SUPPORTING INFORMATION

Maghemite decorated with ultra-small palladium nanoparticles (γ-Fe₂O₃-Pd): applications in Heck-Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes

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**General information.** All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 pre-coated were used, respectively. The spots were visualized with iodine, and UV light.

**Characterization techniques**

X-ray powder diffraction (XRD) patterns for maghemite and maghemite-Pd samples were recorded at room temperature using a X’Pert PRO MPD diffractometer (PANalytical) in Bragg–Brentano geometry with iron-filtered, Co-Kα radiation (40 kV, 30 mA, $\lambda = 0.1789$ nm) equipped with an X’Celerator detector and programmable divergence and diffracted beam antiscatter-slits. The angular range of measurement was set as $2\theta = 10–105^\circ$, with a step size of 0.017$^\circ$. The identification of the crystalline phases in the experimental XRD pattern was obtained using the X’Pert High Score Plus software that includes a PDF-4+ and ICSD databases. Scanning Electron Microscope (SEM) was performed on Hitachi SU6600 with accelerating voltage15 kV. Energy Dispersive Spectrometry (EDS) was acquired in SEM by Thermo Noran System 7 with Si(Li) Detector. Accelerating voltage was 15 kV and acquisition time was 300 s.

Microscopic images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-Energy Dispersive X-ray Spectroscopy (EDS) with acquisition time 20 min. For HRTEM analysis, the powder samples were dispersed in ethanol and 5 min ultrasonicated. One drop of this solution was placed on a copper grid with holey carbon film. The sample was dried at room temperature.

XPS surface investigation has been performed on the PHI 5000 VersaProbe II XPS system (Physical Electronics) with monochromatic Al-Kα source (15 kV, 50 W) and photon energy
of 1486.7 eV was employed. Dual beam charge compensation was used for all measurements. All the spectra were measured in the vacuum of 1.3 x 10⁻⁷ Pa and at the room temperature of 21 °C. The analyzed area on each sample was spot of 200 µm in diameter. The survey spectra was measured with pass energy of 187.850 eV and electronvolt step of 0.8 eV while for the high resolution spectra was used pass energy of 23.500 eV and electronvolt step of 0.2 eV. The spectra were evaluated with the MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the carbon peak C1s at 284.80 eV.

The transmission $^{57}$Fe Mössbauer spectra were recorded on homemade Mössbauer spectrometer operating at a constant acceleration mode and equipped with 50 mCi $^{57}$Co(Rh) source. For low-temperature (5 K) and in-field (5 T) measurements, the sample was placed inside the chamber of the Spectromagcryomagnetic system (Oxford Instruments); with the Mössbauer spectrometer attached to the system, the setup works in a parallel geometry when the external magnetic field is applied in a parallel direction with respect to the propagation of γ-rays. For fitting the Mössbauer spectra, the MossWinn software program was used. The isomer shift values are referred to α-Fe at room temperature. NMR spectra were measured in DMSO-$d_6$ on a JNM-ECA600II NMR spectrometer (JEOL, Japan) at 298 K. Tetramethylsilane (TMS) was used as the internal reference standard for $^1$H and $^{13}$C NMR experiments. The conversion and selectivity of the reactions were analyzed by GC employing chromatograph Agilent 6820 (Agilent, United States), equipped with flame ionisation detector (FID) and chromatographic column DB5 (30x0.250x0.25). Following experimental parameters were applied: initial temperature 100 °C, increased to 250 °C with a rate of 10 °C/min.
Experimental analysis

Fig. S1. Miller indices, corresponding to maghemite and PdO are shown in black and red numbers, respectively.
Fig. S2. (a-b) HRTEM images of maghemite-Pd showing ultrasmall Pd nanoparticles (<5 nm) covering globular (maghemite nanoparticles (ca. 10-20) nm. (c) TEM image of maghemite-Pd nanoparticles in Suzuki reaction after four cycles.

Table S1. Comparison of selected heterogeneous catalysts used for Suzuki reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(0)/C</td>
<td>TBAB, 2 M Na₂CO₃, DME, 80 °C, O/N</td>
<td>21-95%</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Pd/MgLa mixed oxide</td>
<td>80 °C, Ethanol, K₂CO₃, 1-6h</td>
<td>37-98</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Pd^{2+}-sepiolite</td>
<td>100-130 °C, K₂CO₃, DMF, 20-24h</td>
<td>23-94 b</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Pd HAP-1 (2 x 10⁻³)</td>
<td>120 °C, K₂CO₃, o-Xylene, 4-24 h</td>
<td>80-98 b</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Pd (II)-SBA-16</td>
<td>Pd (II)-SBA-16, K₂CO₃, 80 °C, EtOH : H₂O, 2.5-12 h</td>
<td>28-99</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>PANI-Pd</td>
<td>95 °C, K₂CO₃, Dioxane: H₂O, 4h</td>
<td>75-95</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>SBA-15-XH-Pd</td>
<td>100 °C, DMF: H₂O, NaOAc, 15h</td>
<td>67-98</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>Maghemite-Pd</td>
<td>100 °C, K₂CO₃, DMF: H₂O, 2h</td>
<td>60-95</td>
<td>Present work</td>
</tr>
</tbody>
</table>

*a* Isolated yield, *b* GC yield
Table S2. Comparison of selected heterogeneous catalyst used for Heck reaction.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Yield(^a) (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SBA-15-XH-Pd</td>
<td>100 °C, DMF, K₂CO₃, 15h</td>
<td>93-97</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Pd-MCM-41</td>
<td>150 °C, Na₂CO₃, Bu₄NCl, NMP, 3-22h</td>
<td>54-100(^c)</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>PANI-Pd</td>
<td>140 °C, K₂CO₃, DMA, 40 h</td>
<td>41-98</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>{[Pd(NH₃)₄]/NaY}</td>
<td>140 °C, NaOAc, NMP, 6-24 h</td>
<td>23-79</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>C-(KTB-Pd)</td>
<td>120 °C, K₃PO₄·3H₂O, DMF, 2-12h</td>
<td>72-99</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Maghemite-Pd</td>
<td>110 °C, K₂CO₃, DMF, 1h</td>
<td>60-95</td>
<td>Present work</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield, \(^b\) GC yield, \(^c\) Conversion
Table S3. TOF comparison of various supported Pd catalysts for the reaction of 1-bromo-4-methylbenzene with phenyl boronic acid.

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd Catalyst (mol %)</th>
<th>Conditions</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe₂O₃-Bpy-Pd(OAc)₂</td>
<td>K₂CO₃, toluene, 12h, 80 °C</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Pd- Fe₂O₃@C</td>
<td>K₂CO₃, EtOH, 2h, 60 °C</td>
<td>37</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Pd-Fe₂O₃ heterodimer NCs</td>
<td>K₃PO₄, 1,4-dioxane, 24h, reflux</td>
<td>29</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Pd-SBA-16</td>
<td>K₂CO₃, EtOH: H₂O, 8h, 80 °C</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>SBA-15-SH-Pd</td>
<td>K₂CO₃, DMF: H₂O, 15h</td>
<td>54</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Maghemite-Pd</td>
<td>100 °C, K₂CO₃, DMF: H₂O, 2h</td>
<td>43</td>
<td>Present work</td>
</tr>
</tbody>
</table>

\[
\text{TOF} \ (h^{-1}) = \frac{\text{Yield}}{100} \times \frac{\text{mmol of reactant}}{\text{mmol of Pd}} \times \frac{\text{Time (h)}}{\text{mmol of Pd}}
\]
**Table S4.** TOF comparison of various supported Pd catalysts for the reaction of iodobenzene with butyl acrylate.

\[
\begin{array}{cccc}
\text{Entry} & \text{Catalyst} & \text{Conditions} & \text{TOF(h}^{-1}\text{)} & \text{Ref.} \\
1 & \text{Fe}_3\text{O}_4-\text{NH}_2-\text{Pd} & \text{K}_2\text{CO}_3, \text{NMP}, 130 ^\circ\text{C}, 10h & 10 & 16 \\
2 & \text{Pd-PVP@laponite} & \text{Et}_3\text{N}, 100 ^\circ\text{C}, 4h & 70^a & 17 \\
3 & \text{MNP@NHC-Pd} & \text{NaHCO}_3, \text{DMF}, \text{reflux}, 3h & 2 & 18 \\
4 & \text{Maghemite-Pd} & 100 ^\circ\text{C}, \text{K}_2\text{CO}_3, \text{DMF}: \text{H}_2\text{O}, 2h & 31 & \text{Present work} \\
\end{array}
\]

\(^a\) GC yield,
Table S5. Catalyst reusability study.$^a$

\[
\text{苯-碘+硼酸} \xrightarrow{\text{K}_2\text{CO}_3, \text{maghemite-Pd}} \text{苯-醚}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>1$^{\text{st}}$</th>
<th>2$^{\text{nd}}$</th>
<th>3$^{\text{rd}}$</th>
<th>4$^{\text{th}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)$^b$</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;98</td>
<td>&gt;97</td>
</tr>
<tr>
<td>Isolated yield (%)$^c$</td>
<td>&gt;94</td>
<td>&gt;94</td>
<td>&gt;93</td>
<td>&gt;92</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 1-iodo-4-methylbenzene (0.5 mmol), K$_2$CO$_3$ (1 mmol), 4-methoxyphenylboronic acid (0.7 mmol), maghemite-Pd (18 mg, 0.010 mmol of Pd), DMF: H$_2$O (3 mL), 110°C, $^b$Conversion was measured by GC analysis, $^c$Isolated yield.

Fig. S3. XPS spectrum of reused maghemite-Pd sample after first cycle. The position of the metallic Pd$^0$ is denoted by blue color.
Characterization data of compounds

**(E)-Butyl cinnamate (3a)**

![Chemical structure of (E)-Butyl cinnamate](image)

Transparent oil, 94%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 7.72$ (2H, dd, $J=6.6$ Hz, $J=2.8$ Hz), 7.65 (1H, d, $J=15.9$ Hz), 7.42 (3H, m), 6.64 (1H, d, $J=16.5$ Hz), 4.15 (2H, t, $J=6.6$ Hz), 1.62 (2H, qui, $J=7.7$ Hz), 1.38 (2H, sext, $J=7.7$ Hz), 0.91 (3H, t, $J=7.4$ Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta = 166.28, 144.40, 134.01, 130.45, 128.91, 128.36, 118.12, 63.73, 30.28, 18.67, 13.59$ ppm.

**(E)-Butyl 3-p-tolylacrylate (3b)**

![Chemical structure of (E)-Butyl 3-p-tolylacrylate](image)

Transparent oil, 95%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 7.61$ (3H, m), 7.23 (2H, d, $J=8.2$ Hz), 6.57 (1H, d, $J=15.9$ Hz), 4.14 (2H, t, $J=6.6$ Hz), 2.32 (3H, s), 1.61 (2H, qui, $J=7.7$ Hz), 1.37 (2H, sext, $J=7.7$ Hz), 0.91 (3H, t, $J=7.4$ Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta = 166.39, 144.38, 140.43, 131.30, 129.52, 128.35, 117.00, 63.63, 30.30, 21.01, 18.67, 13.58$ ppm.

**(E)-Methyl 3-p-tolylacrylate (3c)**

![Chemical structure of (E)-Methyl 3-p-tolylacrylate](image)

White solid, 93%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta = 7.61$ (3H, m), 7.23 (2H, d, $J=7.7$ Hz), 6.57 (1H, d, $J=15.9$ Hz), 3.71 (3H, s), 2.33 (3H, s) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta = 166.79, 144.54, 140.48, 131.27, 129.52, 128.35, 116.67, 51.39, 21.01$ ppm.
(E)-Butyl 3-(3-methoxyphenyl)acrylate (3d)\textsuperscript{19}

\begin{center}
\includegraphics[width=0.3\textwidth]{fig1}
\end{center}

Transparent oil, 95%. \textsuperscript{1}H NMR (600 MHz, DMSO-$d_6$): $\delta =$ 7.62 (1H, d, $J=15.9$ Hz), 7.32 (2H, m), 7.28 (1H, m), 6.99 (1H, dd, $J=7.7$ Hz, $J=2.2$ Hz), 6.67 (1H, d, $J=15.9$ Hz), 4.15 (2H, t, $J=6.6$ Hz), 3.79 (3H, s), 1.62 (2H, m), 1.38 (2H, sext, $J=7.7$ Hz), 0.91 (3H, t, $J=7.4$ Hz) ppm. \textsuperscript{13}C NMR (600 MHz, DMSO-$d_6$): $\delta =$ 166.29, 159.60, 144.36, 135.44, 129.91, 121.00, 118.46, 116.63, 112.86, 63.72, 55.23, 30.28, 18.67, 13.58 ppm.

(E)-Butyl 3-(3-nitrophenyl)acrylate (3e, 3k)\textsuperscript{20}

\begin{center}
\includegraphics[width=0.3\textwidth]{fig2}
\end{center}

Light yellow solid, 90% and 88%. \textsuperscript{1}H NMR (600 MHz, DMSO-$d_6$): $\delta =$ 8.55 (1H, s), 8.22 (2H, m), 7.76 (1H, d, $J=15.9$ Hz), 7.70 (1H, t, $J=7.8$ Hz), 6.85 (1H, d, $J=16.5$ Hz), 4.16 (2H, t, $J=6.6$ Hz), 1.63 (2H, m), 1.38 (2H, sext, $J=7.5$ Hz), 0.91 (3H, t, $J=7.4$ Hz) ppm. \textsuperscript{13}C NMR (600 MHz, DMSO-$d_6$): $\delta =$ 165.85, 148.28, 141.96, 135.92, 134.11, 130.32, 124.55, 123.02, 121.13, 63.94, 30.23, 18.64, 13.55 ppm.

(E)-Butyl 3-(4-nitrophenyl)acrylate (3f, 3i, 3n)\textsuperscript{20}

\begin{center}
\includegraphics[width=0.3\textwidth]{fig3}
\end{center}

Yellow solid, 85%, 83%, and 30%. \textsuperscript{1}H NMR (600 MHz, DMSO-$d_6$): $\delta =$ 8.23 (2H, m), 8.01 (2H, m), 7.75 (1H, d, $J=16.5$ Hz), 6.85 (1H, d, $J=15.9$ Hz), 4.17 (2H, t, $J=6.6$ Hz), 1.63 (2H, qui, $J=7.7$ Hz), 1.38 (2H, sext, $J=7.7$ Hz), 0.92 (3H, t, $J=7.4$ Hz) ppm. \textsuperscript{13}C NMR (600 MHz,
DMSO-$d_6$: $\delta= 165.73, 148.04, 141.80, 140.47, 129.45, 123.89, 122.43, 64.07, 30.20, 18.63, 13.55$ ppm.

**(E)-Butyl 3-(3-cyanophenyl)acrylate (3g)**

\[
\text{O} \quad \text{CN}
\]

Transparent oil, 62%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta= 8.27$ (1H, s), $8.07$ (1H, d, $J=7.7$ Hz), $7.87$ (1H, d, $J=7.8$ Hz), $7.67$ (1H, d, $J=15.9$ Hz), $7.62$ (1H, t, $J=7.8$ Hz), $6.82$ (1H, d, $J=15.9$ Hz), $4.16$ (2H, $t$, $J=6.6$ Hz), $1.63$ (2H, m), $1.38$ (2H, sext, $J=7.7$ Hz), $0.91$ (3H, t, $J=7.4$ Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta= 165.94, 142.10, 135.35, 133.48, 132.79, 131.89, 130.06, 120.66, 118.36, 112.11, 63.93, 30.23, 18.64, 13.56$ ppm.

**(E)-Butyl 3-(2-methoxyphenyl)acrylate (3h)**

\[
\text{O} \quad \text{O}
\]

Transparent oil, 82%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta= 7.88$ (1H, d, $J=15.9$ Hz), $7.71$ (1H, dd, $J=7.7$ Hz, $J=1.1$ Hz), $7.42$ (1H, t, $J=7.8$ Hz), $7.09$ (1H, d, $J=8.2$ Hz), $6.98$ (1H, t, $J=7.4$ Hz), $6.60$ (1H, d, $J=15.9$ Hz), $4.14$ (2H, t, $J=6.6$ Hz), $3.87$ (3H, s), $1.62$ (2H, qui, $J=7.7$ Hz), $1.36$ (2H, sext, $J=7.7$ Hz), $0.91$ (3H, t, $J=7.4$ Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta= 166.58, 157.83, 139.13, 132.03, 128.65, 122.20, 120.71, 118.15, 111.73, 63.64, 55.65, 30.29, 18.67, 13.57$ ppm.

**(E)-Butyl 3-(4-acetylphenyl)acrylate (3j)**

\[
\text{O} \quad \text{O}
\]

$^1$H NMR (600 MHz, DMSO-$d_6$): $\delta= 7.88$ (1H, d, $J=15.9$ Hz), $7.71$ (1H, dd, $J=7.7$ Hz, $J=1.1$ Hz), $7.42$ (1H, t, $J=7.8$ Hz), $7.09$ (1H, d, $J=8.2$ Hz), $6.98$ (1H, t, $J=7.4$ Hz), $6.60$ (1H, d, $J=15.9$ Hz), $4.14$ (2H, t, $J=6.6$ Hz), $3.87$ (3H, s), $1.62$ (2H, qui, $J=7.7$ Hz), $1.36$ (2H, sext, $J=7.7$ Hz), $0.91$ (3H, t, $J=7.4$ Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta= 166.58, 157.83, 139.13, 132.03, 128.65, 122.20, 120.71, 118.15, 111.73, 63.64, 55.65, 30.29, 18.67, 13.57$ ppm.
Transparent oil, 84%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 7.97 (2H, d, $J$=8.3 Hz), 7.87 (2H, d, $J$=8.3 Hz), 7.70 (1H, d, $J$=15.9 Hz), 6.78 (1H, d, $J$=15.9 Hz), 4.16 (2H, t, $J$=6.6 Hz), 2.60 (3H, s), 1.63 (2H, m), 1.38 (2H, m), 0.92 (3H, t, $J$=7.4 Hz) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta$= 197.43, 165.98, 143.01, 138.31, 137.69, 128.63, 128.54, 120.63, 63.92, 30.24, 26.81, 18.65, 13.56 ppm.

**(E)-Methyl 3-(2-nitrophenyl)acrylate (3l)**

![](image1.png)

Yellow solid, 82%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 8.08 (1H, d, $J$=8.2 Hz), 7.93 (2H, m), 7.78 (1H, t, $J$=7.4 Hz), 7.68 (1H, t, $J$=7.6 Hz), 6.64 (1H, d, $J$=15.9 Hz), 3.75 (3H, s) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta$= 165.96, 148.27, 139.65, 133.91, 131.03, 129.33, 129.20, 124.71, 122.27, 51.80 ppm.

**(E)-methyl-3-(2-cyanophenyl)acrylate (3m)**

![](image2.png)

White solid, 67%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 8.11 (1H, d, $J$= 7.7 Hz), 7.92 (1H, d, $J$=7.7 Hz), 7.80 (1H, d, $J$=15.9 Hz), 7.77 (1H, t, $J$= 7.7 Hz), 7.62 (1H, t, $J$=7.7 Hz), 6.90 (1H, d, $J$=15.9 Hz), 3.77 (3H, s) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta$= 165.97, 138.94, 136.31, 133.64, 133.50, 130.85, 127.44, 122.58, 117.18, 111.70, 51.89 ppm.

**4-methylbiphenyl (6a, 6c)**

![](image3.png)

White solid, 90%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 7.63 (2H, d, $J$=7.6 Hz), 7.55 (2H, d, $J$=7.6 Hz), 7.45 (2H, t, $J$=7.6 Hz), 7.34 (1H, d, $J$=7.3 Hz), 7.27 (2H, d, $J$=7.6 Hz), 2.34 (3H,
13C NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 140.08, 137.29, 136.69, 129.51, 128.87, 127.10, 126.50, 126.41, 20.65 \) ppm.

\textbf{4-methoxy-4'-'methylbiphenyl (6b)}\textsuperscript{25}

![4-methoxy-4'-'methylbiphenyl (6b)](image)

White solid, 94%. \(^1\)H NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 7.55 \) (2H, m), \( 7.49 \) (2H, d, \( J=7.7 \) Hz), \( 7.22 \) (2H, d, \( J=8.2 \) Hz), \( 6.99 \) (2H, m), \( 3.78 \) (3H, s), \( 2.32 \) (3H, s) ppm. \(^{13}\)C NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 158.66, 136.96, 135.84, 132.48, 129.43, 127.44, 125.97, 114.28, 55.10, 20.59 \) ppm.

\textbf{4-methoxy-4'-'nitrobiphenyl (6d)}\textsuperscript{26}

![4-methoxy-4'-'nitrobiphenyl (6d)](image)

Yellow solid, 95%. \(^1\)H NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 8.26 \) (2H, d, \( J=8.8 \) Hz), \( 7.91 \) (2H, d, \( J=8.8 \) Hz), \( 7.76 \) (2H, d, \( J=8.8 \) Hz), \( 7.09 \) (2H, d, \( J=8.8 \) Hz), \( 3.82 \) (3H, s) ppm. \(^{13}\)C NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 160.18, 146.28, 145.99, 129.91, 128.56, 126.99, 124.08, 114.68, 55.31 \) ppm.

\textbf{4-tert-butylbiphenyl (6e)}\textsuperscript{27}

![4-tert-butylbiphenyl (6e)](image)

White solid, 80%. \(^1\)H NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 7.64 \) (2H, m), \( 7.58 \) (2H, m), \( 7.48 \) (2H, m), \( 7.45 \) (2H, m), \( 7.34 \) (1H, m), \( 1.31 \) (9H, s) ppm. \(^{13}\)C NMR (600 MHz, DMSO-\textit{d_6}): \( \delta = 149.82, 140.08, 137.34, 128.86, 127.13, 126.50, 126.35, 125.68, 34.22, 31.09 \) ppm.
1-(4'-methylbiphenyl-4-yl)ethanone (6f)

White solid, 90%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 8.01 (2H, d, $J$=7.5 Hz), 7.79 (2H, d, $J$=7.4 Hz), 7.64 (2H, d, $J$=8.3 Hz), 7.31 (2H, d, $J$=8.3 Hz), 2.60 (3H, s), 2.36 (3H, s) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta$= 197.43, 144.43, 137.90, 135.97, 135.36, 129.68, 128.88, 126.80, 126.51, 26.72, 20.71 ppm.

1-(1,1':4',1''-terphenyl-4-yl)ethanone (6g)

White solid, 88%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$= 8.06 (2H, d, $J$=7.9 Hz), 7.89 (2H, m), 7.87 (2H, m), 7.82 (2H, m), 7.74 (2H, m), 7.50 (2H, t, $J$=7.5 Hz), 7.41 (1H, t, $J$= 7.4 Hz), 2.63 (3H, s) ppm. $^{13}$C NMR (600 MHz, DMSO-$d_6$): $\delta$ = 197.52, 143.94, 140.08, 139.40, 137.82, 135.69, 129.05, 128.98, 127.76, 127.55, 127.35, 126.74, 126.67, 26.81 ppm.

3'-nitrobiphenyl-4-carbonitrile (6h)

Light yellow solid, 60%. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$=8.51 (1H, t), 8.29 (1H, d, $J$=8.2 Hz), 8.22 (1H, d, $J$=7.8 Hz), 8.00 (4H, m), 7.81 (1H, t, $J$=7.9 Hz) ppm. $^{13}$C NMR (600 MHz,
DMSO-$d_6$: \( \delta = 148.47, 142.24, 139.84, 133.68, 133.04, 130.72, 128.06, 123.34, 121.70, 118.60, 111.18 \) ppm.

4'-methylbiphenyl-2-carbonitrile (6i)$^{30}$

![Chemical structure of 4'-methylbiphenyl-2-carbonitrile (6i)](image)

White solid, 82%. \(^1\)H NMR (600 MHz, DMSO-$d_6$): \( \delta = 7.92 \) (1H, dd, \( J = 7.7 \) Hz, \( J = 1.1 \) Hz), 7.76 (1H, td, \( J = 7.7 \) Hz, \( J = 1.1 \) Hz), 7.59 (1H, d, \( J = 7.7 \) Hz), 7.55 (1H, td, \( J = 7.7 \) Hz, \( J = 1.1 \) Hz), 7.46 (2H, d, \( J = 8.3 \) Hz), 7.33 (2H, d, \( J = 8.3 \) Hz), 2.38 (3H, s) ppm. \(^{13}\)C NMR (600 MHz, DMSO-$d_6$): \( \delta = 144.54, 138.26, 134.97, 133.81, 133.46, 129.98, 129.29, 128.55, 127.93, 118.64, 110.08, 20.75 \) ppm.
$^1$H and $^{13}$C NMR spectra of compounds

$(E)$-Butyl cinnamate (3a)

$^1$HNMR

$^{13}$CNMR
(E)-Butyl 3-p-tolylacrylate (3b)

$^1$HNMR

$^{13}$CNMR
(E)-Methyl 3-p-tolylacrylate (3c)

$^1$HNMR

$^{13}$CNMR
(E)-Butyl 3-(3-methoxyphenyl)acrylate (3d)

$^1$HNMR

$^{13}$CNMR
(E)-Butyl 3-(3-nitrophenyl)acrylate (3e)

$^1$H NMR

$^{13}$C NMR
(E)-Butyl 3-(4-nitrophenyl)acrylate (3f)

$^1$HNMR
(E)-Butyl 3-(3-cyanophenyl)acrylate (3g)

1H NMR

13CNMR

13CNMR
(E)-Butyl 3-(2-methoxyphenyl)acrylate (3h)

$^1$HNMR

$^{13}$CNMR
(E)-Butyl 3-(4-acetylphenyl)acrylate (3j)

$^{1}$H NMR

$^{13}$C NMR
(E)-Methyl 3-(2-nitrophenyl)acrylate (3l)

$^{1}$HNMR

$^{13}$CNR
**(E)-methyl-3-(2-cyanophenyl)acrylate (3m)**

**$^1$HNMR**

**$^{13}$CNMR**
4-methylbiphenyl (6a)

$^1$HNMR

$^{13}$CNMR
4-methoxy-4'-methylbiphenyl (6b)

$^1$HNMR

$^{13}$CNRMR
4-methoxy-4′-nitrobiphenyl (6d)

$^1$HNMR

$^{13}$CNMR
4-tert-butylbiphenyl (6e)

$^1$H NMR

$^{13}$C NMR
1-(4'-methylbiphenyl-4-yl)ethanone (6f)

$\text{H}^1$NMR

$\text{C}^{13}$NMR
1-(1,1':4',1''-terphenyl-4-yl)ethanone (6g)

$^1$HNMR

$^{13}$CNMR
3'-nitrobiphenyl-4-carbonitrile (6h)

$^1$HNMR

$^{13}$C NMR
4'-methylbiphenyl-2-carbonitrile (6i)

$^1$HNMR

$^{13}$CNMR
References