Electronic Supplementary Information

Synergistic effect from Lewis acid and the Ni-W₂C/AC catalyst for highly active and selective hydrogenation of aryl nitro to aryl amine†

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Fig. S1 FTIR spectra for (left) NO₂, (middle) N=O and (right) N-O stretching vibrations for NB, NSB and PHA, respectively, in their sole liquids (cyan) and in the presence of Lewis acid (blue), Ni-W2C/AC catalyst (red), dual Lewis acid and Ni-W2C/AC catalyst (black).
Fig. S2 GC of the reaction mixture while the nitrobenzene is used as substrate: (a) before reaction; (b) after reaction.
Fig. S3 GC of the reaction mixture while the nitrosobenzene is used as substrate: (a) before reaction; (b) after reaction.

Fig. S4 GC of the reaction mixture while the phenylhydroxylamine is used as substrate: (a) before reaction; (b) after reaction.
\begin{itemize}
\item Scan 1349 (3.370 min): 20130307 phl-3.D
\item Scan 1503 (0.198 min): 20130307 yhl-4.D
\item Scan 1569 (0.554 min): 20130319 YHL-1.D
\end{itemize}
Fig. S5 Mass spectra of the various products.

aniline: δ6.702-7.201 (m, AR-H); δ6.805 (m, AR-H); δ3.652 (s, NH₂)
\( o\)-chloroaniline: \( \delta 6.742-7.251 \) (m, AR-H); \( \delta 4.034-4.036 \) (s, \( \text{NH}_2 \)); \( \delta 1.226 \) (m, solvent \( \text{C}_2\text{H}_5\text{OH} \))
$m$-chloroaniline: $\delta 7.262$ (s, CHCl$_3$); $\delta 6.533$-$7.060$ (m, AR-H); $\delta 3.709$-$3.727$ (s, NH$_2$); $\delta 1.240$ (m, C$_2$H$_5$OH)

$p$-chloroaniline: $\delta 7.262$ (s, CHCl$_3$); $\delta 6.599$-$7.110$ (m, AR-H); $\delta 3.656$ (S, NH$_2$); $\delta 1.573$ (m, C$_2$H$_5$OH)
o-aminophenol: δ8.959 (s, AR-OH); δ6.378-6.615 (m, AR-H); δ4.457 (s, NH₂); δ3.391 (m, DMSO); δ2.50 (m, C₂H₅OH)

\[
\begin{align*}
\text{NH}_2 \\
\text{OH}
\end{align*}
\]

\( p \)-aminophenol: δ8.364 (s, OH); δ6.454 (m, AR-H); δ4.395 (s, NH₂); δ3.389 (m, DMSO); δ2.503 (s, C₂H₅OH)

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\begin{align*}
\text{NH}_2 \\
\text{COOH}
\end{align*}
\]

\( p \)-aminobenzoic acid: δ7.613 (m, AR-H); δ5.850 (s, NH₂); δ2.499 (m, C₂H₅OH)
$p$-methoxyaniline: $\delta 6.491-6.646$ (m, AR-H); $\delta 4.608$ (s, NH$_2$); $\delta 3.608$ (s, OCH$_3$); $\delta 3.402$ (m, DMSO); $\delta 2.506$ (m, C$_2$H$_5$OH)
o-phenylenediamine: δ7.251 (S, CHCl₃); δ6.687-6.711 (m, AR-H); δ3.337 (s, NH₂)

p-phenylenediamine: δ6.346 (m, Ar-H); δ4.179 (s, NH₂); δ3.380 (DMSO);
1,2,4-triphenylamine: δ6.765 (m, Ar-H); δ5.933 (s, NH₂); δ3.387 (m, DMSO); δ2.50 (m, C₂H₅OH)

ethyl 4-aminobenzoate: δ7.862 (d, 2H, Ar-H); δ6.620 (d, 2H, Ar-H); δ4.339 (q, 2H, CH₃CH-H); δ4.094 (br, 2H, NH₂); δ1.356 (t, 3H, CH₂-H-CH₂)

o-toluidine: δ7.049 (t, 2H, Ar-H)); δ6.702 (t, 1H, Ar-H); δ6.700 (d, 1H, Ar-H); δ3.695 (s, 2H, NH₂); δ2.163 (s, 3H, CH₃); δ1.230 (m, C₂H₅OH)
p-toluidine: δ6.970 (d, 2H, Ar-H); δ6.641 (d, 2H, Ar-H); δ3.652 (s, 2H, NH$_2$); δ2.233 (s, 3H, CH$_3$); δ1.208 (m, C$_2$H$_5$OH)

**Fig. S6** $^1$HNMR of the various products.