Functionalized α,β-Ynones: Efficient ligand for Cu catalyzed Sonogashira-type cross-coupling reaction


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1. General information:

All the reactions and manipulation were performed under dry nitrogen by using standard Schlenk techniques. DMF (N,N-dimethyl formamide) were distilled from calcium hydride, all of the solvents were stored in ampoules with Teflon tap under argon. The TLC (layer chromatography) was on the aluminium plates coating GF254 silica gel. Column Chromatography was performed on 200-300 mesh silica gel and the eluent of petroleum and ethylacetate. All halides and alkynes were purchased from Aldrich and Alfa Aesar. 99.99 % CuI was purchased from Aldrich. NMR spectra were recorded on a spectrometers at 400 MHz ($^1$H NMR), 101 MHz ($^{13}$C NMR). All $^1$H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz).

2. Cu-catalyzed coupling of phenylacetylene with 4-iodoanisole

$$\text{MeO} - \underset{\text{I}}{\text{C}} - \underset{\text{C}}{\text{C}} \rightarrow \text{MeO} - \underset{\text{C}}{\text{C}}$$

To a mixture of Cu salt (0.005 mmol), 1-iodo-4-methoxybenzene (0.5 mmol, 0.11 g), K$_2$CO$_3$ (0.5mmol, 0.068 g), $\alpha,\beta$-Ynones (0.0125mmol) in a Schlenk tube, DMF (3.0 ml) was transferred via cannula. And then, Phenylacetylene (66 μl, 0.6 mmol) are added dropwise. The reaction is stirred under nitrogen atmosphere at 130°C for 24 h. Then cooling to room temperature, after that, the mixture was poured into separating funnel (150 ml) and washed with water (50 ml). And then, it extracted with ethyl acetate (3 times, 15 ml). The organic layer was dried by anhydrous MgSO$_4$, then filtered and evaporated under vacuum. The crude product dissolved in CDCl$_3$ (0.5 ml). The yields were calculated by comparing the integrations of methoxyl protons of starting materials, 4-iodo-anisole, and coupling product, 1-methoxy-4-(phenylethynyl)benzene. And column chromatography separation products on silica gel eluting with 10:1 petroleum ether/dichloromethane, get the target product 1-methoxy-4-(phenylethynyl)benzene, the yield was 96%, nuclear magnetic characterization.
**Table 1.** Optimization of Cu-catalyzed coupling of phenylacetylene with 4-idoanisole.[a]

![Chemical structure]

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<th>Solvent</th>
<th>Yield/%[^b]</th>
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[^a]: Reaction conditions: CuI (1mol%), $L_{11}$ (4 mol%), aryl iodide (0.5 mmol), alkyne (0.6 mmol), K$_2$CO$_3$ (0.5 mmol), 130 °C, 12 h, DMF (3 ml). [^b]: Yield was determined by $^1$H NMR.
3. Cu-catalyzed decarboxylative coupling of alkynylcarboxylic acid with 4-iodoanisole

![Reaction Diagram]

To a mixture of Cu salt (0.005 mmol), aryl iodide (0.5 mmol), K₂CO₃ (0.5 mmol, 0.0680 g), L₁₁ (0.0125 mmol) in a Schlenk tube, DMF (3.0 ml) was transferred via cannula. And then, alkynylcarboxylic acid (0.5 mmol, 0.073 g) are added dropwise. The reaction is stirred under nitrogen atmosphere at 130°C for 24 h. After that, the mixture was poured into water (50 ml). And then, the mixture was extracted with ethyl acetate (3×15 ml). The organic phase was washed with saturation sodium chloride (15 ml). After drying by anhydrous MgSO₄ and evaporating solvent, the brown residue dried in vacuum for at least 24 h. The crude product dissolved in CDCl₃ (0.5 ml). The yields were isolated by column chromatography.
4. Characterization of products

1-methoxy-4-(phenylethynyl)benzene

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.55 (dd, J = 7.7, 1.7 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 7.4 Hz, 3H), 6.90 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). & \\
1^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 159.69, 133.10, 131.50, 128.36, 127.97, 123.67, 115.44, 114.06, 89.46, 88.14, 55.30.
\end{align*}
\]

1-methyl-4-(phenylethynyl)benzene

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.55 – 7.53 (m, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 6.5 Hz, 3H), 7.17 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H). & \\
1^{13}C \text{ NMR (101MHz, CDCl}_3) \delta 139.82, 132.99, 132.94, 130.56, 129.75, 129.51, 124.93, 121.64, 91.00, 90.16, 22.94.
\end{align*}
\]

1-nitro-4-phenylethynylbenzene

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3) \delta 8.22 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.57 (dd, J = 6.5, 3.1 Hz, 2H), 7.39 (dd, J = 5.1, 1.8 Hz, 3H). & \\
1^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 148.40, 133.71, 133.29, 131.69, 130.73, 129.99, 125.08, 123.53, 96.15, 89.00.
\end{align*}
\]

1-ethyl-4-(phenylethynyl)benzene

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.65 – 7.57 (m, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 6.8 Hz, 3H), 7.23 (d, J = 7.9 Hz, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). & \\
1^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 146.16, 133.10, 133.05, 129.81, 129.56, 129.42, 125.02, 121.95, 91.13, 90.25, 30.33, 16.83.
\end{align*}
\]
1-(4-(phenylethynyl)phenyl) ethanone

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.58 – 7.53 (m, 2H), 7.41 – 7.34 (m, 3H), 2.62 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.76, 137.61, 133.19, 133.14, 130.27, 129.90, 129.72, 129.63, 124.08, 94.16, 90.06, 28.07.

1-ethyl-4-(phenylethynyl)benzoate

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.55 (dd, $J = 6.6, 3.0$ Hz, 2H), 7.40 – 7.34 (m, 3H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.41 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.32, 134.51, 133.93, 133.06, 130.62, 129.97, 129.83, 124.28, 123.54, 122.29, 91.62, 89.32, 54.82, 15.56.

1-(phenylethynyl)-4-(trifluoromethyl)benzene

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.7$ Hz, 2H), 7.60 (d, $J = 8.7$ Hz, 2H), 7.55 (dd, $J = 6.1, 3.5$ Hz, 2H), 7.41 – 7.34 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.24, 133.18, 130.27, 129.89, 126.73, 126.69, 124.03, 123.99, 93.18, 89.40.

1-(phenylethynyl)-4-(trifluoromethoxy)benzene

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.8$ Hz, 2H), 7.54 – 7.51 (m, 2H), 7.38 – 7.34 (m, 3H), 7.20 (d, $J = 8.1$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.31, 134.52, 133.06, 129.99, 129.84, 124.27, 123.53, 122.31, 91.62, 89.33.
1-bromo-4-(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, $J = 6.5$, 2.9 Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.37 – 7.33 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.03, 132.52, 131.63, 131.61, 129.21, 128.52, 128.45, 128.41, 122.95, 121.83, 90.53, 88.32.

1-chloro-4-(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (dd, $J = 6.6$, 3.0 Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.38 – 7.29 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.81, 132.51, 131.6, 129.2, 128.7, 128.48, 128.44, 128.39, 121.83, 81.55.

2-diphenylethyne

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (dd, $J = 7.0$, 2.1 Hz, 4H), 7.36 (d, $J = 5.2$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.05, 129.78, 129.69, 124.73, 90.81.

1-methoxy-2-(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (dd, $J = 7.5$, 1.9 Hz, 2H), 7.50 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.38 – 7.27 (m, 4H), 6.93 (dd, $J = 17.3$, 8.1 Hz, 2H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.96, 133.59, 131.67, 129.74, 128.23, 128.09, 123.6, 120.5, 112.51, 110.75, 93.45, 85.72, 55.86.

1-methyl-2-(phenylethynyl)benzene
\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.61 (d, \( J = 6.9 \) Hz, 2H), 7.57 (d, \( J = 7.5 \) Hz, 1H), 7.41 (d, \( J = 6.5 \) Hz, 3H), 7.29 (d, \( J = 4.2 \) Hz, 2H), 7.23 (dt, \( J = 8.4, 4.3 \) Hz, 1H), 2.59 (s, 3H). \[ ^13C \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 140.17, 131.84, 131.51, 129.46, 128.35, 128.30, 128.16, 125.58, 123.58, 123.05, 93.37, 88.37, 20.73.

**1-trifluoromethyl-2-(phenylethynyl)benzene**

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) = 7.64 (t, \( J = 7.5 \), 2H), 7.58-7.51 (m, 2H), 7.46 (t, \( J = 7.6 \), 1H), 7.37 (d, \( J = 8.0 \), 1H), 7.35-7.30 (m, 3H). \[ ^13C \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 133.76, 131.75, 131.43, 128.87, 128.46, 127.96, 125.95, 125.90, 125.86, 122.82, 122.37, 121.65, 95.03, 85.45.

**1-chloro-2-(phenylethynyl)benzene**

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.61 (td, \( J = 8.0, 3.4 \) Hz, 3H), 7.49 – 7.44 (m, 1H), 7.40 (dd, \( J = 4.9, 1.6 \) Hz, 3H), 7.30 – 7.26 (m, 2H). \[ ^13C \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 135.97, 133.24, 132.53, 131.77, 129.33, 129.27, 128.67, 128.47, 128.4, 126.48, 123.27, 122.96, 95.13, 92.14, 89.06.

**1-iodo-3-(phenylethynyl)benzene**

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.90 (s, 1H), 7.67 (d, \( J = 7.9 \) Hz, 1H), 7.56 – 7.47 (m, 3H), 7.39 – 7.34 (m, 3H), 7.08 (t, \( J = 7.8 \) Hz, 1H). \[ ^13C \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 141.58, 138.66, 133.09, 132.14, 131.28, 130.04, 129.84, 126.81, 124.21, 95.13, 92.14, 89.06.
1,3-bis(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (s, 1H), 7.55 (d, $J =$ 4.3 Hz, 2H), 7.53 (d, $J =$ 2.0 Hz, 2H), 7.50 (d, $J =$ 1.4 Hz, 1H), 7.48 (d, $J =$ 1.5 Hz, 1H), 7.38 – 7.32 (m, 7H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.04, 133.09, 132.71, 129.90, 129.88, 129.82, 125.07, 124.45, 91.39, 89.97.

1-methoxy-3-(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 – 7.53 (m, 2H), 7.42 – 7.35 (m, 3H), 7.32 – 7.25 (m, 2H), 7.16 (d, $J =$ 7.6 Hz, 1H), 7.09 (s, 1H), 6.92 (dd, $J =$ 8.3, 2.3 Hz, 1H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.84, 133.06, 130.83, 129.77, 129.72, 125.69, 125.66, 117.77, 116.38, 90.79, 90.59, 56.73.

1-methoxy-3-(phenylethynyl)benzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (dd, $J =$ 7.4, 1.8 Hz, 2H), 7.41 (dd, $J =$ 11.4, 8.8 Hz, 5H), 7.29 (t, $J =$ 7.6 Hz, 1H), 7.20 (d, $J =$ 7.6 Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.50, 133.70, 133.10, 130.67, 130.20, 129.83, 129.75, 129.67, 124.90, 124.59, 91.11, 90.57, 22.72.

1-(phenylethynyl)-3-(trifluoromethyl)benzene
1H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.48 (t, J = 7.8 Hz, 1H), 7.40 – 7.34 (m, 3H). 13C NMR (101 MHz, CDCl₃) δ 136.07, 133.13, 130.29, 130.17, 129.87, 126.19, 126.16, 125.70, 124.03, 92.32, 89.20.

\[ \text{oct-1-ynylbenzene} \]

1H NMR (400 MHz, CDCl₃) δ 7.46–7.31 (m, 2H), 7.37–7.17 (m, 3H), 2.52–2.31 (m, 2H), 1.51 (m, 2H), 1.53–1.36 (m, 2H), 1.33–1.21 (m, 4H), 0.90 (m, 3H). 13C NMR (101 MHz, CDCl₃) δ 143.46, 131.60, 131.56, 128.50, 128.34, 128.08, 123.59, 120.46, 89.67, 88.79, 35.92, 31.49, 30.96, 22.57, 14.05.

\[ \text{1-methoxy-4-(p-tolylethynyl)benzene} \]

1H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.83 (s, 2H), 2.37 (s, 2H). 13C NMR (101 MHz, CDCl₃) δ 159.51, 138.03, 132.99, 131.36, 129.10, 120.53, 115.62, 113.99, 88.68, 88.22, 55.30, 21.49.

\[ \text{1-ethyl-4-(4-ethyl-methoxyphenyl)ethynyl)benzene} \]

1H NMR (400 MHz, CDCl₃) δ 7.45 (dd, J = 12.3, 8.5 Hz, 4H), 7.17 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.66 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). 13C NMR (101 MHz, CDCl₃) δ 160.90, 145.76, 134.41, 132.85, 129.31, 122.16, 117.05, 115.35, 90.06, 89.64, 56.73, 30.24, 16.79

\[ \text{1-butyl-4-((4-methoxyphenyl)ethynyl)benzene} \]

1H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 2.67 – 2.57 (m, 2H), 1.59 (dd, J = 15.3, 7.8 Hz, 2H), 1.36 (dd, J =
14.9, 7.4 Hz, 2H), 0.93 (d, J = 7.3 Hz, 3H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.49, 143.04, 132.98, 131.35, 128.43, 120.71, 115.66, 113.97, 88.65, 88.24, 55.3, 35.58, 33.41, 22.31, 13.93.

\[ \text{1,2-bis(4-methoxyphenyl)ethyne} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J$ = 8.6 Hz, 4H), 6.87 (d, $J$ = 8.7 Hz, 4H), 3.82 (s, 6H).

\[ \text{1-(hex-1-ynyl)-4-methoxybenzene} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 8.7 Hz, 2H), 6.81 (d, $J$ = 8.7 Hz, 2H), 6.48 (t, $J$ = 7.1 Hz, 1H), 1.64 – 1.55 (m, 1H), 1.51 – 1.40 (m, 1H), 1.25 (dd, $J$ = 3.4 Hz, 3H), 0.91 (t, $J$ = 6.8 Hz, 2H).

\[ \text{1-(hept-1-ynyl)-4-methoxybenzene} \]

$^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.97, 132.84, 116.33, 113.81, 88.78, 80.27, 55.24, 31.07, 28.62, 22.57, 19.42, 14.06.

\[ \text{1-methoxy-4-(oct-1-ynyl)benzene} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.8 Hz, 2H), 6.80 (d, $J$ = 8.9 Hz, 2H), 3.79 (s, 2H), 2.39 (t, $J$ = 7.1 Hz, 1H), 1.68 – 1.56 (m, 1H), 1.42 (dddt, $J$ = 28.8, 21.5, 14.5, 7.2 Hz, 2H), 0.94 (t, $J$ = 7.2 Hz, 2H).
$J=7.0$, 3H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.01, 132.85, 116.35, 113.81, 88.78, 80.27, 55.20, 31.41, 28.89, 28.64, 22.59, 19.43, 14.06.

![Chemical structure of 3-(4-methoxyphenyl)ethyl]yl]aniline](attachment:structure.png)

3-((4-methoxyphenyl)ethynyl)aniline

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J=8.8$ Hz, 2H), 7.12 (t, $J=7.8$ Hz, 1H), 6.92 (d, $J=7.6$ Hz, 1H), 6.90 – 6.82 (m, 2H), 6.64 (dd, $J=8.0$, 1.6 Hz, 1H), 5.29 (s, 1H), 3.82 (s, 2H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.98, 147.68, 134.48, 130.69, 125.68, 123.39, 119.15, 116.90, 116.52, 115.41, 90.21, 89.71, 56.73, 54.

![Chemical structure of 1-((4-methoxyphenyl)ethynyl)-3-methylbenzene](attachment:structure.png)

1-((4-methoxyphenyl)ethynyl)-3-methylbenzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J=8.7$ Hz, 2H), 7.37 – 7.28 (m, 2H), 7.22 (t, $J=7.6$ Hz, 1H), 7.13 (d, $J=7.6$ Hz, 1H), 6.88 (d, $J=8.7$ Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.58, 137.96, 133.03, 132.04, 128.84, 128.53, 128.2, 123.4, 115.52, 113.99, 89.01, 88.23, 55.3, 21.24.

![Chemical structure of 2-(phenylethynyl)naphthalene](attachment:structure.png)

2-(phenylethynyl)naphthalene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J=8.3$ Hz, 1H), 7.94 – 7.85 (m, 2H), 7.83 (d, $J=7.1$ Hz, 1H), 7.76 – 7.69 (m, 2H), 7.65 (t, $J=7.5$ Hz, 1H), 7.58 (t, $J=7.4$ Hz, 1H), 7.50 (t, $J=7.7$ Hz, 1H), 7.44 (d, $J=7.6$ Hz, 3H). $^1$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.31, 133.25, 131.69, 130.39, 128.78, 128.45, 128.4, 128.34, 126.8, 126.45, 126.25, 125.3, 123.45, 120.94, 94.37, 87.59.
5. 1H NMR and 13C NMR spectra of alkynes