Supporting for

Recyclable Cu/C₃N₄ composite materials catalyzed homo- and cross-coupling of terminal alkynes under mild conditions

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1. Preparation and characterization of catalyst

The Cu/C₃N₄ catalyst was synthesized following the reported method. Typically, melamide (2g) was uniformly mixed with copper(II) acetate (625mg). The resulting mixture was then heated to 550 °C with 2°C/min in a tube furnace under N₂ atmosphere and kept for 2 h. After cooling to room temperature, the final solid product (Cu-doped C₃N₄) was collected without further purification.

![XRD patterns of pure C₃N₄ and Cu/C₃N₄](image)

**Figure S1.** XRD patterns of pure C₃N₄ and Cu/C₃N₄.

Figure S1 shows the XRD patterns of pure C₃N₄ and 20% Cu/C₃N₄. It was found that the XRD pattern of 20% Cu/C₃N₄ was similar to pure C₃N₄. This result indicates that the structure of C₃N₄ remains unchanged when copper species were host by coordination with the N atom.
2. Experimental section

2.1 General information
All experiments were carried out under oxygen atmosphere. Flash column chromatography was performed over silica gel 200-300 mesh. $^1$H NMR spectra were acquired by 400 MHz, and $^{13}$C NMR spectra were acquired by 101 MHz. Compound 3g and 3j are unknown compounds and were characterized by m.p., $^1$H & $^{13}$C NMR, LR & HR MS. All of the known compounds described in the paper were characterized by comparing their $^1$H & $^{13}$C NMR to the previously reported data.

2.2 Condition optimization for the homo-coupling of phenylacetylene(1a)

Table S1 Screening bases for the homo-coupling of phenylacetylene catalyzed by 5% Cu/C$_3$N$_4$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield(%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>K$_2$CO$_3$</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>NaHCO$_3$</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Na$_2$CO$_3$</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Et$_3$N</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>NaOH</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>Py</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>KOH</td>
<td>74</td>
</tr>
<tr>
<td>9 $^c$</td>
<td>KOH</td>
<td>65</td>
</tr>
</tbody>
</table>

$^a$ The reaction was carried out using 1a (0.2 mmol) and base (2 eq) in the presence of catalyst (10 mol%) in IPA (0.5 mL) at rt under O$_2$. $^b$ Isolated yields. $^c$ KOH 1eq.
2.3 Condition optimization for the cross-coupling of phenylacetylene (1a) and \( p \)-Methoxyphenlacetylene (1b)

**Table S2** Screening ratio for the cross-coupling of phenylacetylene and \( p \)-Methoxyphenlacetylene catalyzed by 20% Cu/C₃N₄.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>1b (mmol)</th>
<th>1a (mmol)</th>
<th>Yield(%) b</th>
<th>Yield(%) c</th>
<th>Yield(%) d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>43 (0.043)</td>
<td>49 (0.025)</td>
<td>38 (0.019)</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.2</td>
<td>60 (0.060)</td>
<td>59 (0.059)</td>
<td>38 (0.019)</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.5</td>
<td>78 (0.078)</td>
<td>65 (0.163)</td>
<td>15 (0.011)</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.1</td>
<td>65 (0.065)</td>
<td>30 (0.015)</td>
<td>61 (0.076)</td>
</tr>
<tr>
<td>5e</td>
<td>0.1</td>
<td>0.5</td>
<td>65 (0.065)</td>
<td>65 (0.163)</td>
<td>8 (0.008)</td>
</tr>
<tr>
<td>6f</td>
<td>0.1</td>
<td>0.5</td>
<td>trace</td>
<td>34 (0.084)</td>
<td>8 (0.008)</td>
</tr>
<tr>
<td>7g</td>
<td>0.1</td>
<td>0.5</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
</tr>
</tbody>
</table>

\( a \) The reaction was carried out using 20% Cu/C₃N₄ (10 mmol%) and KOH (2 eq) in IPA (0.5 mL) at rt under O₂; Isolated yield. \( b \) the numbers in the parentheses are amounts of 3a (mmol). \( c \) Yields based on 1a; the numbers in the parentheses are amounts of 2a (mmol). \( d \) Yields based on 1b; the numbers in the parentheses are amounts of 2b (mmol). \( e \) With 4 equiv. of IPA. \( f \) Neat. \( g \) CH₃CN (0.5 mL) as solvent.
2.4 Typical procedure for the synthesis of symmetric 1,3-diynes

Phenylacetylene (1a, 0.2 mmol), 20% Cu/C₃N₄ (10 mol%), KOH (2 eq) and 0.5 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O₂. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (pure hexanes). Compound 2a was obtained in 99% of yield.

2-Methylbut-3-yn-2-ol (1l, 1 mmol), 20% Cu/C₃N₄ (10 mol%), KOH (2 eq) were added into a 10 mL sealed tube under O₂. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (hexanes/ethyl acetate=5:1). Compound 2l was obtained in 55% of yield.

2.5 Typical procedure for the synthesis of unsymmetrical 1,3-diynes

Phenylacetylene (1a, 0.5 mmol), p-methoxyphenylacetylene (1b, 0.1 mmol), 20% Cu/C₃N₄ (10 mol%), KOH (2 eq) and 0.5 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O₂. The mixture was stirred at room temperature for 6 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (pure hexanes). Compound 3a was obtained in 78% of yield.
2.6 The experiments of catalyst recycle

Phenylacetylene (1a, 1 mmol), 20% Cu/C₃N₄ (10 mol%), KOH (2 eq) and 2 mL of isopropanol (0.5 mL) were added into a 10 mL sealed tube under O₂. The mixture was stirred at room temperature for 6 hours. After completion of the reaction, the catalyst was separated by centrifugation and washed by water and ether, and then, dried under vacuum at 60 °C. The recovered catalyst was reused for the next cycle with fresh starting materials and solvent.

Table S3. Recycling of the Cu/C₃N₄ catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>Fresh</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield(%)b</td>
<td>98</td>
<td>97</td>
<td>98</td>
<td>97</td>
<td>93</td>
<td>91</td>
<td>91</td>
<td>92</td>
<td>93</td>
<td>92</td>
<td>91</td>
</tr>
</tbody>
</table>

* The reaction was carried out using 1a (1.0 mmol) and KOH (2eq) in the presence of 20% Cu/C₃N₄ (10mol%) in IPA (2 mL) at rt under O₂. bIsolated yields
Characterization for compounds 2 & 3

1,4-diphenyl buta-1,3-diyne (2a) \textsuperscript{12}: White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.54-7.51 (m, 4 H), 7.36-7.31 (m, 6 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 132.79, 129.09, 128.45, 121.82, 81.56, 73.92.

1,4-bis(p-methoxyphenyl)buta-1,3-diyne (2b) \textsuperscript{12}: White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.46 (d, J = 9.2 Hz, 4 H), 6.85 (d, J = 8.8 Hz, 4 H), 3.82 (s, 6 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 160.25, 134.05, 114.14, 113.97, 81.32, 72.95, 55.35.

1,4-Bis(4-ethylphenyl)buta-1,3-diyne (2c) \textsuperscript{3}: White solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.42 (d, J = 7.6 Hz, 4 H), 7.14 (d, J = 7.6 Hz, 4 H), 2.36 (s, 6 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 139.53, 132.43, 129.25, 118.84, 81.58, 73.48, 21.66.

1,4-Bis(4-n-propylphenyl)buta-1,3-diyne (2e) \textsuperscript{12}: Yellow solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 4 H), 7.14 (d, J = 7.6 Hz, 4 H), 2.59 (t, J = 7.6 Hz, 4 H), 1.68-1.59 (m, 4 H), 0.94 (t, J = 7.2 Hz, 4 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) δ 145.67, 132.50, 128.03, 119.41, 81.58, 73.38, 28.93, 15.25.

1,4-Bis(4-n-pentylphenyl)buta-1,3-diyne (2f) \textsuperscript{3}: Yellow solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 4 H), 7.14 (d, J = 7.6 Hz, 4 H), 2.60 (t, J = 7.6 Hz, 4 H), 1.64-1.57 (m, 4 H), 1.32 (m, 8 H), 0.90-0.87 (m, 6 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) δ
144.51, 132.42, 128.57, 119.05, 81.59, 73.48, 35.97, 31.44, 30.86, 22.51, 14.01.

\[
\begin{align*}
\text{F}_3\text{C} & \equiv \equiv \equiv \text{CF}_3 \\
\text{2g}
\end{align*}
\]

1,4-Bis(4-trifluoromethyl)buta-1,3-diyne (2g): Yellow solid; \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz): \(\delta 7.63 \ (q, J = 8.4 \text{ Hz}, J = 4.0 \text{ Hz}, 8 \text{ H})\); \(^{13}\text{C NMR}\) (CDCl\(_3\), 101 MHz): 132.83, 131.13 (q, \(J = 33.0 \text{ Hz}\)), 125.48 (q, \(J = 3.7 \text{ Hz}\)), 123.70 (q, \(J = 273.4 \text{ Hz}\)), 80.98, 75.65.

\[
\begin{align*}
\text{2h}
\end{align*}
\]

1,4-Bis(4-fluorophenyl)buta-1,3-diyne (2h): White solid; \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta 7.53-7.50 \ (m, 4 \text{ H}), 7.04 \ (t, J = 8.4 \text{ Hz}, 4 \text{ H})\); \(^{13}\text{C NMR}\) (CDCl\(_3\), 101 MHz) \(\delta 163.1, 134.57 \ (d, J = 8.0 \text{ Hz}), 117.86 \ (d, J = 3.0 \text{ Hz}), 115.94 \ (d, J = 22.2 \text{ Hz})\), 80.46, 73.57.

\[
\begin{align*}
\text{2i}
\end{align*}
\]

1,4-bis(m-methylphenyl)buta-1,3-diyne (2i): White solid. \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta 7.28-7.25 \ (m, 4 \text{ H}), 7.17-7.10 \ (m, 4 \text{ H}), 2.27 \ (s, 6 \text{ H})\); \(^{13}\text{C NMR}\) (CDCl\(_3\), 101 MHz) \(\delta 138.1, 133.0, 130.1, 129.6, 128.3, 121.7, 81.6, 73.7, 21.2\).

\[
\begin{align*}
\text{2j}
\end{align*}
\]

3,3'-(Buta-1,3-diyne-1,4-diyl)dibenzenamine (2j): Yellow solid; \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta 7.11 \ (t, J = 7.6 \text{ Hz}, 2 \text{ H}), 6.93 \ (d, J = 7.6 \text{ Hz}, 2 \text{ H}), 6.82 \ (s, 2 \text{ H}), 6.68 \ (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 3.71 \ (s, 4 \text{ H})\); \(^{13}\text{C NMR}\) (CDCl\(_3\), 101 MHz) \(\delta 146.34, 129.41, 123.00, 122.51, 118.44, 116.30, 81.68, 73.42\).

\[
\begin{align*}
\text{2k}
\end{align*}
\]

1,4-Bis(2-thienyl) buta-1,3-diyne (2i): Yellow solid; \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta 7.35-7.31 \ (m, 4\text{ H}), 7.00-6.98 \ (m, 2\text{ H})\); \(^{13}\text{C NMR}\) (CDCl\(_3\), 101 MHz) \(\delta 134.41, 128.92, 127.22, 121.91, 77.83, 76.64\).
2,7-dimethyl octa-3,5-diyne-2,7-diol (2l) \textsuperscript{s5}: Colorless liquid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): $\delta$ 1.47 (s, 12 H), 1.36 (s, 2 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): $\delta$ 83.99, 66.33, 65.59, 31.05.

Dodeca-5,7-diyne (2m) \textsuperscript{s2}: Yellow liquid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): $\delta$ 2.18 (t, $J$ = 6.8 Hz, 4 H), 1.47-1.30 (m, 8 H), 0.83 (t, $J$ = 7.2 Hz, 6 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): $\delta$ 77.49, 65.26, 30.41, 21.94, 18.90, 13.54.

1,4-dicyclohexylbuta-1,3-diyne (2n) \textsuperscript{s5}: Colorless liquid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) $\delta$ 2.46-2.40 (m, 2 H), 1.81-1.77 (m, 4 H), 1.71-1.68 (m, 4 H), 1.49-1.41 (m, 6 H), 1.33-1.26 (m, 6 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): $\delta$ 80.86, 64.08, 31.27, 28.48, 24.47, 23.77.

1-methoxy-4-(phenylbuta-1, 3-diyn-1-yl) benzene (3a) \textsuperscript{s2}: Colorless solid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.52 (d, $J$ = 6.8 Hz, 2 H), 7.47 (d, $J$ = 8.4 Hz, 2 H), 7.36-7.31 (m, 3 H), 6.86 (d, $J$ = 8.4 Hz, 2 H), 3.83 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): $\delta$ 160.38, 134.13, 132.44, 129.02, 128.42, 122.03, 114.17, 113.72, 81.82, 81.03, 74.18, 72.74, 55.35.

1-((4-methoxyphenyl)buta-1,3-diynyl)-4-methylbenzene (3b) \textsuperscript{s2}: White solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): $\delta$ 7.39 (d, $J$ = 8.8 Hz, 2 H), 7.34 (d, $J$ = 8.0 Hz, 2 H), 7.06 (d, $J$ = 8.0 Hz, 2 H), 6.78 (d, $J$ = 8.8 Hz, 2 H), 3.74 (s, 3 H), 2.29 (s, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): $\delta$ 160.30, 139.41, 134.09, 132.36, 129.21, 118.89, 114.08, 113.86, 81.46, 81.32, 73.52, 72.86, 55.35, 21.63.
1-Ethyl-4-((4-methoxyphenyl)buta-1,3-diynyl)benzene (3c) \textsuperscript{s2}: White solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.45 (t, \( J = 9.2 \) Hz, 4 H), 7.16 (d, \( J = 7.6 \) Hz, 2 H), 6.86 (d, \( J = 8.0 \) Hz, 2 H), 3.83 (s, 3 H), 2.66 (q, \( J = 7.6 \) Hz, 2 H), 1.25-1.21 (m, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): \( \delta \) 160.30, 145.67, 134.09, 132.46, 128.02, 119.11, 114.15, 113.86, 81.45, 81.36, 73.51, 72.89, 55.35, 28.92, 15.26.

1-Propyl-4-((4-methoxyphenyl)buta-1,3-diynyl)benzene (3d) \textsuperscript{s2}: Yellow solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.48-7.42 (m, 4 H), 7.14 (d, \( J = 8.0 \) Hz, 2 H), 6.85 (d, \( J = 8.4 \) Hz, 2 H), 3.82 (s, 3 H), 2.59 (t, \( J = 7.6 \) Hz, 2 H), 1.68-1.59 (m, 2 H), 0.93 (t, \( J = 7.2 \)Hz, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): \( \delta \) 160.33, 144.19, 134.12, 132.40, 128.65, 119.15, 114.18, 113.90, 81.49, 81.41, 73.57, 72.94, 55.38, 38.08, 24.31, 13.79.

1-methoxy-4-((4-pentylphenyl)buta-1,3-diynyl)benzene (3e) \textsuperscript{s6}: Yellow solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 7.48-7.42 (m, 4 H), 7.14 (d, \( J = 7.2 \) Hz, 2 H), 6.86 (d, \( J = 8.0 \) Hz 2 H), 3.83 (s, 3 H), 2.60 (t, \( J = 7.6 \) Hz, 2 H), 1.64-1.57 (m, 2 H), 1.36-1.31 (m, 4 H), 0.91-0.87 (m, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) \( \delta \) 160.39, 144.48, 134.09, 132.38, 128.56, 119.07, 114.02, 81.42, 73.53, 72.91, 55.35, 35.97, 31.43, 30.86, 22.51, 14.07.

1-(4-Methoxyphenyl)-4-(m-toluenyl)-buta-1,3-diyne (3f) \textsuperscript{s7}: White solid; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \( \delta \) 7.47 (d, \( J = 8.4 \) Hz, 2 H), 7.34-7.32 (m, 2 H), 7.24-7.16 (m, 2 H), 6.86 (d, \( J = 8.4 \) Hz, 2 H), 3.82 (s, 3 H), 2.33 (s, 3 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz): \( \delta \) 160.34, 138.14, 134.12, 132.93, 129.99, 129.56, 128.31, 121.80, 114.16, 113.80, 81.61, 81.27, 73.81, 72.82, 55.35, 21.22.
3-((4-methoxyphenyl)buta-1,3-diyln-1-yl)aniline (3g): Yellow solid; MP. 78-81°C

$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.46 (d, $J = 8.4$ Hz, 2 H), 7.13-7.09 (m, 2 H), 6.93 (d, $J = 7.6$ Hz, 1 H), 6.87-6.82 (m, 3 H), 3.82 (s, 3 H), 3.70 (s, 2 H); $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 160.33, 146.28, 134.11, 129.35, 122.93, 122.64, 118.36, 116.13, 114.15, 1113.80, 81.52, 81.36, 73.52, 72.84, 55.35; MS (EI) m/z (%): 247(M$^+$), 232, 205(100), 190, 149, 121. HRMS calc for C$_{17}$H$_{13}$NO: 247.0997; found 247.0999.

![3g](image)

1-(4-Methoxyphenyl)-4-(4-fluorophenyl)-buta-1,3-diyne (3h) $^{32}$: White solid; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.48 (m, 4 H), 7.03-7.00 (m, 2 H), 6.89-6.85 (m, 2 H), 3.83 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 162.93 (d, $J = 250$ Hz), 160.44, 134.44 (d, $J = 8.0$ Hz), 134.15, 118.16 (d, $J = 8.0$ Hz), 115.85 (d, $J = 22$ Hz), 114.2, 113.61, 81.82, 79.92, 73.96, 72.59, 55.36.

![3h](image)

1-(4-Methoxyphenyl)-4-(4-trifluorophenyl)-buta-1,3-diyne (3i) $^{48}$: Yellow solid; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.53 (dd, $J_1 = 8.6$ Hz, $J_2 = 11.4$ Hz, 4 H), 7.41 (d, $J = 8.3$ Hz, 2 H), 6.80 (d, $J = 8.3$ Hz, 2 H), 3.76 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 160.68, 134.30, 132.64, 130.58 (q, $J = 32.9$ Hz), 125.99 (d, $J = 1.1$ Hz), 125.38 (dd, $J_1 = 3.7$ Hz, $J_2 = 7.5$ Hz), 123.82 (q, $J = 273.3$ Hz), 114.28, 113.28, 83.24, 79.36, 76.60, 72.36, 55.40.

![3i](image)

1-(4-Methylphenyl)-1,3-octadiyne (3j) $^{69}$: White liquid; $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.34 (d, $J = 8.4$ Hz, 2 H), 6.75 (d, $J = 8.0$ Hz, 2 H), 3.74 (s, 3 H), 2.29 (t, $J = 6.8$ Hz, 2 H), 1.50-1.45 (m, 2 H), 1.42-1.33(m, 2 H), 0.85 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 160.06, 134.08, 114.07, 84.19, 74.85, 73.16, 65.22, 55.34, 30.38, 29.74, 21.98, 19.31, 13.57.

![3j](image)
3-(p-tolylbuta-1,3-diyn-1-yl)aniline (3k): Yellow solid; MP. 105-107 °C. \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta \) 7.41 (d, \( J = 7.6 \) Hz, 2 H), 7.15-7.09 (m, 3 H), 6.93 (d, \( J = 7.6 \) Hz, 1 H), 6.82 (s, 1 H, \( J = 8.0 \) Hz), 6.68 (d, \( J = 8.0 \) Hz, 1 H), 3.70 (s, 2 H), 2.36 (s, 3 H); \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta \) 146.35, 139.60, 132.45, 129.41, 129.27, 122.98, 118.77, 118.42, 116.26, 81.65, 81.52, 73.47, 21.67; MS (EI) m/z (%): 231(M\(^+\), 100), 202, 163, 139, 115, 101, 88. HRMS calcd for C\(_{17}\)H\(_{13}\)N: 231.1048; found 231.1047.

\[
\begin{align*}
\text{H}_2\text{N} & \equiv \equiv \equiv \text{C} \\
\end{align*}
\]

3-(phenylbuta-1,3-diyn-1-yl)aniline (3l) \(^{10}\): Yellow solid; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.45 (d, \( J = 6.8 \) Hz, 2 H), 7.31-7.24 (m, 3 H), 7.04 (t, \( J = 7.2 \) Hz, 1 H), 6.86 (d, \( J = 7.6 \) Hz, 1 H), 6.76 (s, 1 H), 6.62 (d, \( J = 7.6 \) Hz, 1 H), 3.65 (s, 2 H); \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 145.29, 131.47, 128.37, 128.13, 127.41, 121.96, 121.40, 120.86, 117.38, 115.29, 80.91, 80.26, 73.02, 72.25.

References:

2l

$\text{HO} - \equiv - \equiv - \text{OH}$

$\delta$ (ppm)

- 7.195
- 8.39
- 77.56
- 77.23
- 66.33
- 65.59
- 31.05

$\text{HO} - \equiv - \equiv - \text{OH}$

$\delta$ (ppm)

- 12.46
- 12.18
- 1.466
- 1.363
- 1.184

S24
3e

\[
\begin{align*}
O & \quad \text{160.39} \\
\text{134.09} & \quad \text{128.56} \\
\text{119.07} & \quad \text{114.15} \\
\text{113.88} & \quad \text{81.45} \\
\text{81.39} & \quad \text{77.34} \\
\text{77.52} & \quad \text{77.70} \\
\text{72.91} & \quad \text{72.53} \\
\text{73.53} & \quad \text{72.91} \\
\text{14.01} & \quad \text{-55.35} \\
\text{35.97} & \quad \text{31.43} \\
\text{30.86} & \quad \text{119.07} \\
\end{align*}
\]

3e

\[
\begin{align*}
\text{3.07} & \quad \text{4.11} \\
\text{2.04} & \quad \text{2.01} \\
\text{2.88} & \quad \text{2.00} \\
\text{2.00} & \quad \text{3.87} \\
\text{4.07} & \quad \text{-3.825} \\
\end{align*}
\]