Palladium(II)-Catalyzed C-C Bond Formation of Arylhydrazines with Olefins via Carbon-Nitrogen Bond Cleavage

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Supporting Information

Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Methods</td>
<td>S-1</td>
</tr>
<tr>
<td>Screening of the optimal conditions</td>
<td>S-2</td>
</tr>
<tr>
<td>Procedure for Palladium(II)-Catalyzed C-C bond formation of aniline with tert-butyl acrylate</td>
<td>S-3</td>
</tr>
<tr>
<td>General Procedure for Palladium(II)-Catalyzed C-C bond formation of Arylhydrazines with Olefins</td>
<td>S-3</td>
</tr>
<tr>
<td>Procedure for synthesis of (2,9-dimethyl-1,10-phenanthroline)- 4-cyanophenyl-palladium(II) chloride (1h’)</td>
<td>S-4</td>
</tr>
<tr>
<td>Procedure for Palladium(II)-Catalyzed C-C bond formation of N’-phenyl-acetohydrazide with tert-butyl acrylate:</td>
<td>S-4</td>
</tr>
<tr>
<td>Characterization Data for the product</td>
<td>S-5</td>
</tr>
<tr>
<td>Mechanistic study by employing ESI-MS</td>
<td>S-14</td>
</tr>
<tr>
<td>$^1$H NMR, $^{13}$C NMR, and High Resolution Mass (HRMS) spectra</td>
<td>S-16</td>
</tr>
</tbody>
</table>
General Methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Commercial grade solvents and reagents were used without further purification. Hexane, ethyl acetate were fractionally distilled.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditions.

High Resolution Mass (HRMS) spectra were obtained using Waters Q-Tof Permie Mass Spectrometer.

Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer (CDCl₃ as solvent). Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (¹³C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet).
Screening of the optimal conditions:

\[
\begin{align*}
\text{entry} & \quad \text{Pd} & \quad \text{Ligand} & \quad \text{Solvent} & \quad \text{Time (h)} & \quad \text{yield (3a) (%)}^b \\
1 & \text{NO} & \text{NO} & \text{DCE} & 2h & \text{trace} \\
2 & \text{Pd(OAc)}_2 & \text{NO} & \text{DCE} & 4h & 22\% \\
3 & \text{Pd(OAc)}_2 & \text{A} & \text{DCE} & 2h & 68\% \\
4 & \text{PdCl}_2 & \text{A} & \text{DCE} & 2h & 61\% \\
5 & \text{Pd(OOCOCF}_3\text{)}_2 & \text{A} & \text{DCE} & 2h & 57\% \\
6 & \text{Pd(dba)}_2 & \text{A} & \text{DCE} & 2h & 41\% \\
7 & \text{Pd(OAc)}_2 & \text{B} & \text{DCE} & 2h & 72\% \\
8 & \text{Pd(OAc)}_2 & \text{C} & \text{DCE} & 2h & 81\% \\
9 & \text{Pd(OAc)}_2 & \text{D} & \text{DCE} & 2h & 83\% \\
10 & \text{Pd(OAc)}_2 & \text{E} & \text{DCE} & 2h & 23\% \\
11 & \text{Pd(OAc)}_2 & \text{F} & \text{DCE} & 2h & 77\% \\
12 & \text{Pd(OAc)}_2 & \text{D} & \text{THF} & 2h & 75\% \\
13 & \text{Pd(OAc)}_2 & \text{D} & \text{toluene} & 2h & 80\% \\
14 & \text{Pd(OAc)}_2 & \text{D} & \text{CH}_3\text{CN} & 2h & 75\% \\
15 & \text{Pd(OAc)}_2 & \text{D} & \text{DMSO} & 2h & 51\% \\
16 & \text{Pd(OAc)}_2 & \text{D} & \text{CHCl}_3 & 2h & 78\% \\
17 & \text{Pd(OAc)}_2 & \text{D} & \text{PhCl} & 2h & 92\% \\
18 & \text{Pd(OAc)}_2 & \text{D} & 1,4\text{-dioxiane} & 2h & 72\% \\
19 & \text{Pd(OAc)}_2 & \text{D} & \text{MeOH} & 2h & 85\% \\
20^c & \text{Pd(OAc)}_2 & \text{D} & \text{PhCl} & 2h & 91\% \\
21^d & \text{Pd(OAc)}_2 & \text{D} & \text{PhCl} & 2h & 91\% \\
21^d,e & \text{Pd(OAc)}_2 & \text{D} & \text{PhCl/MeOH} & 2h & 92\%
\end{align*}
\]

*a* Unless noted otherwise, the reactions were carried out on a 0.30 mmol scale of 1a with 4 equiv of HOAc (1.2 mmol), and 2.0 equiv 2a (0.6 mmol) in solvent (0.5 mL). ° Isolated yield. † 50 mg 4APMS was added. ‡ with 3% Pd(OAc)$_2$. *reaction was done in PhCl/MeOH=4:1 (0.4 mL/0.1 mL).
Procedure for Palladium(II)-Catalyzed C-C bond formation of aniline with tert-butyl acrylate:

A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with aniline (0.30 mmol), Pd(OAc)$_2$ (10 mol %, 0.03 mmol), 1,10-phenanthroline (3.6 mol %, 0.036 mmol), tert-butyl acrylate (0.60 mmol) and 4 equiv of HOAc (1.2 mmol) a in DCE. The flask was stirred at 40 °C in air (1 atm) for 12 h and judged by TLC. The reaction mixture was cooled to room temperature, The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.

General Procedure for Palladium(II)-Catalyzed C-C bond formation of arylhydrazines with olefins:

A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with arylhydrazine (0.30 mmol), Pd(OAc)$_2$ (3 mol %, 0.009 mmol), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (3.6 mol %, 0.0108 mmol), and 4 equiv of HOAc (1.2 mmol) a in Ph / MeOH = 4:1 (0.4 mL:0.1 mL). The flask was stirred at 40 °C in air (1 atm) for 2-12 h and judged by TLC. The reaction mixture was cooled to room temperature, The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.
Procedure for synthesis of (2,9-dimethyl-1,10-phenanthroline)-4-cyanophenyl-palladium(II) chloride (1h’):

A solution of preformed Pd(OAc)$_2$ (67.3 mg, 0.3 mmol), 2,9-dimethyl-1,10-phenanthroline (75 mg, 0.36 mmol) in 2 mL of chloroform-d was treated with the 4-hydrazinylbenzonitrile (40 mg, 0.30 mmol) and the resulting mixture was stirred at room temperature for 12 h in glove-box. The solvent is removed under reduced pressure to a volume of approx. 0.2 mL and the crude product is precipitated by addition of 4 mL of absolute diethylether. The crude product is washed with further diethyl ether and the dried under reduced pressure. It is taken up in 3 mL of dichloromethane and filtered through a pad of Celite. The remaining solution is evaporated to dryness under reduced pressure to leave the product as a white solid.

Procedure for Palladium(II)-Catalyzed C-C bond formation of N'-phenyl-acetohydrazide with tert-butyl acrylate:

A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with N'-phenyl-acetohydrazide (0.30 mmol), Pd(OAc)$_2$ (5 mol %, 0.015 mmol), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (6 mol %, 0.018 mmol), tert-butyl acrylate (0.60 mmol) and 4 equiv of HOAc (1.2 mmol) in PhCl / MeOH = 4:1 (0.4 mL:0.1 mL). The
flask was stirred at 40 °C in air (1 atm) for 12 h and judged by TLC. The reaction mixture was cooled to room temperature. The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.

**Characterization Data for the product**

**(E)-tert-butyl 3-(2-((E)-3-tert-butoxy-3-oxoprop-1-enyl)phenylamino)acrylate:** This compound was prepared by the general procedure described above and was obtained as a yellow oil in 28% yield: $R_f = 0.65$ (hexane : ethyl acetate = 7:1); $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 10.70 (d, 1H, $J = 12.8$ Hz, NH), 7.70 (d, 1H, $J = 13.2$ Hz, ArH), 7.32-7.40 (m, 3H), 7.04-7.10 (m, 3H), 6.06 (d, 1H, $J = 15.6$ Hz, CH), 1.58 (s, 9H, 3CH$_3$), 1.50 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.4, 167.9, 146.5, 141.8, 139.7, 129.8, 124.0, 116.5, 112.4, 99.8, 81.4, 79.4, 28.4, 28.3 ppm; HRMS (ESI, m/z): calcd. for C$_{20}$H$_{27}$NO$_4$H$^+$ 346.2018, found 346.2022.

**tert-butyl cinnamate (3a):** This compound was prepared by the general procedure described above and was obtained as a yellow oil in 91% yield: $R_f = 0.72$ (hexane : ethyl acetate = 7:1); $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 7.59 (d, 1H, $J = 16.0$ Hz, CH), 7.45 (d, 2H, $J = 8.4$ Hz, ArH), 6.88 (d, 2H, $J = 8.8$ Hz, ArH), 6.24 (d, 1H, $J = 16.0$ Hz, CH), 3.82 (s, 3H, OCH$_3$), 1.52 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 161.1, 143.2, 129.6, 117.4, 114.3, 80.2, 55.3, 28.2 ppm; HRMS (ESI, m/z): calcd. for C$_{13}$H$_{16}$O$_2$Na$^+$ 227.1048, found 227.1042.

**(E)-tert-butyl 3-(4-methoxyphenyl)acrylate (3b):** This compound was prepared by the general procedure described above and was obtained as a yellow solid in 90% yield: $R_f = 0.70$ (hexane : ethyl acetate = 7:1); $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 7.54 (d, 1H, $J = 16.0$ Hz, CH), 7.45 (d, 2H, $J = 8.4$ Hz, ArH), 6.88 (d, 2H, $J = 8.8$ Hz, ArH), 6.24 (d, 1H, $J = 16.0$ Hz, CH), 3.82 (s, 3H, OCH$_3$), 1.52 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.7, 161.1, 143.2, 129.6, 117.4, 114.3, 80.2, 55.3, 28.2 ppm; HRMS (ESI, m/z): calcd. for C$_{14}$H$_{18}$O$_3$Na$^+$ 257.1154, found 257.1158.

**(E)-tert-butyl 3-p-tolylacrylate (3c):** This compound was prepared by the general procedure
described above and was obtained as a yellow oil in 92% yield: \( R_f = 0.74 \) (hexane : ethyl acetate = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.57 (d, 1H, \( J = 16.0 \) Hz, CH), 7.40 (d, 2H, \( J = 8.0 \) Hz, ArH), 7.17 (d, 2H, \( J = 7.6 \) Hz, ArH), 6.33 (d, 1H, \( J = 16.0 \) Hz, CH), 2.36 (s, 3H, CH\(_3\)), 1.54 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.5, 143.6, 140.3, 132.0, 129.6, 128.0, 119.1, 80.3, 28.2, 21.4 ppm; HRMS (ESI, m/z): calcd. for C\(_{14}\)H\(_{18}\)O\(_2\)Na\(^+\) 241.1204, found 241.1199.

\((E)-\text{tert-butyl 3-(4-fluorophenyl)acrylate} \) (3d): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 85% yield: \( R_f = 0.75 \) (hexane : ethyl acetate = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.54 (d, 1H, \( J = 16.0 \) Hz, CH), 7.46-7.49 (m, 2H, ArH), 7.02-7.07 (m, 2H, ArH), 6.28 (d, 1H, \( J = 16.0 \) Hz, CH), 1.52 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.2, 163.6 (d, \( J = 237.0 \) Hz), 142.2, 130.9 (d, \( J = 3.3 \) Hz), 129.8 (d, \( J = 8.6 \) Hz), 120.0 (d, \( J = 2.1\)Hz), 115.9 (d, \( J = 21.9 \) Hz), 80.6, 28.2 ppm; HRMS (ESI, m/z): calcd. for C\(_{13}\)H\(_{15}\)O\(_2\)FNa\(^+\) 245.0954, found 245.0950.

\((E)-\text{tert-butyl 3-(4-chlorophenyl)acrylate} \) (3e): This compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: \( R_f = 0.75 \) (hexane : ethyl acetate = 7:1); Mp = 67.3-68.5 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.52 (d, 1H, \( J = 16.0 \) Hz, CH), 7.49 (d, 2H, \( J = 8.4 \) Hz, ArH), 7.33 (d, 2H, \( J = 8.4 \) Hz, ArH), 6.33 (d, 1H, \( J = 16.0 \) Hz, CH), 1.52 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.0, 142.1, 135.8, 133.2, 129.1, 120.8, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for C\(_{13}\)H\(_{16}\)O\(_2\)H\(^+\) 239.0839, found 239.0832.

\((E)-\text{tert-butyl 3-(4-bromophenyl)acrylate} \) (3f): This is compound was prepared by the general procedure described above and was obtained as a white solid in 81% yield: \( R_f = 0.74 \) (hexane : ethyl acetate = 7:1); Mp = 64.8-65.9 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.50 (d, 1H, \( J = 16.0 \) Hz, CH), 7.49 (d, 2H, \( J = 8.0 \) Hz, ArH), 7.35 (d, 2H, \( J = 8.4 \) Hz, ArH), 6.34 (d, 1H, \( J = 16.0 \) Hz, CH), 1.52 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.0, 142.1, 133.6,
132.1, 129.3, 124.1, 120.9, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for C₁₃H₁₅O₂Na⁺ 305.0153, found 305.0148.

**(E)-tert-butyl 3-(4-iodophenyl)acrylate (3g):** This compound was prepared by the general procedure described above and was obtained as a yellow solid in 80% yield: R₇ = 0.74 (hexane : ethyl acetate = 7:1); Mp = 66.2-67.4 °C; ^1^H NMR (400 MHz, CDCl₃): δ 7.70 (d, 2H, J = 8.0 Hz, ArH), 7.48 (d, 1H, J = 16.0 Hz, ArH), 7.22 (d, 2H, J = 8.4 Hz, ArH), 6.36 (d, 1H, J = 16.0 Hz, CH), 1.52 (s, 9H, 3CH₃) ppm; ^1^C NMR (100 MHz, CDCl₃): δ 166.0, 142.3, 138.0, 134.2, 129.4, 121.0, 96.1, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for C₁₃H₁₅O₂Na⁺ 353.0015, found 353.0020.

**(E)-tert-butyl 3-(4-cyanophenyl)acrylate (3h):** This compound was prepared by the general procedure described above and was obtained as a white solid in 93% yield: R₇ = 0.62 (hexane : ethyl acetate = 7:1); Mp = 154.8-155.9 °C; ^1^H NMR (400 MHz, CDCl₃): δ 7.65 (d, 2H, J = 8.0 Hz, ArH), 7.58 (d, 2H, J = 8.0 Hz, ArH), 7.55 (d, 1H, J = 16.0 Hz, CH), 6.44 (d, 1H, J = 16.0 Hz, CH), 1.53 (s, 9H, 3CH₃) ppm; ^1^C NMR (100 MHz, CDCl₃): δ 165.4, 141.1, 139.0, 132.6, 128.3, 123.8, 118.4, 113.1, 81.2, 28.1 ppm; HRMS (ESI, m/z): calcd. for C₁₄H₁₄NO₂Na⁺ 252.0995.

**(E)-4-(3-tert-butoxy-3-oxoprop-1-enyl)benzoic acid (3i):** This compound was prepared by the general procedure described above and was obtained as a white solid in 98% yield: R₇ = 0.35 (dichloromethane : ethyl acetate = 3:1); ^1^H NMR (400 MHz, CDCl₃): δ 10.96 (b, 1H, COOH), 8.11 (d, 2H, J = 8.0 Hz, ArH), 7.61 (d, 1H, J = 16.0 Hz, CH), 7.59 (d, 2H, J = 8.0 Hz, ArH), 6.73 (d, 1H, J = 16.0 Hz, CH), 1.54 (s, 9H, 3CH₃) ppm; ^1^C NMR (100 MHz, CDCl₃): δ 171.5, 165.8, 142.0, 139.8, 130.7, 130.3, 127.9, 123.0, 81.1, 28.2 ppm; HRMS (ESI, m/z): calcd. for C₁₄H₁₆O₄Na⁺ 271.0946, found 271.0941.

**(E)-tert-butyl(E)-tert-butyl 3-(4-(trifluoromethyl)phenyl)acrylate (3j):** This compound was prepared by the general procedure described above and was obtained as a yellow oil in 85% yield: R₇ = 0.71 (hexane : ethyl acetate = 7:1); ^1^H NMR (400 MHz, CDCl₃): δ 7.57-7.63.
(E)-

**tert-butyl 3-(4-sulfamoylphenyl)acrylate (3k):** This compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: R<sub>f</sub> = 0.46 (dichloromethane : methanol= 7:1); Mp = 91.8-92.9 °C; <sup>1</sup>H NMR (400 MHz, DMSO-<sub>d</sub>6): δ 7.71-7.88 (m, 4H, ArH), 7.58 (d, 1H, <i>J</i> = 16.0 Hz, CH), 7.41 (b, 2H, NH<sub>2</sub>), 6.63 (d, 1H, <i>J</i> = 16.0 Hz, CH), 1.52 (s, 9H, 3CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-<sub>d</sub>6): δ 165.7, 145.5, 142.3, 137.8, 129.1, 126.6, 122.9, 80.8, 28.3 ppm; HRMS (ESI, m/z): calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>4</sub>SNa<sup>+</sup> 306.0776, found 306.0782.

**tert-butyl 3-m-tolylacrylate (3l):** This compound was prepared by the general procedure described above and was obtained as a yellow oil in 93% yield: R<sub>f</sub> = 0.74 (hexane : ethyl acetate = 7:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.56 (d, 1H, <i>J</i> = 16.0 Hz, CH), 7.29-7.31 (m, 2H, ArH), 7.23-7.27 (m, 1H, ArH), 7.16 (d, 1H, <i>J</i> = 7.3 Hz, ArH), 6.35 (d, 1H, <i>J</i> = 16.0 Hz, CH), 2.35 (s, 3H, CH<sub>3</sub>), 1.53 (s, 9H, 3CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.4, 143.7, 138.4, 134.6, 130.8, 128.7, 128.6, 125.2, 120.0, 80.4, 28.2, 21.3 ppm; HRMS (ESI, m/z): calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>Na<sup>+</sup> 241.1204, found 241.1202.

**tert-butyl 3-(3-bromophenyl)acrylate (3m):** This compound was prepared by the general procedure described above and was obtained as a yellow oil in 93% yield: R<sub>f</sub> = 0.72 (hexane : ethyl acetate = 7:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.65 (s, 1H, ArH), 7.49 (d, 1H, <i>J</i> = 16.0 Hz, CH), 7.47-7.48 (m, 1H, ArH), 7.41 (d, 1H, <i>J</i> = 7.7 Hz, ArH), 7.21-7.25 (m, 1H, ArH), 6.36 (d, 1H, <i>J</i> = 16.0 Hz, CH), 1.53 (s, 9H, 3CH<sub>3</sub>) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.8, 141.8, 136.8, 132.7, 130.6, 130.3, 126.6, 123.0, 121.7, 80.8, 28.2 ppm; HRMS (ESI, m/z): calcd. for C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>BrNa<sup>+</sup> 305.0153, found 305.0155.
(E)-3-(3-tert-butoxy-3-oxoprop-1-enyl)benzoic acid (3n): This compound was prepared by the general procedure described above and was obtained as a white solid in 94% yield: \( R_f = 0.38 \) (dichloromethane : ethyl acetate = 3:1); \( Mp = 159.5-160.7 \) °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.8 (b, 1H, COOH), 8.26 (s, 1H, ArH), 8.10 (d, 1H, \( J = 7.8 \) Hz, ArH), 7.73 (d, 1H, \( J = 7.7 \) Hz, ArH), 7.63 (d, 1H, \( J = 16.0 \) Hz, CH), 7.49 (t, 1H, \( J = 7.7 \) Hz, ArH), 6.47 (d, 1H, \( J = 16.0 \) Hz, CH), 1.54 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 171.5, 166.0, 142.2, 135.2, 132.9, 131.4, 130.1, 129.5, 129.1, 121.7, 80.9, 28.2 ppm; HRMS (ESI, m/z): calcd. for C\(_{14}\)H\(_{16}\)O\(_4\)Na\(^+\) 271.0946, found 271.0937.

(E)-tert-butyl 3-o-tolylacrylate (3o): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 73% yield: \( R_f = 0.71 \) (hexane : ethyl acetate = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.89 (d, 1H, \( J = 16.0 \) Hz, CH), 7.54 (d, 1H, \( J = 8.3 \) Hz, ArH), 7.23-7.25 (m, 1H, ArH), 7.17-7.20 (m, 2H, ArH), 6.29 (d, 1H, \( J = 15.9 \) Hz, CH), 2.43 (s, 3H, CH\(_3\)), 1.54 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.5, 141.3, 137.5, 133.6, 130.7, 129.7, 126.4, 126.3, 121.1, 80.5, 28.2, 19.8 ppm; HRMS (ESI, m/z): calcd. for C\(_{14}\)H\(_{18}\)O\(_2\)Na\(^+\) 241.1204, found 241.1201.

(E)-tert-butyl 3-(2-nitrophenyl)acrylate (3p): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 75% yield: \( R_f = 0.65 \) (hexane : ethyl acetate = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.00 (d, 1H, \( J = 16.0 \) Hz, CH), 7.99-8.00 (m, 1H, ArH), 7.62-7.63 (m, 1H, ArH), 7.49-7.53 (m, 1H, ArH), 6.29 (d, 1H, \( J = 15.9 \) Hz, CH), 1.53 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 165.1, 148.4, 138.7, 133.4, 130.8, 130.0, 129.1, 125.3, 124.9, 81.2, 28.1 ppm; HRMS (ESI, m/z): calcd. for C\(_{13}\)H\(_{16}\)NO\(_4\)Na\(^+\) 272.0899, found 272.0896.

(E)-tert-butyl 3-(3,4-dimethoxyphenyl)acrylate (3q): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 88% yield: \( R_f = 0.61 \) (hexane : ethyl acetate = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.54 (d, 1H, \( J = 16.0 \) Hz, 1H, ArH), 7.31-7.33 (m, 2H, ArH), 6.70-6.72 (m, 2H, ArH), 6.53 (d, 1H, \( J = 15.9 \) Hz, CH), 1.54 (s, 9H, 3CH\(_3\)) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 166.5, 141.3, 137.5, 133.6, 130.7, 129.7, 126.4, 126.3, 121.1, 80.5, 28.2, 19.8 ppm; HRMS (ESI, m/z): calcd. for C\(_{14}\)H\(_{18}\)O\(_2\)Na\(^+\) 241.1204, found 241.1201.
Hz, CH), 7.27 (s, 1H, ArH), 7.24 (d, 1H, J = 6.7 Hz, ArH), 7.11 (d, 1H, J = 7.8 Hz, ArH),
6.31 (d, 1H, J = 15.9 Hz, CH), 2.26 (s, 6H, 2OCH$_3$), 1.54 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.6, 143.7, 139.0, 137.0, 132.4, 130.1, 129.2, 125.6, 118.9, 80.3, 28.2, 19.8, 19.7 ppm; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{20}$O$_4$Na$^+$ 287.1259, found 278.1261.

(E)-**tert**-butyl 3-(3-chloro-4-fluorophenyl)acrylate (3r): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 82% yield: R$_f$ = 0.66 (hexane : ethyl acetate = 7:1);
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.54 (dd, 1H, J = 1.8 Hz, J = 6.9 Hz, ArH), 7.46 (d, 1H, J = 16.0 Hz, CH), 7.34-7.37 (m, 1H, ArH), 7.13 (t, 1H, J = 8.6 Hz, ArH), 6.29 (d, 1H, J = 16.0 Hz, CH), 1.52 (s, 9H, 3CH$_3$) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.7, 158.9 (d, J = 252.9 Hz), 140.9, 132.1 (d, J = 4.2 Hz), 129.9, 127.8 (d, J = 7.4 Hz), 121.7 (d, J = 18.3 Hz), 121.4 (d, J = 2.2 Hz), 117.0 (d, J = 21.6 Hz), 80.9, 28.2 ppm; HRMS (ESI, m/z): calcd. for C$_{13}$H$_{14}$O$_2$ClFNa$^+$ 279.0564, found 279.0566.

(E)-**tert**-butyl 3-(3,5-dichlorophenyl)acrylate (3s): This compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: R$_f$ = 0.67 (hexane : ethyl acetate = 7:1); Mp = 53.6-54.5 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.42 (d, 1H, J = 16.0 Hz, CH), 7.347 (s, 1H, ArH), 7.349 (s, 1H, ArH), 7.32 (s, 1H, ArH), 6.35 (d, 1H, J = 16.0 Hz, CH), 1.52 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.4, 140.4, 137.7, 135.5, 129.5, 126.1, 123.1, 81.1, 28.1 ppm; HRMS (ESI, m/z): calcd. for C$_{13}$H$_{14}$O$_2$Cl$_2$Na$^+$ 295.0269, found 295.0272.

(E)-**tert**-butyl 3-(2,5-difluorophenyl)acrylate (3t): This compound was prepared by the general procedure described above and was obtained as a solid in 73% yield: R$_f$ = 0.66 (hexane : ethyl acetate = 7:1); Mp = 50.1-51.0 °C;
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, 1H, J = 16.0 Hz, CH), 7.17-7.21 (m, 1H, ArH), 7.01-7.06 (m, 2H, ArH), 6.42 (d, 1H, J = 16.0 Hz, CH), 1.53 (s, 9H, 3CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.6, 158.7 (d, J = 242.8 Hz), 157.2 (d, J = 249.4 Hz), 134.8 (t, J = 2.3 Hz), 124.0, 123.9 (d, J = 5.8 Hz), 117.8
(dd, $J = 8.9$ Hz, $J = 24.4$ Hz), 117.3 (dd, $J = 8.6$ Hz, $J = 25.2$ Hz), 114.5 (dd, $J = 3.5$ Hz, $J = 24.5$ Hz), 81.0, 28.1 ppm; HRMS (ESI, m/z): calcd. for C$_{13}$H$_{14}$F$_2$O$_2$Na$^+$ 263.0860, found 263.0870.

**(E)-4-(3-butoxy-3-oxoprop-1-enyl)benzoic acid (3u):** This is compound was prepared by the general procedure described above and was obtained as a white solid in 97% yield: $R_f = 0.35$ (dichloromethane : ethyl acetate = 3:1); $\text{Mp} = 88.6-89.3 \degree \text{C}$; $^1\text{H NMR}$ (400 MHz, DMSO-$d_6$): $\delta$ 7.95 (d, 2H, $J = 8.0$ Hz, ArH), 7.80 (d, 2H, $J = 8.0$ Hz, ArH), 7.67 (d, 1H, $J = 15.9$ Hz, CH), 6.70 (d, 1H, $J = 16.0$ Hz, CH), 4.13 (t, 2H, $J = 6.5$ Hz, OCH$_2$), 1.58-1.61 (m, 2H, CH$_2$), 1.32-1.38 (m, 2H, CH$_2$), 0.88 (t, 3H, $J = 7.3$ Hz, CH$_3$) ppm; $^{13}\text{C NMR}$ (100 MHz, DMSO-$d_6$): $\delta$ 166.8, 166.0, 143.1, 138.1, 132.1, 129.7, 128.4, 120.4, 63.9, 30.3, 18.7, 13.6 ppm; HRMS (ESI, m/z): calcd. for C$_{13}$H$_{14}$O$_2$Na$^+$ 271.0946, found 271.0940

**(E)-4-(3-ethoxy-3-oxoprop-1-enyl)benzoic acid (3v):** This compound was prepared by the general procedure described above and was obtained as a white solid in 96% yield: $R_f = 0.34$ (dichloromethane : ethyl acetate = 3:1); $\text{Mp} = 109.5-110.2 \degree \text{C}$; $^1\text{H NMR}$ (400 MHz, DMSO-$d_6$): $\delta$ 7.95 (d, 2H, $J = 8.0$ Hz, ArH), 7.80 (d, 2H, $J = 8.0$ Hz, ArH), 7.67 (d, 1H, $J = 16.0$ Hz, CH), 6.70 (d, 1H, $J = 16.0$ Hz, CH), 4.18 (q, 2H, $J = 7.1$ Hz, OCH$_2$), 1.25 (t, 3H, $J = 7.1$ Hz, CH$_3$) ppm; $^{13}\text{C NMR}$ (100 MHz, DMSO-$d_6$): $\delta$ 166.8, 165.9, 143.1, 138.1, 132.1, 129.7, 128.4, 120.5, 60.2, 14.2 ppm; HRMS (ESI, m/z): calcd. for C$_{12}$H$_{12}$O$_4$Na$^+$ 243.0633, found 243.0636

**(E)-4-(3-methoxy-3-oxoprop-1-enyl)benzoic acid (3w):** This compound was prepared by the general procedure described above and was obtained as a white solid in 98% yield: $R_f = 0.32$ (dichloromethane : ethyl acetate = 3:1); $\text{Mp} = 149.6-150.5 \degree \text{C}$; $^1\text{H NMR}$ (400 MHz, DMSO-$d_6$): $\delta$ 7.95 (d, 2H, $J = 8.0$ Hz, ArH), 7.80 (d, 2H, $J = 8.0$ Hz, ArH), 7.68 (d, 1H, $J = 15.8$ Hz, CH), 6.71 (d, 1H, $J = 16.0$ Hz, CH), 3.73 (s, 3H, OCH$_3$) ppm; $^{13}\text{C NMR}$ (100 MHz, DMSO-$d_6$): $\delta$ 166.8, 165.9, 143.2, 138.2, 132.1, 129.7, 128.4, 120.1, 51.6 ppm; HRMS (ESI, m/z): calcd. for C$_{11}$H$_{10}$O$_4$Na$^+$ 229.0477, found 229.0477
(E)-butyl 3-p-tolylacrylate (3x): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 89% yield: $R_f = 0.69$ (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, 1H, $J = 15.9$ Hz, CH), 7.42 (d, 2H, $J = 8.0$ Hz, ArH), 7.18 (d, 2H, $J = 8.0$ Hz, ArH), 6.40 (d, 1H, $J = 16.0$ Hz, CH), 4.20 (t, 2H, $J = 6.7$ Hz, OCH$_2$), 2.37 (s, 3H, CH$_3$), 1.67-1.72 (m, 2H, CH), 1.41-1.47 (m, 2H, CH), 0.97 (t, 3H, $J = 7.4$ Hz, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.3, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 64.3, 30.8, 21.4, 19.2, 13.8 ppm; HRMS (ESI, m/z): calcd. for C$_{14}$H$_{18}$O$_2$Na$^+$ 241.1204, found 241.1202

(E)-ethyl 3-p-tolylacrylate (3y): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 86% yield: $R_f = 0.68$ (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, 1H, $J = 15.9$ Hz, CH), 7.42 (d, 2H, $J = 8.0$ Hz, ArH), 7.18 (d, 2H, $J = 8.0$ Hz, ArH), 6.39 (d, 1H, $J = 16.0$ Hz, CH), 4.26 (q, 2H, $J = 7.1$ Hz, OCH$_2$), 2.37 (s, 3H, CH$_3$), 1.33 (t, 3H, $J = 7.1$ Hz, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.2, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4 ppm; HRMS (ESI, m/z): calcd. for C$_{12}$H$_{14}$O$_2$Na$^+$ 213.0891, found 213.0894

(E)-methyl 3-p-tolylacrylate (3z): This compound was prepared by the general procedure described above and was obtained as a yellow solid in 84% yield: $R_f = 0.63$ (hexane : ethyl acetate = 7:1); Mp = 53.2-54.1 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.67 (d, 1H, $J = 15.9$ Hz, CH), 7.42 (d, 2H, $J = 8.0$ Hz, ArH), 7.19 (d, 2H, $J = 7.6$ Hz, ArH), 6.39 (d, 1H, $J = 16.0$ Hz, CH), 3.80 (s, 3H, OCH$_3$), 2.37 (s, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.6, 144.9, 140.7, 131.7, 129.6, 128.1, 116.7, 51.6, 21.5 ppm; HRMS (ESI, m/z): calcd. for C$_{11}$H$_{12}$O$_2$Na$^+$ 199.0735, found 199.0732

(E)-ethyl 3-phenylbut-2-enoate (4): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 72% yield: $R_f = 0.70$ (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.47-7.53 (m, 2H, ArH), 7.36-7.40 (m, 3H, ArH), 6.14 (s,
1H, CH), 4.22 (q, 2H, J = 7.2 Hz, OCH$_2$), 2.58 (s, 3H, CH$_3$), 1.32 (t, 3H, J = 7.2 Hz, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.8, 155.5, 142.3, 129.0, 128.5, 126.3, 117.2, 59.8, 17.9, 14.4 ppm; HRMS (ESI, m/z): calcd. for C$_{12}$H$_{14}$O$_2$Na$^+$ 213.0888, found 213.0891

$^{(E)}$-ethyl 3-(4-cyanophenyl)-5-phenylpent-2-enoate (5): This compound was prepared by the general procedure described above and was obtained as a solid in 45% yield: $R_f = 0.65$ (hexane : ethyl acetate = 7:1); Mp = 51.3-52.5 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, 2H, J = 8.2 Hz, ArH), 7.49 (d, 2H, J = 8.3 Hz, ArH), 7.23-7.27 (m, 2H, ArH), 7.16-7.18 (m, 3H, ArH), 6.06 (s, 1H, CH), 4.22 (q, 2H, J = 7.1 Hz, OCH$_2$), 3.37-3.41 (m, 2H, CH$_2$), 2.70-2.74 (m, 2H, CH$_2$), 1.31 (t, 3H, J = 7.1 Hz, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) (major): δ 165.7, 157.1, 145.9, 140.8, 132.4, 128.4, 127.5, 126.2, 120.3, 118.5, 112.5, 60.3, 35.0, 32.9, 14.3 ppm; HRMS (ESI, m/z): calcd. for C$_{22}$H$_{23}$NO$_2$Na$^+$ 356.1626, found 356.1624

N-phenylcinnamamide (6): This compound was prepared by the general procedure described above and was obtained as a white solid in 78% yield: $R_f = 0.35$ (hexane : ethyl acetate = 3:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.35 (b, 1H, NH), 7.72 (d, 1H, J = 15.9 Hz, CH), 7.66-7.68 (m, 2H, ArH), 7.38-7.40 (m, 2H, ArH), 7.24-7.30 (m, 5H, ArH), 7.07-7.11 (m, 1H, ArH), 6.67 (d, 1H, J = 15.9 Hz, CH) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 164.6, 142.3, 138.2, 134.6, 130.0, 129.1, 128.8, 128.0, 124.5, 121.2, 120.4 ppm; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{13}$NOna$^+$ 246.0895, found 246.0901

cinnamic acid (7): This compound was prepared by the general procedure described above and was obtained as a white solid in 73% yield: $R_f = 0.38$ (dichloromethane : ethyl acetate = 2:1); $^1$H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, 1H, J = 15.9 Hz, CH), 7.42 (d, 2H, J = 8.0 Hz, ArH), 6.39 (d, 1H, J = 8.0 Hz, ArH), 7.81 (d, 1H, J = 16.0 Hz, CH), 7.42 (d, 2H, J = 8.0 Hz, ArH), 7.18 (d, 2H, J = 8.0 Hz, ArH), 6.39 (d, 1H, J = 16.0 Hz, CH), 4.26 (q, 2H, J = 7.1 Hz, OCH$_2$), 2.37 (s, 3H, CH$_3$), 1.33 (t, 3H, J = 7.1 Hz, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.2, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4 ppm; HRMS (ESI, m/z): calcd. for C$_9$H$_6$O$_2$Na$^+$ 171.0422, found 171.0424
(E)-1,2-diphenylethene (8): This compound was prepared by the general procedure described above and was obtained as a white solid in 93% yield: $R_f = 0.78$ (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55-7.57 (m, 4H, ArH), 7.39-7.42 (m, 4H, ArH), 7.29-7.32 (m, 2H, ArH), 7.16 (s, 2H, CH) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.4, 128.8, 128.7, 127.7, 126.6 ppm; HRMS (ESI, m/z): calcd. for C$_{14}$H$_{12}$N$^+$ 181.1017, found 181.1015.

4-(cyclopent-2-enyl)benzonitrile (9) and 4-cyclopentenylbenzonitrile (10): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 80% yield: $R_f = 0.58$ (hexane : ethyl acetate = 7:1) (9:10 = 80:20); $^1$H NMR (400 MHz, CDCl$_3$) (9): $\delta$ 7.57 (d, 2H, $J = 8.0$ Hz, ArH), 7.28 (d, 2H, $J = 8.4$ Hz, ArH), 6.00-6.01 (m, 1H, CH), 5.72-5.74 (m, 1H, CH), 3.93-3.94 (m, 1H, CH), 2.41-2.51 (m, 3H, CH$_2$), 1.63-1.72 (m, 1H, CH$_2$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.2, 133.4, 132.8, 132.3, 128.0, 119.2, 109.8, 51.4, 33.6, 32.5 ppm; HRMS (ESI, m/z): calcd. for C$_{12}$H$_{11}$N$^+$ 170.0970, found 170.0972; $^1$H NMR (400 MHz, CDCl$_3$) (10): $\delta$ 7.57 (d, 2H, $J = 8.0$ Hz, ArH), 7.34 (d, 2H, $J = 8.0$ Hz, ArH), 3.48-3.52 (m, 1H, CH), 2.83-2.89 (m, 2H, CH$_2$), 2.71-2.73 (m, 1H, CH$_2$), 2.41-2.51 (m, 2H, CH$_2$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.3, 132.1, 130.7, 129.7, 127.7, 126.0, 109.6, 43.0, 41.2, 32.9 ppm; HRMS (ESI, m/z): calcd. for C$_{12}$H$_{11}$N$^+$ 170.0970, found 170.0972.

(E)-4-p-tolylbut-3-enenitrile (11): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 71% yield: $R_f = 0.58$ (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25 (d, 2H, $J = 7.9$ Hz, ArH), 7.14 (d, 2H, $J = 7.8$ Hz, ArH), 6.69 (d, 1H, $J = 15.8$ Hz, CH), 5.99 (td, 1H, $J = 5.6$ Hz, $J = 15.7$ Hz, CH), 3.26 (d, 2H, $J = 5.5$ Hz, CH$_2$), 2.34 (s, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.3, 134.5, 132.9, 129.4, 126.4, 117.5, 115.7, 21.2, 20.8 ppm; HRMS (ESI, m/z): calcd. for C$_{11}$H$_{11}$N$^+$ 158.0970, found 158.0969.

3-p-tolylbut-3-enenitrile (12): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 14% yield: $R_f =
0.63 (hexane : ethyl acetate = 7:1); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29 (d, 2H, $J = 8.1$ Hz, ArH), 7.18 (d, 2H, $J = 8.0$ Hz, ArH), 5.60 (s, 1H, CH$_2$), 5.48 (s, 1H, CH$_2$), 3.52 (s, 2H, CH$_2$), 2.36 (s, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.6, 136.8, 135.0, 129.4, 125.4, 117.5, 115.2, 23.9, 21.1 ppm; HRMS (ESI, m/z): calcd. for C$_{11}$H$_{11}$NH$^+$ 158.0970, found 158.0969.

(2,9-dimethyl-1,10-phenanthroline)-4-cyanophenyl-palladium(II) chloride (1h'): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 35% yield: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (d, 2H, $J = 8.4$ Hz, ArH), 7.86 (s, 2H, ArH), 7.55 (b, 2H, ArH), 7.26-7.29 (m, 2H, ArH), 7.15 (d, 2H, $J = 8.0$ Hz, ArH), 3.27 (b, 3H, CH$_3$), 2.08 (b, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.2, 153.6, 137.8, 136.8, 128.8, 127.6, 126.7, 125.3, 120.1, 106.7, 28.5, 26.7 ppm; HRMS (ESI, m/z): calcd. for C$_{21}$H$_{16}$ClN$_3$PdH$^+$ 452.0146, found 452.0141.
Mechanistic study by employing ESI-MS:

Figure 1 shows the ESI-MS spectrum of the reaction mixture of cross-coupling between 4-methoxy phenylhydrazine and tert-butyl acrylate. The reaction mixture was injected directly to ESI-MS after reaction time of 2 hours. Aryl palladium ion 14 (m/z 573) and 18 (m/z 932) and four palladiaziridine complexes 13 (m/z 497), 15 (m/z 603), 16 (m/z 709) and 17 (m/z 731) could be detected as stable species (Figure 1).

Figure 1. ESI(+-)MS spectrum of the reaction mixture of cross-coupling between 4-methoxy phenylhydrazine and tert-butyl acrylate.
37
45