Ferrocenyl palladacycles derived from unsymmetrical pincer-type ligands: Evidences of Pd(0) nanoparticles generation during Suzuki-Miyaura reaction and applications in direct arylation of thiazole and isoxazole

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Details of 1H-NMR and 13C-NMR spectra of direct arylation products

1H-NMR and 13C-NMR spectra of SMC cross-coupling products

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<table>
<thead>
<tr>
<th>Compound</th>
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<td>484(3825), 332(22690), 290(20850), 251 (23850)</td>
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<td>L$^2$H</td>
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</tr>
<tr>
<td>Complex 2</td>
<td>535(1350), 355(2590), 243(21700).</td>
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$GOF = \frac{\sum [w(F_o^2 - F_c^2)^2]}{M - N}$ (M = number of reflections, N = number of parameters refined).

$R_1 = \frac{\sum \left|F_o\right| - \left|F_c\right|}{\sum \left|F_o\right|}$.

$wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]^{1/2}}$.

**Table S3.** Selected bond lengths and bond angles of complex Pd1 and their theoretical comparison.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
<th>Bond lengths (Å)</th>
<th>Bond angles (°)</th>
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<td><strong>Theoretical</strong></td>
<td><strong>Experimental</strong></td>
<td><strong>Theoretical</strong></td>
</tr>
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<td>Pd1—C11</td>
<td>1.968(6)</td>
<td>1.98675</td>
<td>C11—Pd1—N3</td>
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<td>Pd1—N3</td>
<td>1.986(5)</td>
<td>2.03894</td>
<td>C11—Pd1—N1</td>
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<td>Pd1—N1</td>
<td>2.125(5)</td>
<td>2.19720</td>
<td>N3—Pd1—N1</td>
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<td>2.33925</td>
<td>C11—Pd1—C11</td>
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<td>N3—Pd1—C11</td>
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<td>N1—Pd1—C11</td>
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**Table S4.** Selected bond lengths and bond angles of complex Pd2 and their theoretical comparison.

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<td><strong>Theoretical</strong></td>
<td><strong>Experimental</strong></td>
<td><strong>Theoretical</strong></td>
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<td>Pd1—C11</td>
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<td>N3—Pd1—C11</td>
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<td></td>
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<td>N1—Pd1—C11</td>
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</table>
DFT calculation

Optimized structure:

Complexes Pd1 and Pd2 are diamagnetic at room temperature indicating their singlet ground state. The geometry optimization of these complexes was performed using their crystallographic coordinates in gas phase in their singlet spin state without any ligand simplification by DFT method using the (R)B3LYP hybrid functional approach incorporated in GAUSSIAN 09 program package. In the ground state (S0), HOMO of all the complexes mainly on metal centre (Fe-71% for Pd1 and Fe-80% for Pd2) and ligand moity (L-26% for Pd1 and L-15% for Pd2). Ongoing to the more stabilized H-1 contribution iron Fe-76% for Pd1 and Fe-71% for Pd2). But going to H-2 state its mainly contribute ligand orbital L (L-65% for Pd1 and L-69% for Pd2) and d orbital of Pd (15%). On the other hand, first vacant orbital LUMO mainly composed of π* orbital delocalized mainly ligands (L-84% for Pd1 and L-79% for Pd2) But on the other hand L+1 composed π* orbital delocalized L (L-45% for Pd1 and L-69% for Pd2) and d orbital of Pd (Pd-43% for Pd1 and Pd-24% for Pd2). The energy difference between HOMO and LUMO are ~3.72 eV (Complex Pd1) and 3.82 eV (Complex Pd2).

![Optimized molecular structures of complex Pd1 and Pd2](image)

**Figure S17.** Optimized molecular structures of complex Pd1 and Pd2. (Pd: Deep red, cyan, Fe: Blue Cl: green, N: blue, O: red, C: grey.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy(eV)</th>
<th>Pd</th>
<th>Fe</th>
<th>Cl</th>
<th>L</th>
<th>Main orbital contribution</th>
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<td>L+5</td>
<td>-0.33</td>
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<td>54</td>
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<tr>
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<td>1</td>
<td>1</td>
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<td>0</td>
<td>95</td>
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<td>2</td>
<td>10</td>
<td>45</td>
<td>dxy (Pd) + π*(L)</td>
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<tr>
<td>H</td>
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<td>71</td>
<td>1</td>
<td>26</td>
<td>dx2-y2(Fe)+ π(L)</td>
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<tr>
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<td>76</td>
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<td>26</td>
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<td>65</td>
<td>dx2-y2(Fe)+ π(L)</td>
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**Table S5.** Frontier Molecular Orbital Composition (%) in the ground state for complex Pd1.
Table S6. Frontier Molecular Orbital Composition (%) in the ground state for complex Pd2.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy(eV)</th>
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<td>π*(L)</td>
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<td>69</td>
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<tr>
<td>H-5</td>
<td>-6.56</td>
<td>36</td>
<td>6</td>
<td>28</td>
<td>31</td>
<td>dz2 (Fe) + dz2 (Pd)</td>
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Scheme 1. Screening of reaction conditions for the direct arylation reaction of 4-methylthiazole with bromobenzene.

Table S7. Optimization of arylation reaction.

<table>
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<th>% Yield</th>
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<td>18</td>
<td>K2CO3</td>
<td>DMA</td>
<td>43&lt;sup&gt;d&lt;/sup&gt;</td>
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</table>

Reaction conditions: Pd1 (0.1 mol%), 2a (1.0 mmol), 3a (1.2 mmol), base (2 mmol), 0.3 mol% PivOH, solvent (2.0 mL), 140 °C, 10 h. <sup>a</sup>only ligand L1H, <sup>b</sup>No base, <sup>c</sup>In presence of Na2PdCl4, <sup>d</sup>In the absence of PivOH.
Figure S18. XPS survey scan of Pd1.

Figure S19. XPS survey scan of SMC reaction mixture in the presence of Pd1.
Figure S20. XPS spectrum of 2p3/2 of iron(II) of catalyst Pd1.

Figure S21. XPS spectrum of 2p3/2 of iron(II) of catalyst Pd1 during SMC reaction.
[1,1'-biphenyl]-4-carbaldehyde\textsuperscript{3}(3aa) White colored solid, Yield 167.6 mg 92% (Complex Pd1), 173 mg 95% (Complex Pd2); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 10.04 (s, 1H), 7.94 (d, \(J = 8.4\) Hz, 2H), 7.74 (d, \(J = 8.3\) Hz, 2H), 7.62 (d, \(J = 8.1\) Hz, 2H), 7.47 (t, \(J = 7.3\) Hz, 2H), 7.40 (t, \(J = 7.3\) Hz, 1H). \textsuperscript{13}C-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 192.15, 147.29, 139.78, 135.23, 130.41, 129.15, 128.60, 127.80, 127.48.

1-([1,1'-biphenyl]-4-yl)ethanone (3ab) White colored solid, Yield 184.4 mg 92% (Complex Pd1), 188.4 mg 95% (Complex Pd2); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.01 (d, \(J = 8.4\) Hz, 2H), 7.67 (d, \(J = 8.4\) Hz, 2H), 7.61 (d, \(J = 7.3\) Hz, 2H), 7.45 (t, \(J = 7.4\) Hz, 2H), 7.38 (t, \(J = 7.3\) Hz, 1H), 2.62 (s, 3H). \textsuperscript{13}C-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 198.01, 145.87, 139.92, 135.86, 129.07, 129.03, 128.35, 127.37, 127.32, 26.85.

4-nitro-1,1'-biphenyl (3ac) Off-white colored solid, Yield 181.3 mg 91% (Complex Pd1), 185.2 mg 93% (Complex Pd2); \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.28 (d, \(J = 8.8\) Hz, 2H), 7.72 (d, \(J = 8.2\) Hz, 2H), 7.61 (d, \(J = 7.3\) Hz, 2H), 7.46 (dt, \(J = 13.6, 7.1\) Hz, 3H) \textsuperscript{13}C-NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 129.25, 129.01, 127.90, 127.48, 127.47, 124.21, 124.20.

2-nitro-1,1'-biphenyl (3ad) Off-white colored solid, Yield 151.4 mg 76% (Complex Pd1), 151.4 mg 76% (Complex Pd2); \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50–7.45 (m, 4H), 7.40–7.37 (m, 1H), 7.19 (dd, \(J = 17.0, 7.8\) Hz, 2H), 6.87 (t, \(J = 7.4\) Hz, 1H), 6.81 (d, \(J = 7.9\) Hz, 1H). \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 143.50, 139.53, 130.47, 129.11, 128.83, 128.51, 127.66, 127.18, 118.67, 115.62.

[1,1'-biphenyl]-4-carbonitrile\textsuperscript{4} (3ae) White colored solid, Yield 167.6 mg 92% (Complex Pd1), 170.1 mg 95% (Complex Pd2); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.69 (q, \(J = 8.6\) Hz, 4H), 7.57 (d, \(J = 7.0\) Hz, 2H), 7.47 (t, \(J = 7.3\) Hz, 2H), 7.40 (t, \(J = 6.6\) Hz, 1H). \textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 145.77, 139.27, 132.68, 129.19, 128.74, 127.82, 127.31, 119.02, 111.00.

2-phenylquinoline (3af) White colored solid, Yield 133.40 mg 65% (Complex Pd1), 158.0 mg 77% (Complex Pd2); \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.21 (d, \(J = 8.6\) Hz, 1H), 8.15 (t, \(J = 8.5\) Hz, 3H), 7.86 (d, \(J = 8.6\) Hz, 1H), 7.82 (d, \(J = 8.1\) Hz, 1H), 7.71 (t, \(J = 7.0\) Hz, 1H), 7.52 (t, \(J = 7.5\) Hz, 3H), 7.45 (t, \(J = 7.3\) Hz, 1H). \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 157.40, 148.32, 139.72, 136.76, 129.76, 129.64, 129.31, 128.83, 127.58, 127.45, 127.20, 126.28, 119.01.

2-phenylpyridine\textsuperscript{3} (3ag) Oil liquid, Yield 116.4 mg 75% (Complex Pd1), 121.1 mg 78% (Complex Pd2); \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 8.66(d, \(J = 4.81\)H), 8.00-7.98 (m,2H), 7.65-7.59 (m, 2H), 7.46-7.42 (m, 2H) 7.38-7.36 (m, 1H) 7.14-7.10 (m, 1H) \textsuperscript{13}C-NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 157.47, 149.66, 139.40, 136.80, 128.99, 128.78, 126.95, 122.13, 120.60.

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2,6-diphenylpyridine (3ah) White colored solid, Yield 152.6 mg 66% (Complex Pd1), 164.2 mg 71% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.23 (d, J = 7.9 Hz, 4H), 7.84 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 4H), 7.52 – 7.48 (m, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 156.85, 139.54, 137.48, 129.00, 128.71, 127.02, 118.67

1-phenylnaphthalene (3ak) White colored liquid Yield 176.5 mg 86% (Complex Pd1), 194 mg 95% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.98 (t, J = 9.4 Hz, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.62 – 7.53 (m, 6H), 7.49 (t, J = 6.9 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 140.94, 140.44, 133.98, 131.80, 130.27, 128.46, 127.83, 127.42, 127.12, 126.22, 125.96, 125.57

4’-ethyl-[1,1’-biphenyl]-4-carbaldehyde (3al) White colored solid, Yield 176.5 mg 84% (Complex Pd1), 180.7 mg 86% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 10.04 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 192.07, 147.22, 144.98, 137.09, 135.06, 130.40, 128.76, 128.66, 127.52, 127.41, 28.70, 15.68.

1-(4’-ethyl-[1,1’-biphenyl]-4-yl)ethanone (3am) White colored solid, Yield 190.6 mg 85% (Complex Pd1), 195.1 mg 87% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.01 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 197.96, 145.86, 144.69, 137.27, 135.64, 129.01, 128.60, 127.29, 127.09, 28.65, 26.78, 15.65.

4’-ethyl-4-nitro-1,1’-biphenyl (3an) Yellow colored solid, Yield 171.1 mg 86% (Complex Pd1), 177.1 mg 89% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 146.32 (s), 145.76 (s), 137.30, 133.25, 129.35, 128.18, 127.84, 119.73, 111.22, 29.23, 16.21.

4’-ethyl-2-nitro-1,1’-biphenyl (3ao) Yellow colored solid, Yield 195.4 mg 86% (Complex Pd1), 202.2 mg 89% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 7.41 (d, J = 7.8 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.17 (dd, J = 12.2, 7.6 Hz, 2H), 6.85 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 2.72 (t, J = 6.5 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 143.58, 143.18, 136.74, 130.49, 129.01, 128.30, 127.70, 118.65, 115.56, 28.60, 15.57.

4’-ethyl-[1,1’-biphenyl]-4-carbonitrile (3ap) White colored solid, Yield 178.2 mg 86% (Complex Pd1), 188.6 mg 91% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.68 (q, J = 8.7 Hz, 4H), 7.51 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.27
(t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 145.72, 145.16, 136.59, 132.65, 128.75, 127.58, 127.24, 119.11, 110.62, 28.66, 15.57.

2-(4-ethylphenyl)quinolone (3aq) White colored solid, Yield 158.6 mg 68% (Complex Pd$_1$), 167.9 mg 72% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.18 (dd, J = 8.2, 5.4 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 9.3 Hz, 1H), 7.72 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 157.51, 148.37, 145.85, 137.24, 136.86, 128.40, 127.72, 127.53, 127.18, 119.04, 28.83, 15.73.

2-(4-ethylphenyl)pyridine (3ar) Off-white colored solid, Yield 130.0 mg 71% (Complex Pd$_1$), 139.3 mg 76% (Complex Pd$_2$); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.68 (d, J = 4.6 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.20 (ddd, J = 6.8, 4.9, 2.2 Hz, 1H), 2.71 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 157.60, 149.61, 145.39, 136.88, 128.52, 128.29, 126.97, 120.44, 28.70, 15.61.

2,6-bis(4-ethylphenyl)pyridine (3as) White colored solid, Yield 186.8 mg 65% (Complex Pd$_1$), 201.2 mg 70% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 8.3 Hz, 4H), 7.79 – 7.74 (m, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 8.4 Hz, 4H), 2.71 (q, J = 7.6 Hz, 4H), 1.28 (t, J = 7.6 Hz, 6H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 156.87, 145.45, 137.33, 137.15, 128.31, 127.05, 118.21, 28.81, 15.74.

1-(4-ethylphenyl)naphthalene (3at) White colored liquid, Yield 197.0 mg 85% (Complex Pd$_1$), 211.2 mg 91% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.12 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.97 (d, J = 10.3 Hz, 1H), 7.68 – 7.52 (m, 6H), 7.46 (d, J = 7.8 Hz, 2H), 2.93 – 2.85 (m, 2H), 1.47 (t, J = 6.8 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 143.45, 140.54, 138.30, 134.06, 131.99, 130.28, 128.51, 128.03, 127.70, 127.17, 126.40, 126.18, 125.97, 125.67, 28.90, 15.88.

3-phenylpyridine (3au) White colored liquid, Yield 122.6 mg 79% (Complex Pd$_1$), 127.2 mg 82% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.82 (d, J = 3.1 Hz, 1H), 8.55 (dd, J = 4.8, 1.6 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.53 (dd, J = 5.3, 3.3 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 (dd, J = 8.6, 4.8 Hz, 1H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 148.37, 137.85, 136.69, 134.43, 129.13, 128.17, 127.20, 123.71.

3-(4-ethylphenyl)pyridine (3av) White colored liquid, Yield 125.7 mg 81% (Complex Pd$_1$), 131.9 mg 85% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.83 (d, J = 3.1 Hz, 1H), 8.54 (dd, J = 4.8, 1.6 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.28 (dd, J = 8.1, 2.5 Hz, 3H), 2.67 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 148.29, 144.43, 136.63, 135.21, 134.21, 128.78, 127.10, 123.57, 28.51, 15.77.
1-(4'-chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (3ba) White colored solid, Yield 205.3 mg 89% (Complex Pd1), 209.9 mg 91% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.01 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H), 2.62 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 197.79, 144.55, 138.36, 136.15, 134.54, 129.28, 128.83, 127.14, 26.66.

4'-chloro-[1,1'-biphenyl]-4-carbonitrile (3bb) White colored solid, Yield 196.5 mg 92% (Complex Pd1), 202.9 mg 95% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.8$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 7.6$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 2H), 7.40 – 7.34 (m, 1H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 148.44, 137.67, 135.05, 132.79, 129.40, 128.55, 127.65, 118.84, 111.35.

3-(4-chlorophenyl)pyridine (3bc) White colored liquid, Yield 162.1 mg 85% (Complex Pd1), 168.7 mg 89% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.82 (s, 1H), 8.61 (s, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 2H), 7.40 – 7.34 (m, 1H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 148.74, 148.07, 136.25, 135.52, 134.28, 129.29, 128.39, 123.63.

2-(4-chlorophenyl)quinoline (3bd) White colored solid, Yield 174.9 mg 73% (Complex Pd1), 184.56 mg 77% (Complex Pd2); $^1$H-NMR (400 MHz, CDCl$_3$) δ 8.22 (d, $J = 8.6$ Hz, 1H), 8.13 (dd, $J = 14.3$, 8.8 Hz, 3H), 7.83 (dd, $J = 7.9$, 3.6 Hz, 2H), 7.73 (t, $J = 7.7$ Hz, 1H), 7.51 (dd, $J = 20.7$, 7.8 Hz, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) δ 156.12, 148.07, 136.25, 135.52, 134.28, 129.29, 128.39, 123.63.

4'-chloro-3-nitro-1,1'-biphenyl (3be) Yellow colored solid, Yield 165.9 mg 71% (Complex Pd1), 179.9 mg 79% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 7.9$ Hz, 1H), 7.57 (d, $J = 7.7$ Hz, 2H), 7.48 (d, $J = 7.8$ Hz, 2H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 148.77, 141.61, 137.09, 134.85, 132.84, 129.90, 128.37, 128.42, 122.34, 121.76.

4'-chloro-2-nitro-1,1'-biphenyl (3bf) Yellow colored solid, Yield 163.55 mg 70% (Complex Pd1), 179.9 mg 77% (Complex Pd2); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J = 6.8$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.52 – 7.47 (m, 1H), 7.41 – 7.38 (m, 3H), 7.24 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.15, 135.99, 135.31, 134.55, 132.57, 131.91, 129.37, 128.00, 128.64 124.36.

1-(4'-fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (3ca) White colored solid, Yield 197.1 mg 92% (Complex Pd1), 203.52 mg 95% (Complex Pd2); $^1$H-NMR (500 MHz, CDCl$_3$) δ 8.05 (d, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.64 – 7.59 (m, 2H), 7.18 (t, $J = 8.1$ Hz, 2H), 2.66 (s, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) δ 197.68, 144.75, 135.87, 128.98, 127.07, 116.01, 26.64.
4'-fluoro-[1,1'-biphenyl]-4-carbonitrile (3cb) White colored solid, Yield 183.4 mg 93% (Complex Pd1), 187.34 mg 95% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 7.71\) (d, \(J = 8.0\) Hz, 2H), 7.62 (d, \(J = 8.6\) Hz, 2H), 7.55 (dd, \(J = 8.5, 4.9\) Hz, 2H), 7.16 (t, \(J = 8.7\) Hz, 2H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta 164.51, 162.04, 144.70, 135.37, 132.74, 129.09, 127.66, 118.92, 116.12, 111.03.

3-(4-fluorophenyl)pyridine (3cc) White colored oil, Yield 150.6 mg 87% (Complex Pd1), 155.87 mg 90% (Complex Pd2); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta 8.83\) (s, 1H), 8.61 (s, 1H), 7.84 (d, \(J = 7.8\) Hz, 1H), 7.58 – 7.52 (m, 2H), 7.39 (s, 1H), 7.18 (t, \(J = 8.2\) Hz, 2H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta 163.92, 161.95, 148.42, 135.81, 134.25, 133.92, 128.85, 123.64, 116.16.

2-(4-fluorophenyl)quinoline (3cd) White colored solid, Yield 167.43 mg 75% (Complex Pd1), 180.83 mg 81% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.22\) – 8.13 (m, 4H), 7.81 (d, \(J = 8.1\) Hz, 1H), 7.72 (t, \(J = 7.7\) Hz, 1H), 7.63 (dd, \(J = 14.5, 7.4\) Hz, 3H), 7.21 (t, \(J = 8.2\) Hz, 2H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta 165.12, 162.65, 156.32, 148.30, 136.98, 135.91, 129.84, 127.57, 126.43, 118.72, 115.80.

4'-fluoro-3-nitro-1,1'-biphenyl (3ce) Yellow colored solid, Yield 175.23 mg 75% (Complex Pd1), 207.9 mg 79% (Complex Pd2); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta 8.43\) (s, 1H), 8.23 (d, \(J = 8.1\) Hz, 1H), 7.89 (d, \(J = 7.7\) Hz, 1H), 7.63 (dd, \(J = 14.5, 7.4\) Hz, 3H), 7.21 (t, \(J = 8.2\) Hz, 2H). \(^{13}\)C-NMR (126 MHz, CDCl\(_3\)) \(\delta 141.92, 134.85, 132.87, 129.80, 128.87, 122.06, 121.83, 116.26, 116.09.

4'-fluoro-2-nitro-1,1'-biphenyl (3cf) Yellow colored solid, Yield 156.37 mg 72% (Complex Pd1), 169.33 mg 78% (Complex Pd2); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.85\) (d, \(J = 8.1\) Hz, 1H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.50 – 7.46 (m, 1H), 7.41 (d, \(J = 7.6\) Hz, 1H), 7.28 (dd, \(J = 8.8, 5.2\) Hz, 2H), 7.10 (t, \(J = 8.7\) Hz, 2H).

4-methyl-5-phenylthiazole\(^5\) (6a) Off-white colored solid, Yield 149 mg 85% (Complex Pd1), 156 mg 89% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.66\) (s, 1H), 7.45 – 7.38 (m, 5H), 7.35 (dd, \(J = 5.9, 2.9\) Hz, 1H), 2.52 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta 150.46, 148.56, 132.02, 129.41, 128.79, 127.98, 126.39, 16.15.

5-(4-chlorophenyl)-4-methylthiazole\(^5\) (6b) Off-white colored solid, Yield 186.6 mg 89% (Complex Pd1), 192.8 mg 92% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.68\) (s, 1H), 7.45 – 7.30 (m, 4H), 2.50 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta 150.73, 148.94, 134.07, 130.79, 130.49, 129.11, 128.99, 16.18.

5-(4-fluorophenyl)-4-methylthiazole\(^5\) (6c) Off-white colored solid, Yield 175.8 mg 91% (Complex Pd1), 181.6 mg 94% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta 8.66\) (s, 1H),
7.39 (dd, \(J = 8.8, 5.3\) Hz, 2H), 7.10 (d, \(J = 8.7\) Hz, 2H), 2.49 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.75, 161.28, 150.40, 148.68, 131.13, 127.97, 115.91, 16.01.

1-(4-(4-methylthiazol-5-yl)phenyl)ethanone\(^5\) (6d) Off-white colored solid, Yield 195.5 mg 90\% (Complex Pd\(_1\)), 206.4 mg 95\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.72 (s, 1H), 7.99 (d, \(J = 8.4\) Hz, 2H), 7.53 (d, \(J = 8.5\) Hz, 2H), 2.62 (s, 3H), 2.55 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 197.51, 151.29, 149.66, 136.91, 136.21, 130.95, 129.37, 128.85, 26.77, 16.47.

5-(4-methoxyphenyl)-4-methylthiazole\(^5\) (6e) Off-white colored solid, Yield 154 mg 75\% (Complex Pd\(_1\)), 162.1 mg 79\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.62 (s, 1H), 7.34 (d, \(J = 8.8\) Hz, 2H), 6.94 (d, \(J = 8.8\) Hz, 2H), 3.82 (s, 3H), 2.49 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 159.45, 149.80, 147.99, 131.82, 130.63, 124.25, 114.25, 55.43, 16.03.

4-methyl-5-(p-tolyl)thiazole\(^5\) (6f) Off-white colored solid, Yield 145.7 mg 77\% (Complex Pd\(_1\)), 153.3 mg 81\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.64 (s, 1H), 7.32 (d, \(J = 8.1\) Hz, 2H), 7.22 (d, \(J = 7.9\) Hz, 2H), 2.52 (s, 3H), 2.38 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.07, 148.27, 137.94, 132.06, 129.50, 129.26, 129.05, 21.28, 16.12.

4-(4-methylthiazol-5-yl)benzaldehyde\(^5\) (6g) White colored solid, Yield 181.2 mg 89\% (Complex Pd\(_1\)), 184.9 mg 91\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.03 (s, 1H), 8.74 (s, 1H), 7.93 (d, \(J = 8.3\) Hz, 2H), 7.61 (d, \(J = 8.3\) Hz, 2H), 2.57 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 191.61, 151.53, 149.97, 138.33, 135.47, 130.83, 130.17, 129.77, 16.53.

4-methyl-5-(pyridin-3-yl)thiazole\(^6\) (6h) Off-white colored solid, Yield 155.0 mg 88\% (Complex Pd\(_1\)), 162.1 mg 92\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.72 (s, 1H), 8.67 (s, 1H), 8.56 (d, \(J = 4.9\) Hz, 1H), 7.72 (d, \(J = 7.9\) Hz, 1H), 7.34 (d, \(J = 3.9\) Hz, 1H), 2.51 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.35, 149.79, 148.98, 136.52, 128.35, 128.13, 123.51, 21.60, 16.06.

5-(3-methoxyphenyl)-4-methylthiazole\(^5\) (6i) Off-white colored solid, Yield 143.7 mg 70\% (Complex Pd\(_1\)), 153.9 mg 75\% (Complex Pd\(_2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.65 (s, 1H), 8.74 (s, 1H), 8.56 (d, \(J = 4.9\) Hz, 1H), 7.72 (d, \(J = 7.9\) Hz, 1H), 2.52 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.35, 149.79, 148.98, 136.52, 128.35, 128.13, 123.51, 21.60, 16.06.

4-methyl-5-(3-nitrophenyl)thiazole\(^5\) (6j) Off-white colored solid, Yield 165.2 mg 75\% (Complex Pd\(_1\)), 178.4 mg 81\% (Complex Pd\(_2\)); \(^1\)H- NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.75 (s, 1H), 8.30 (t, \(J = 2.0\) Hz, 1H), 8.21 (d, \(J = 8.2\) Hz, 1H), 7.76 (d, \(J = 7.8\) Hz, 1H), 7.60 (d, \(J = 7.9\) Hz, 1H), 2.56 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.48, 150.10, 135.15, 133.92, 129.88, 129.48, 124.05, 122.76, 16.22.
4-(4-methylthiazol-5-yl)benzonitrile\(^5\) (6k) White colored solid, Yield 176.2 mg 88% (Complex Pd1), 190.2 mg 95% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 (s, 1H), 7.71 (d, \(J = 8.5\) Hz, 2H), 7.55 (d, \(J = 8.5\) Hz, 2H), 2.55 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.68, 150.13, 136.95, 132.60, 130.18, 129.80, 118.55, 111.58, 16.43.

4-methyl-5-(4-nitrophenyl)thiazole\(^5\) (6l) Yellow colored solid, Yield 198.2 mg 90% (Complex Pd1), 211.4 mg 96% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.77 (s, 1H), 8.28 (d, \(J = 8.9\) Hz, 2H), 7.61 (d, \(J = 8.9\) Hz, 2H), 2.58 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.96, 150.46, 147.18, 138.87, 129.91, 126.33, 124.14, 16.50.

4-methyl-5-(naphthalen-1-yl)thiazole\(^5\) (6m) White colored solid, Yield 193.7 mg 86% (Complex Pd1), 207.2 mg 92% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.82 (s, 1H), 7.90 (d, \(J = 10.6\) Hz, 2H), 7.67 (d, \(J = 10.7\) Hz, 1H), 7.48 (dt, \(J = 11.3, 8.5\) Hz, 4H), 2.28 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.67, 150.46, 136.95, 132.60, 130.18, 129.80, 118.55, 111.58, 16.43.

3,5-dimethyl-4-phenylisoxazole\(^7\) (8a) Yellow colored solid, Yield 138.5 mg 80% (Complex Pd1), 143.7 mg 83% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 (t, \(J = 7.4\) Hz, 2H), 7.35 (t, \(J = 7.4\) Hz, 1H), 7.24 (d, \(J = 7.0\) Hz, 2H), 2.40 (s, 3H), 2.27 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.26, 158.79, 130.56, 129.17, 128.86, 127.58, 116.73, 11.62, 10.87.

4-(4-chlorophenyl)-3,5-dimethylisoxazole (8b)\(^6\) Off-white colored solid, Yield 176.5 mg 85% (Complex Pd1), 184.7 mg 89% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (d, \(J = 8.7\) Hz, 2H), 7.16 (d, \(J = 8.7\) Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.45, 158.55, 133.69, 130.44, 129.15, 129.00, 11.60, 10.81.

4-(4-fluorophenyl)-3,5-dimethylisoxazole (8c) Off-white colored solid, Yield 162.5 mg 85% (Complex Pd1), 174 mg 91% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (dd, \(J = 8.8, 5.3\) Hz, 2H), 7.11 (t, \(J = 8.7\) Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.30, 163.52, 161.06, 158.70, 130.83, 115.83, 11.55, 10.78.

1-(4-(3,5-dimethylisoxazol-4-yl)phenyl)ethanone (8d) Off-white colored solid Yield 180.8 mg 84% (Complex Pd1), 191.5 mg 89% (Complex Pd2); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.01 (d, \(J = 8.4\) Hz, 2H), 7.34 (d, \(J = 8.4\) Hz, 2H), 2.61 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 165.10, 158.89, 137.42, 129.61, 129.08, 127.57, 116.64, 21.31, 11.63, 10.90.

4-(4-methoxyphenyl)-3,5-dimethylisoxazole (8e) Off-white colored solid Yield 142.2 mg 70% (Complex Pd1), 152.4 mg 75% (Complex Pd2); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 (d, \(J = 8.8\) Hz, 2H), 6.96 (d, \(J = 8.8\) Hz, 2H), 3.83 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H). \(^{13}\)C-NMR
(101 MHz, CDCl$_3$) $\delta$ 164.92, 159.07, 158.93, 130.34, 122.70, 116.34, 114.34, 55.40, 11.59, 10.87.

3,5-dimethyl-4-(p-tolyl)isoxazole$^7$ (8f) Off-white colored solid, Yield 121.7 mg 65% (Complex Pd$_1$), 136.7 mg 73% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 2.38 (d, $J = 1.5$ Hz, 6H), 2.25 (s, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 165.10, 158.89, 137.42, 129.61, 129.08, 127.57, 116.64, 21.31, 11.63, 10.90.

4-(3,5-dimethylisoxazol-4-yl)benzaldehyde$^7$ (8g) Off-white colored solid, Yield 157 mg 78% (Complex Pd$_1$), 163 mg 81% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 191.67, 166.11, 158.37, 137.00, 135.37, 130.24, 129.58, 115.93, 11.85, 10.98.

3,5-dimethyl-4-(pyridin-3-yl)isoxazole$^6$ (8h) Off-white colored solid, Yield 139.3 mg 80% (Complex Pd$_1$), 144.6 mg 83% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 4.8, 1.7 Hz, 1H), 8.52 (d, $J = 3.0$ Hz, 1H), 7.59 – 7.56 (m, 1H), 7.38-7.35 (1H), 2.41 (s, 3H), 2.26 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 166.24, 158.27, 158.36, 131.89, 129.90, 121.58, 116.63, 115.18, 112.68, 55.36, 11.66, 10.89.

4-(3-methoxyphenyl)-3,5-dimethylisoxazole$^7$ (8i) Off-white colored solid, Yield 132.0 mg 65% (Complex Pd$_1$), 144.3 mg 71% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.32 (m, 1H), 6.89 (d, $J = 5.8$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 1H), 6.77 (d, $J = 4.1$ Hz, 1H), 3.83 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 165.38, 159.88, 158.76, 131.89, 129.90, 121.58, 116.63, 115.18, 112.68, 55.36, 11.66, 10.89.

3,5-dimethyl-4-(3-nitrophenyl)isoxazole$^7$ (8j) Off-white colored solid, Yield 154.9 mg 71% (Complex Pd$_1$), 165.8 mg 76% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J = 8.0$ Hz, 1H), 8.12 (t, $J = 1.9$ Hz, 1H), 7.64 (t, $J = 7.9$ Hz, 1H), 7.59 (dt, $J = 7.7$, 1.5 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H). $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 166.14, 158.59, 149.95, 148.89, 136.36, 126.68, 122.70, 113.56, 11.64, 10.80.

4-(3-methoxyphenyl)-3,5-dimethylisoxazole$^7$ (8k) Off-white colored solid, Yield 160.5 mg 81% (Complex Pd$_1$), 170.5 mg 86% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J = 8.0$ Hz, 1H), 8.12 (t, $J = 1.9$ Hz, 1H), 7.64 (t, $J = 7.9$ Hz, 1H), 7.59 (dt, $J = 7.7$, 1.5 Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 166.23, 158.22, 135.63, 132.75, 129.70, 118.60, 115.54, 111.52, 11.83, 10.93.

3,5-dimethyl-4-(4-nitrophenyl)isoxazole$^7$ (8l) Off-white colored solid, Yield 183.3 mg 84% (Complex Pd$_1$), 194.2 mg 89% (Complex Pd$_2$); $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.29 (d, $J = 8.9$ Hz, 2H), 7.43 (d, $J = 8.9$ Hz, 2H), 2.44 (s, 3H), 2.29 (s, 3H). $^{13}$C-NMR (126 MHz, CDCl$_3$) $\delta$ 166.35, 158.09, 147.06, 137.50, 129.68, 124.13, 115.16, 11.78, 10.86.
3,5-dimethyl-4-(naphthalen-1-yl)isoxazole\(^7\) (8m) Off-white colored solid, Yield 176.3 mg 79\% (Complex Pd\(^1\)), 189.7 mg 85\% (Complex Pd\(^2\)); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (t, \(J = 7.0\) Hz, 2H), 7.60 – 7.44 (m, 4H), 7.32 (d, \(J = 7.0\) Hz, 1H), 2.25 (s, 3H), 2.09 (s, 3H). \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \(\delta\) 191.67, 166.11, 158.37, 137.00, 135.37, 130.24, 129.58, 115.93, 11.85, 10.98.
Figure S22. $^1$H-NMR spectrum of 3aa in CDCl$_3$.

Figure S23. $^{13}$C-NMR spectrum of 3aa in CDCl$_3$. 
Figure S24. $^1$H-NMR spectrum of 3ab in CDCl$_3$.

Figure S25. $^{13}$C-NMR spectrum of 3ab in CDCl$_3$.
Figure S26. \(^1\)H-NMR spectrum of 3ac in CDCl\(_3\).

Figure S27. \(^{13}\)C-NMR spectrum of 3ac in CDCl\(_3\).
Figure S28. $^1$H-NMR spectrum of 3ad in CDCl$_3$.

Figure S29. $^{13}$C-NMR spectrum of 3ad in CDCl$_3$. 
Figure S30. $^1$H-NMR spectrum of 3ae in CDCl$_3$.

Figure S31. $^{13}$C-NMR spectrum of 3ae in CDCl$_3$. 
Figure S32. $^1$H-NMR spectrum of 3af in CDCl$_3$.

Figure S33. $^{13}$C-NMR spectrum of 3af in CDCl$_3$. 
Figure S3. $^1$H-NMR spectrum of 3ag in CDCl$_3$.

Figure S35. $^{13}$C-NMR spectrum of 3ag in CDCl$_3$. 
Figure S36. $^1$H-NMR spectrum of 3ah in CDCl₃.

Figure S37. $^{13}$C-NMR spectrum of 3ah in CDCl₃.
Figure S38. $^1$H-NMR spectrum of 3ak in CDCl$_3$.

Figure S39. $^{13}$C-NMR spectrum of 3ak in CDCl$_3$. 
Figure S40. $^1$H-NMR spectrum of 3al in CDCl$_3$.

Figure S41. $^{13}$C-NMR spectrum of 3al in CDCl$_3$. 

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Figure S42. $^1$H-NMR spectrum of 3am in CDCl$_3$.

Figure S43. $^{13}$C-NMR spectrum of 3am in CDCl$_3$. 
Figure S44. $^1$H-NMR spectrum of 3a in CDCl$_3$.

Figure S45. $^{13}$C-NMR spectrum of 3a in CDCl$_3$. 
Figure S46. $^1$H-NMR spectrum of 3ao in CDCl$_3$.

Figure S47. $^{13}$C-NMR spectrum of 3ao in CDCl$_3$. 
**Figure S48.** $^1$H-NMR spectrum of 3ap in CDCl$_3$.

**Figure S49.** $^{13}$C-NMR spectrum of 3ap in CDCl$_3$. 
Figure S50. $^1\text{H}-\text{NMR}$ spectrum of 3aq in CDCl$_3$.

Figure S51. $^{13}\text{C}-\text{NMR}$ spectrum of 3aq in CDCl$_3$. 
Figure S52. $^1$H-NMR spectrum of 3ar in CDCl$_3$.

Figure S53. $^{13}$C-NMR spectrum of 3ar in CDCl$_3$. 
Figure S5. $^1$H-NMR spectrum of 3as in CDCl$_3$.

Figure S55. $^{13}$C-NMR spectrum of 3as in CDCl$_3$. 
Figure S5. $^1$H-NMR spectrum of 3at in CDCl$_3$.

Figure S6. $^1$H-NMR spectrum of 3at in CDCl$_3$.

Figure S7. $^{13}$C-NMR spectrum of 3at in CDCl$_3$. 
Figure S58. $^1$H-NMR spectrum of 3au in CDCl$_3$.

Figure S59. $^{13}$C-NMR spectrum of 3au in CDCl$_3$. 
Figure S60. $^1$H-NMR spectrum of 3av in CDCl$_3$.

Figure S61. $^{13}$C-NMR spectrum of 3av in CDCl$_3$.
Figure S62. $^1$H-NMR spectrum of 3ba in CDCl$_3$.

Figure S63. $^{13}$C-NMR spectrum of 3ba in CDCl$_3$. 
Figure S64. $^1$H-NMR spectrum of 3bb in CDCl$_3$.

Figure S65. $^{13}$C-NMR spectrum of 3bb in CDCl$_3$. 
Figure S64. $^1$H-NMR spectrum of 3bc in CDCl$_3$.

Figure S67. $^{13}$C-NMR spectrum of 3bc in CDCl$_3$. 
Figure S68. $^1$H-NMR spectrum of 3bd in CDCl$_3$.

Figure S69. $^{13}$C-NMR spectrum of 3bd in CDCl$_3$. 

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Figure S70. $^1$H-NMR spectrum of 3be in CDCl$_3$.

Figure S71. $^{13}$C-NMR spectrum of 3be in CDCl$_3$. 
Figure S72. $^1$H-NMR spectrum of 3bf in CDCl$_3$.

Figure S73. $^{13}$C-NMR spectrum of 3bf in CDCl$_3$. 
Figure S74. $^1$H-NMR spectrum of 3ca in CDCl$_3$.

Figure S75. $^{13}$C-NMR spectrum of 3ca in CDCl$_3$. 
Figure S76. $^1$H-NMR spectrum of 3cb in CDCl$_3$.

Figure S77. $^{13}$C-NMR spectrum of 3cb in CDCl$_3$. 
Figure S78. $^1$H-NMR spectrum of 3cc in CDCl$_3$.

Figure S79. $^{13}$C-NMR spectrum of 3cc in CDCl$_3$. 

N  F
Figure S80. $^1$H-NMR spectrum of 3cd in CDCl$_3$.

Figure S81. $^{13}$C-NMR spectrum of 3cd in CDCl$_3$. 
Figure S82. $^1$H-NMR spectrum of 3ce in CDCl$_3$.

Figure S83. $^{13}$C-NMR spectrum of 3ce in CDCl$_3$. 
Figure S84. $^1$H-NMR spectrum of 3cf in CDCl$_3$.

Figure S85. $^{13}$C-NMR spectrum of 3cf in CDCl$_3$. 
Figure S86. $^1$H-NMR spectrum of 6a in CDCl$_3$.

Figure S87. $^{13}$C-NMR spectrum of 6a in CDCl$_3$. 
Figure S88. $^1$H-NMR spectrum of 6b in CDCl$_3$.

Figure S89. $^{13}$C-NMR spectrum of 6b in CDCl$_3$. 
Figure S90. $^1$H-NMR spectrum of 6c in CDCl$_3$.

Figure S91. $^{13}$C-NMR spectrum of 6c in CDCl$_3$. 
Figure S92. $^1$H-NMR spectrum of 6d in CDCl$_3$.

Figure S93. $^{13}$C-NMR spectrum of 6d in CDCl$_3$. 
Figure S94. $^1$H-NMR spectrum of 6e in CDCl$_3$.

Figure S95. $^{13}$C-NMR spectrum of 6e in CDCl$_3$. 
Figure S96. $^1$H-NMR spectrum of 6f in CDCl$_3$.

Figure S97. $^{13}$C-NMR spectrum of 6f in CDCl$_3$. 
Figure S98. $^1$H-NMR spectrum of 6g in CDCl$_3$.

Figure 99. $^{13}$C-NMR spectrum of 6g in CDCl$_3$. 
Figure S100. $^1$H-NMR spectrum of 6h in CDCl$_3$.

Figure S101. $^{13}$C-NMR spectrum of 6h in CDCl$_3$. 
Figure S102. $^1$H-NMR spectrum of 6i in CDCl$_3$. 

Figure S103. $^{13}$C-NMR spectrum of 6i in CDCl$_3$. 

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Figure S104. $^1$H-NMR spectrum of 6j in CDCl$_3$.

Figure S105. $^{13}$C-NMR spectrum of 6j in CDCl$_3$. 

NO$_2$
Figure S106. $^1$H-NMR spectrum of 6k in CDCl$_3$.

Figure S107. $^{13}$C-NMR spectrum of 6k in CDCl$_3$. 
Figure S108. $^1$H-NMR spectrum of 6l in CDCl$_3$.

Figure S109. $^{13}$C-NMR spectrum of 6l in CDCl$_3$.
Figure S110. $^1$H-NMR spectrum of 6m in CDCl$_3$.

Figure S111. $^{13}$C-NMR spectrum of 6m in CDCl$_3$. 
Figure S112. $^1$H-NMR spectrum of 8a in CDCl$_3$.

Figure S113. $^{13}$C-NMR spectrum of 8a in CDCl$_3$. 
Figure S114. $^1$H-NMR spectrum of 8b in CDCl$_3$.

Figure S115. $^{13}$C-NMR spectrum of 8b in CDCl$_3$. 

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Figure S116. $^1$H-NMR spectrum of 8c in CDCl$_3$.

Figure S117. $^{13}$C-NMR spectrum of 8c in CDCl$_3$. 
Figure S118. $^1$H-NMR spectrum of 8d in CDCl$_3$.

Figure S119. $^{13}$C-NMR spectrum of 8d in CDCl$_3$. 

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Figure S120. $^{13}$C-NMR spectrum of 8e in CDCl$_3$.

Figure S121. $^{13}$C-NMR spectrum of 8e in CDCl$_3$. 
Figure S122. $^1$H-NMR spectrum of 8f in CDCl$_3$.

Figure S123. $^{13}$C-NMR spectrum of 8f in CDCl$_3$. 
**Figure S124.** $^1$H-NMR spectrum of 8g in CDCl$_3$.

**Figure S125.** $^{13}$C-NMR spectrum of 8g in CDCl$_3$. 
Figure S126. $^1$H-NMR spectrum of 8h in CDCl$_3$.

Figure S127. $^{13}$C-NMR spectrum of 8h in CDCl$_3$. 
Figure S128. $^1$H-NMR spectrum of 8i in CDCl$_3$.

Figure S129. $^{13}$C-NMR spectrum of 8i in CDCl$_3$. 
Figure S130. $^1$H-NMR spectrum of 8j in CDCl$_3$.

Figure S131. $^{13}$C-NMR spectrum of 8j in CDCl$_3$. 
**Figure S132.** $^1$H-NMR spectrum of 8k in CDCl$_3$.

**Figure S133.** $^{13}$C-NMR spectrum of 8k in CDCl$_3$. 
Figure S134. $^1$H-NMR spectrum of 8l in CDCl$_3$.

Figure S135. $^{13}$C-NMR spectrum of 8l in CDCl$_3$. 
Figure S136. $^1$H-NMR spectrum of 8m in CDCl$_3$.

Figure S137. $^{13}$C-NMR spectrum of 8m in CDCl$_3$. 
Figure S138. GC-MS mass spectrum of 6k.

Figure S139. GC-MS mass spectrum of 6l.

Figure S140. GC-MS mass spectrum of 8b.
Figure S141. GC-MS mass spectrum of 8k.

References