Cu$^{II}$–hydrotalcite catalyzed one–pot three component synthesis of 2$H$-indazoles by consecutive condensation, C–N and N–N bond formations

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5. $^1$H NMR and $^{13}$C NMR spectra of isolated compounds
1. **Characterization techniques of Cu$^{II}$–hydrotalcite (Cu$^{II}$–HT) catalysts:** The X-ray powder diffraction (XRD) patterns of the prepared catalysts were acquired with a Siemens D-5005 diffractometer using a Ni-filtered Cu-Kα radiation (0.15418 nm) source and a Scintillation counter detector. From XRD, we observed typical reflection peaks at 2θ = 11.7, 23.6, 34.6, 35.6, 37.7, 40.4 and 53.31 which are almost identical to the characteristic peaks of the hydrotalcite phase (JCPDC # 460099). The FTIR spectra were recorded on a Nicolet 740 FT–IR spectrometer at ambient conditions, using KBr disks, with a nominal resolution of 4 cm$^{-1}$ and an average of 100 spectra. From FTIR, we observed the intense absorption bands at around 1,350–1,410 and 800–890 cm$^{-1}$ due to symmetric stretching ($\nu_3$) and out-of-plane deformation vibrations ($\nu_2$) of the interlayer carbonate anions, respectively, and broad band at ~3450 cm$^{-1}$ is due to OH$^-$ stretching vibration of brucite-like layers caused by the interlayer water molecules and the hydroxyl groups of the layers. The absorption band at around 445 cm$^{-1}$ ($\delta$ O–M–O) is ascribed to the lattice vibrations of the octahedral sheets of the hydrotalcites.
Figure 1. Powder X-ray diffraction patterns of the Cu$^{II}$–HT materials.
Figure 2. FT–IR spectra of Cu$^{II}$–HT materials.
2. **Recyclability of the Cu$^{II}$–HT catalyst:** We carried out catalyst-recycling experiments by using 2-bromobenzaldehyde, aniline and sodium azide as the model reaction. Remarkably, the used Cu$^{II}$–HT catalyst exhibited without any significant loss of activity and selectivity in terms of desired product (2$H$-indazole) up to three cycles.

![Figure 3. Recycling of Cu$^{II}$–HT catalyst for the reaction between 2-bromobenzaldehyde, aniline and sodium azide.](image)
3. **General information:** $^1$H and $^{13}$C NMR spectra were recorded on a Varian VXR-Unity 200 MHz, Bruker UXNMR/XWIN-NMR Avance-300 MHz, and GEMINI spectrometer. Chemical shifts ($\delta$) are given in parts per million (ppm) relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants ($J$) are reported in hertz (Hz). Splitting patterns of proton are described as s, d, dd, t, q, br s and m stand for the resonance multiplicities singlet, doublet, doublet of doublet, triplet, quartet, broad singlet and multiplet, respectively. Only the most important IR absorptions (cm$^{-1}$) and the molecular ions and/or base peaks in MS are given.
4. \(^1\)H NMR, \(^13\)C NMR, FTIR and MS data of isolated compounds:

**Table 2, Entry 1: 2-Phenyl-2\(H\)-indazole:**

\[^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.38 (s, 1H), 7.92-7.88 (m, 3H), 7.77-7.73 (m, 1H), 7.67-7.63 (m, 1H), 7.53-7.48 (m, 2H), 7.40-7.30 (m, 1H), 7.10-7.05 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 149.8, 140.5, 129.6, 127.9, 126.8, 122.4, 121.0, 120.5, 120.4, 117.9, 116.9; IR (KBr) \(\nu\) 1628, 1518, 1497, 1385, 1317, 1204, 1046, 950, 908, 752, 686 cm\(^{-1}\); MS (EI) \(m/z\): 195 [M\(^{+}\)+1].

**Table 2, Entry 2: 2-(Pyridine-3-yl)-2\(H\)-indazole:**

\[^1\)H NMR (CDCl\(_3\)): \(\delta\) 9.11 (s, 1H), 8.56-8.48 (m, 1H), 8.33-8.25 (m, 1H), 7.96-7.87 (m, 1H), 7.77-7.72 (m, 2H), 7.36-7.28 (m, 2H), 7.13-7.08 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 150.2, 148.2, 138.8, 127.5, 122.7, 122.6, 122.1, 120.5, 117.9, 114.0; IR (KBr) \(\nu\) 1612, 1520, 1475, 1437, 1382, 1203, 1145, 1059, 909, 780, 731 cm\(^{-1}\); MS (EI) \(m/z\): 196 [M\(^{+}\)+1].

**Table 2, Entry 3: 2-(3,4-Dimethylphenyl)-2\(H\)-indazole:**

\[^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.37 (s, 1H), 7.79 (d, \(J = 8.68\) Hz, 1H), 7.70 (d, \(J = 8.49\) Hz, 2H), 7.59-7.56 (m, 1H), 7.34-7.27 (m, 2H), 7.13-7.08 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 149.5, 138.3, 138.0, 136.5, 130.4, 126.5, 122.1, 122.0, 120.2, 118.0, 117.7, 19.8, 19.3; IR (KBr) \(\nu\) 2919, 2860, 1617, 1512, 1458, 1381, 1340, 1138, 1056, 967, 883, 811, 752, 562 cm\(^{-1}\); MS (ESI) \(m/z\): 223 [M\(^{+}\)+1].

**Table 2, Entry 4: 2-\(p\)-Tolyl-2\(H\)-indazole:**

\[^1\)H NMR (CDCl\(_3\)): \(\delta\) 8.37 (s, 1H), 7.79-7.69 (m, 4H), 7.33-7.26 (m, 3H), 7.13-7.08 (m, 1H), 2.42 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 149.5, 137.8, 130.0, 129.5,
126.6, 122.6, 122.2, 120.7, 120.2, 119.7, 117.7, 20.9; IR (KBr) ν 2922, 2858, 1626, 1522, 1384, 1313, 1204, 1118, 1046, 908, 816, 782, 730, 508 cm⁻¹; MS (ESI) m/z: 209 [M⁺+1].

Table 2, Entry 5: 2-(4-Methoxy-2-nitrophenyl)-2H-indazole:

![2-(4-Methoxy-2-nitrophenyl)-2H-indazole](image1)

\(^1\)H NMR (CDCl₃): δ 8.91 (d, \(J = 9.82\) Hz, 1H), 8.00-7.96 (m, 2H), 7.75-7.72 (m, 1H), 7.60-7.50 (m, 3H), 7.33-7.28 (m, 1H), 3.89 (s, 3H); \(^1^3\)C NMR (CDCl₃): δ 178.3, 165.9, 155.3, 132.5, 129.1, 129.0, 127.3, 125.5, 124.0, 123.7, 120.2, 108.9, 108.6, 55.9; IR (KBr) ν 2923, 2853, 1686, 1516, 1459, 1343, 1278, 1039, 757, 697 cm⁻¹; MS (ESI) m/z: 271 [M⁺+2].

Table 2, Entry 6: 2-(4-Methoxyphenyl)-2H-indazole:

![2-(4-Methoxyphenyl)-2H-indazole](image2)

\(^1\)H NMR (CDCl₃): δ 8.37 (s, 1H), 7.84 (t, \(J = 9.00\) Hz, 3H), 7.75 (d, \(J = 8.00\) Hz, 1H), 7.36 (t, \(J = 9.00\) Hz, 1H), 7.15 (t, \(J = 8.00\) Hz, 1H), 7.08 (d, \(J = 9.00\) Hz, 2H), 3.92 (s, 3H); \(^1^3\)C NMR (CDCl₃): δ 159.2, 149.2, 134.0, 126.5, 122.6, 122.3,122.1, 120.2, 117.7, 114.5, 55.5; IR (KBr) ν 2924, 2854, 1597, 1500, 1462, 1252, 1148, 1024, 842, 740, 550 cm⁻¹; MS (ESI) m/z: 225 [M⁺+1].

Table 2, Entry 7: 2-(2-Chlorophenyl)-2H-indazole:

![2-(2-Chlorophenyl)-2H-indazole](image3)

\(^1\)H NMR (CDCl₃): δ 8.34 (s, 1H), 7.80-7.76 (m, 1H), 7.71-7.67 (m, 1H), 7.60-7.57 (m, 1H), 7.50-7.42 m, 3H), 7.32-7.28 (m, 1H), 7.18-7.12 (m, 1H); \(^1^3\)C NMR (CDCl₃): δ 148.3, 146.0, 139.0, 135.1, 130.6, 129.9, 128.5, 127.7, 126.9, 125.2, 122.4, 120.5, 117.9; IR (KBr) ν 1628, 1518, 1484, 1385, 1193, 1060, 953, 757, 611, 537 cm⁻¹; MS (ESI) m/z: 229 [M⁺].
Table 2, Entry 8: 2-(4-Bromophenyl)-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.37 \text{ (s, 1H)}, 7.81-7.77 \text{ (m, 4H)}, 7.74-7.62 \text{ (m, 4H)}; \\
\text{13C NMR (CDCl}_3\text{): } & \delta 149.8, 139.4, 132.6, 127.1, 122.8, 122.7, 122.2, 121.4, 120.3, 120.2, 117.8; \\
\text{IR (KBr) } & \nu 2926, 2856, 1631, 1591, 1492, 1384, 1304, 1020, 1007, 952, 909, 817, 752 \text{ cm}^{-1}; \\
\text{MS (ESI) } & m/z: 273 \text{ [M}^+\text{]+1].
\end{align*}
\]

Table 2, Entry 9: 5-Fluoro-2-(3,4-dimethylphenyl)-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.32 \text{ (s, 1H)}, 7.77-7.74 \text{ (m, 1H)}, 7.70-7.67 \text{ (m, 1H)}, 7.57-7.52 \text{ (m, 2H)}, 7.50-7.48 \text{ (m, 2H)}, 7.48-7.45 \text{ (m, 1H)}, 7.23-7.20 \text{ (m, 3H)}, 7.08-7.05 \text{ (m, 3H)}; \\
\text{13C NMR (CDCl}_3\text{): } & \delta 160.1, 156.9, 138.1, 136.7, 130.4, 121.9, 120.4, 120.2, 119.8, 119.7, 118.2, 117.9, 19.8, 19.3; \\
\text{IR (KBr) } & \nu 2924, 2855, 1640, 1522, 1457, 1382, 1230, 1171, 964, 806, 732 \text{ cm}^{-1}; \\
\text{MS (ESI) } & m/z: 241 \text{ [M}^+\text{]+1].
\end{align*}
\]

Table 2, Entry 10: 2-(2-Methoxy-4-methylphenyl)-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.52 \text{ (s, 1H)}, 7.79-7.70 \text{ (m, 2H)}, 7.39-7.28 \text{ (m, 1H), 7.22-7.17 \text{ (m, 1H), 7.13-7.06 \text{ (m, 1H), 7.03-6.98 \text{ (m, 1H), 3.87 \text{ (s, 3H), 2.37 \text{ (s, 3H)}; } \\
\text{13C NMR (CDCl}_3\text{): } & \delta 156.8, 148.6, 135.6, 130.8, 129.5, 126.9, 126.8, 126.4, 125.5, 121.7, 120.4, 117.5, 112.3, 56.1, 20.3; \\
\text{IR (KBr) } & \nu 2925, 2853, 1689, 1514, 1460, 1383, 1251, 1141, 1026, 911, 803, 735, 608 \text{ cm}^{-1}; \\
\text{MS (ESI) } & m/z: 239 \text{ [M}^+\text{]+1].
\end{align*}
\]

Table 2, Entry 11: 5-Fluoro-2-phenyl-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.37 \text{ (s, 1H)}, 7.89-7.87 \text{ (d, } J = 7.72 \text{ Hz, 2H), 7.78-7.75 \text{ (m, 1H), 7.53 \text{ (t, } J = 7.72 \text{ Hz, 2H), 7.41 \text{ (t, } J = 7.72 \text{ Hz, 1H), 7.29-7.26 \text{ (m, 1H), 7.15-7.11 \text{ (m, 1H); } \\
\text{13C NMR (CDCl}_3\text{): } & \delta
\end{align*}
\]
157.0, 147.1, 140.3, 129.5, 128.0, 120.8, 120.4, 120.0, 119.9, 118.6, 118.2, 102.7, 102.4; IR (KBr) ν 1682, 1526, 1374, 1214, 1149, 1079, 907, 732, 650 cm⁻¹; MS (ESI) m/z: 213 [M⁺+1].

Table 2, Entry 12: 5-Fluoro2-adamantyl-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 7.99 (s, 1H), 7.71-7.68 (m, 1H), \\
& 7.24-7.21 (m, 1H), 7.07-7.03 (m, 1H), 2.32-2.27 (m, 9H), 1.82-1.80 (m, 6H); \\
\text{13C NMR (CDCl}_3\text{): } & \delta 145.4, 119.4, 119.3, 118.6, 118.5, 117.0, 116.6, 60.4, 43.1, 36.0, 29.5; IR (KBr) ν 2917, 2854, 1516, 1455, 1373, 1310, 857, 808, 766, 730 cm⁻¹; MS (ESI) m/z: 271 [M⁺+1].
\end{align*}
\]

Table 2, Entry 13: 2-Adamantyl-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.05 (s, 1H), 7.75 (d, J = 8.39 Hz, 1H), \\
& 7.66 (d, J = 8.39 Hz, 1H), 7.26 (t, J = 8.39 Hz, 1H), \\
& 7.05 (t, J = 8.39 Hz, 1H), 2.34-2.28 (m, 9H), 1.83-1.80 (m, 6H); \\
\text{13C NMR (CDCl}_3\text{): } & \delta 148.0, 125.4, 121.0, 120.9, 120.1, 118.4, 117.4, 60.1, 43.1, 36.0, 29.5; IR (KBr) ν 2915, 2856, 1516, 1454, 1385, 1309, 1149, 1052, 908, 730, 647 cm⁻¹; MS (ESI) m/z: 253 [M⁺+1].
\end{align*}
\]

Table 2, Entry 14: 2-(4-Bromo-2,6-dimethylphenyl)-2H-indazole:

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{): } & \delta 8.58 (s, 1H), 8.25-8.21(m, 1H), \\
& 7.64-7.60 (m, 1H), 7.46-7.32 (m, 2H), 7.24-7.20 (m, 2H), 2.13 (s, 6H); \\
\text{13C NMR (CDCl}_3\text{): } & \delta 162.6, 149.9, 134.3, 133.2, 132.6, 131.6, 130.6, 129.2, 128.6, 127.7, 125.8, 116.6, 18.1; IR (KBr) ν 2924, 2855, 1726, 1463, 1279, 1186, 1079, 967, 746, 606, 543 cm⁻¹; MS (ESI) m/z: 301 [M⁺+1].
\end{align*}
\]
Table 2, Entry 15: 2-(4-Bromo-2,6-dimethylphenyl)-5-fluoro-2H-indazole:

$^1$H NMR (CDCl$_3$): $\delta$ 8.52 (d, $J = 2.26$ Hz, 1H), 7.98-7.94 (m, 1H), 7.64-7.57 (m, 2H), 7.24-7.21 (m, 2H), 2.13 (s, 6H); $^{13}$C NMR (CDCl$_3$): $\delta$ 161.5, 149.4, 138.8, 134.6, 134.5, 131.4, 130.7, 129.2, 120.2, 119.9, 116.9, 115.4, 115.1, 18.2; IR (KBr) $\nu$ 2923, 2855, 1522, 1459, 1375, 1244, 910, 724, 628, 520 cm$^{-1}$; MS (ESI) $m/z$: 319 [M$^+$+1].
5. $^1$H NMR and $^{13}$C NMR spectra of isolated compounds

Table 2, Entry 1: 2-Phenyl-2$H$-indazole:
Table 2, Entry 2: 2-(Pyridine-3-yl)-2H-indazole:

![Diagram of the molecule](image_url)
Table 2, Entry 3: 2-(3,4-Dimethylphenyl)-2H-indazole:
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Table 2, Entry 15: 2-(4-Bromo-2,6-dimethylphenyl)-5-fluoro-2H-indazole: