**Supplementary Information**

For

**Visible-Light-Mediated Photocatalytic Cross-Coupling of Acetenyl Ketones with Benzyl Trifluoroborate**

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1. General information

**General methods.** All reagents were purchased from commercial suppliers such as Aldrich, Energy Chemical Chemicals and Aladdin. All were used as received. Unless other noted, all photochemical reactions were carried out in a 10 ml, flame-dried glass tube under nitrogen atmosphere. $^1$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) were recorded on Bruker AV-400 instrument in CDCl$_3$ with TMS as internal standard. The chemical shifts ($\delta$) are given in parts per million relative to the chemical shift of TMS at 0.00 ppm in CDCl$_3$ for $^1$H, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and for $^{13}$C NMR spectra were relative to the center line signal of the CDCl$_3$ triplet at 77.00 ppm. Cyclic voltammogram was obtained with CHI 620E electrochemical analyzer. HRMS (ESI) spectra were recorded on a Bruker ESI mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent. Fluorescence spectra were measured on a Shimadzu RF-5301PC Spectrofluorometer at room temperature. For irradiation with blue light NVC SLED 320B (blue, 18W) was used. The reaction process was monitored by thin-layer chromatography on silica gel GF 254. Flash column chromatography was performed using 200-300 mesh silica gel with petroleum and ethyl acetate as eluent. The removal of solvent was performed on a rotary evaporator.

**Solvents.** All the relevant solvents were purified according to the procedure from “Purification of Laboratory Chemicals book”.

**Photocatalytic reactions.** The photocatalytic reactions were carried out in a dried glass tube, which was sealed with a rubber septum and a coiled seal film. The used light source is blue LEDs with a power output of 36 W. To maintain the temperature at room temperature, a clip fan was placed in front of the reaction system.

The picture of irradiation equipment is as below.

2. The preparation procedure for acetenyl ketones.

2.1 General procedure for the preparation of acetenyl ketones

To a dry, 50 ml two-neck flask was added acid chloride (6 mmol), alkyne (4 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.02 equiv) and Cul (0.02 equiv). The flask was filled with N$_2$ for three times by evacuating air. Then degassed THF (8 ml) was added to the flask by syringe. After stirring at room temperature for 2 min, Et$_3$N (5 mmol) was added. The reaction system was stirred for 5 hours then diluted by EtOAc (20 ml) and washed by H$_2$O for three times. The organic layer was combined and dried by anhydrous Na$_2$SO$_4$ overnight. The suspension was filtered and the filtrate was evacuated under
reduced pressure. The resulting residue was purified by column chromatography (PE/EtOAc as eluent) to afford corresponding acetenyl ketones.

2.2 Characterization of acetenyl ketones.

\[
\text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}} \text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}}
\]

1,3-diphenylprop-2-yn-1-one (1a), colorless oil. Yield = 97%. Prepared according to the general method by employing benzoyl chloride and ethynylbenzene.

\( \text{\chem{^1H NMR (400 MHz, CDCl}_3)} \delta 8.28 – 8.17 (m, 2H), 7.72 – 7.65 (m, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.54 – 7.37 (m, 5H); \text{\chem{^{13C NMR (101 MHz, CDCl}_3)} \delta 177.91, 136.77, 134.05, 132.98, 130.73, 129.47, 128.61, 128.55, 119.99, 93.03, 86.81.} \)

HRMS (ESI): calc. for C\(_{15}\)H\(_{10}\)NaO \([\text{M+Na}]^+\): 229.0624, found: 229.0623.
The \(\text{\chem{^1H}}\) and \(\text{\chem{^{13C}}}\) NMR data are consistent with previous literature.²

\[
\text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}} \text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}}
\]

1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (1b), slightly brown oil. Yield = 80%. Prepared according to the general method by employing 4-methoxybenzoyl chloride and ethynylbenzene.

\( \text{\chem{^1H NMR (400 MHz, CDCl}_3)} \delta 8.23 – 8.04 (m, 2H), 7.69 – 7.56 (m, 2H), 7.48 – 7.29 (m, 3H), 7.00 – 6.84 (m, 2H), 3.81 (s, 3H); \text{\chem{^{13C NMR (101 MHz, CDCl}_3)} \delta 176.63, 164.44, 132.91, 131.94, 130.55, 130.25, 128.61, 120.30, 113.84, 92.27, 86.87, 55.55.} \)

HRMS (ESI): calc. for C\(_{16}\)H\(_{12}\)NaO\(_2\) \([\text{M+Na}]^+\): 259.0730, found: 259.0734.
The \(\text{\chem{^1H}}\) and \(\text{\chem{^{13C}}}\) NMR data are consistent with previous literature.³

\[
\text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}} \text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}}
\]

3-phenyl-1-(m-tolyl)prop-2-yn-1-one (1d), colorless oil. Yield = 87%. Prepared according to the general method by employing 3-methylbenzoyl chloride and ethynylbenzene.

\( \text{\chem{^1H NMR (400 MHz, CDCl}_3)} \delta 8.15 – 7.99 (m, 2H), 7.75 – 7.65 (m, 2H), 7.55 – 7.37 (m, 5H), 2.46 (d, J = 3.5 Hz, 3H); \text{\chem{^{13C NMR (101 MHz, CDCl}_3)} \delta 177.99, 138.32, 136.73, 134.84, 132.87, 130.61, 129.59, 128.53, 128.37, 126.95, 119.99, 92.72, 86.87, 21.17.} \)

The \(\text{\chem{^1H}}\) and \(\text{\chem{^{13C}}}\) NMR data are consistent with previous literature.³

\[
\text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}} \text{\chem{\begin{array}{c} \text{O} \\ \text{C} \end{array}}}
\]

1-(4-(tert-butyl)phenyl)-3-phenylprop-2-yn-1-one (1e), colorless oil. Yield = 80%. Prepared according to the general method by employing 4-(tert-butyl)benzoyl chloride and ethynylbenzene.
1H NMR (400 MHz, CDCl$_3$) δ 8.20 – 8.12 (m, 2H), 7.71 – 7.63 (m, 2H), 7.55 – 7.50 (m, 2H), 7.42 (ddd, $J$ = 14.6, 7.9, 6.4 Hz, 3H), 1.35 (s, 9H); 13C NMR (101 MHz, CDCl$_3$) δ 177.58, 158.00, 134.42, 132.92, 130.60, 129.46, 128.57, 125.53, 120.15, 92.52, 86.94, 35.17, 30.96.


1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (1f), slightly yellow oil. Yield = 85%. Prepared according to the general method by employing 4-chlorobenzoyl chloride and ethynylbenzene.

1H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, $J$ = 8.6 Hz, 2H), 7.74 – 7.62 (m, 2H), 7.58 – 7.32 (m, 5H);

13C NMR (101 MHz, CDCl$_3$) δ 176.64, 140.68, 135.25, 133.08, 130.96, 130.84, 128.97, 128.71, 119.84, 93.61, 86.54.


3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1g), colorless oil. Yield = 73%. Prepared according to the general method by employing 4-(trifluoromethyl)benzoyl chloride and ethynylbenzene.

1H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, $J$ = 8.1 Hz, 2H), 7.89 – 7.65 (m, 4H), 7.59 – 7.36 (m, 3H);

13C NMR (101 MHz, CDCl$_3$) δ 176.70, 139.35, 135.15 (q, $J$ = 32.7 Hz), 133.18, 131.19, 129.78, 128.78, 125.69 (q, $J$ = 3.7 Hz), 123.51 (q, $J$ = 272.9 Hz), 119.63, 94.46, 86.55.


The 1H and 13C NMR data are consistent with previous literature.

1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-one (1h), colorless solid. Yield = 92%. Prepared according to the general method by employing 2-naphthoyl chloride and ethynylbenzene.

1H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 1H), 8.21 (dd, $J$ = 8.6, 1.7 Hz, 1H), 8.10 – 7.84 (m, 3H), 7.79 – 7.70 (m, 2H), 7.68 – 7.35 (m, 5H); 13C NMR (101 MHz, CDCl$_3$) δ 177.92, 136.13, 134.38, 133.04, 132.64, 132.38, 130.76, 129.86, 129.00, 128.69, 128.52, 127.89, 126.93, 123.94, 120.18, 93.03, 87.03.


The 1H and 13C NMR data are consistent with previous literature.

1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one (1i), colorless solid. Yield = 70%. Prepared according to the general method by employing 1-naphthoyl chloride and ethynylbenzene.
1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.24 (d, \(J = 8.7\) Hz, 1H), 8.64 (dd, \(J = 7.3, 1.1\) Hz, 1H), 8.08 (d, \(J = 8.2\) Hz, 1H), 7.90 (d, \(J = 8.1\) Hz, 1H), 7.74 – 7.64 (m, 3H), 7.57 (dt, \(J = 8.1, 4.6\) Hz, 2H), 7.51 – 7.35 (m, 3H); 13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 179.70, 135.08, 134.51, 133.83, 132.91, 130.69, 130.58, 128.93, 128.62, 128.54, 126.73, 125.95, 124.44, 120.30, 91.66, 88.45.

HRMS (ESI): calc. for C\textsubscript{19}H\textsubscript{12}NaO [M+Na]\textsuperscript{+}: 279.0780, found: 279.0783.

The 1H and 13C NMR data are consistent with previous literature.\textsuperscript{5}

\[
\text{1-(furan-2-yl)-3-phenylprop-2-yn-1-one (1j), colorless oil. Yield = 79%. Prepared according to the general method by employing furan-2-carbonyl chloride and ethynylbenzene.}
\]

1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.80 – 7.59 (m, 3H), 7.53 – 7.34 (m, 4H), 6.61 (dd, \(J = 3.6, 1.6\) Hz, 1H); 13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 164.59, 153.03, 147.97, 132.90, 128.56, 120.92, 119.67, 112.59, 91.75, 86.09.

HRMS (ESI): calc. for C\textsubscript{13}H\textsubscript{8}NaO\textsubscript{2} [M+Na]\textsuperscript{+}: 219.0417, found: 219.0419.

The 1H and 13C NMR data are consistent with previous literature.\textsuperscript{6}

\[
\text{3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-one (1k), colorless oil. Yield = 95%. Prepared according to the general method by employing thiophene-2-carbonyl chloride and ethynylbenzene.}
\]

1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.91 (dd, \(J = 3.8, 1.2\) Hz, 1H), 7.71 – 7.49 (m, 3H), 7.45 – 7.27 (m, 3H), 7.09 (dd, \(J = 4.9, 3.9\) Hz, 1H); 13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 169.69, 144.81, 135.21, 135.05, 132.94, 130.78, 128.61, 128.29, 119.79, 91.66, 86.38.

HRMS (ESI): calc. for C\textsubscript{13}H\textsubscript{8}NaOS [M+Na]\textsuperscript{+}: 235.0188, found: 235.0189.

The 1H and 13C NMR data are consistent with previous literature.\textsuperscript{7}

\[
\text{3-phenyl-1-(pyridin-3-yl)prop-2-yn-1-one (1l), brown oil. Yield = 86%. Prepared according to the general method by employing nicotinoyl chloride and ethynylbenzene.}
\]

1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 9.45 – 9.26 (m, 1H), 8.77 (dd, \(J = 4.8, 1.7\) Hz, 1H), 8.36 (dt, \(J = 8.0, 1.9\) Hz, 1H), 7.75 – 7.56 (m, 2H), 7.53 – 7.30 (m, 4H); 13C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 176.37, 154.20, 151.41, 136.16, 133.22, 132.16, 131.23, 128.76, 123.52, 119.51, 94.70, 86.23.

HRMS (ESI): calc. for C\textsubscript{14}H\textsubscript{9}NNaO [M+Na]\textsuperscript{+}: 230.0576, found: 230.0575.
4-phenylbut-3-yn-2-one (1m), colorless oil. Yield = 36%. Prepared according to the general method by employing acetyl chloride and ethynylbenzene.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.52 (m, 2H), 7.49 – 7.41 (m, 1H), 7.41 – 7.34 (m, 2H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.44, 132.89, 130.61, 128.50, 119.73, 90.17, 88.13, 32.59.


The $^1$H and $^{13}$C NMR data are consistent with previous literature.$^6$

4,4-dimethyl-1-phenylpent-1-yn-3-one (1n), slightly yellow oil. Yield = 87%. Prepared according to the general method by employing pivaloyl chloride and ethynylbenzene.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.54 (m, 2H), 7.50 – 7.35 (m, 3H), 1.28 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 194.30, 132.94, 130.53, 128.58, 120.24, 92.21, 85.97, 44.87, 26.12.


The $^1$H and $^{13}$C NMR data are consistent with previous literature.$^6$

1-cyclopentyl-3-phenylprop-2-yn-1-one (1o), colorless oil. Yield = 57%. Prepared according to the general method by employing cyclopentanecarbonyl chloride and ethynylbenzene.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.52 (m, 2H), 7.48 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 3.17 – 2.92 (m, 1H), 2.07 – 1.89 (m, 4H), 1.78 – 1.59 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.01, 132.89, 130.49, 128.51, 120.07, 91.08, 87.19, 53.67, 29.04, 25.91.

HRMS (ESI): calc. for C$_{14}$H$_{14}$NaO [M+Na]$^+$: 221.0937, found: 221.0938.

1-phenylhex-4-en-1-yn-3-one (1p), slightly yellow oil. Yield = 57%. Prepared according to the general method by employing but-2-enoyl chloride and ethynylbenzene.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.55 (m, 2H), 7.48 – 7.34 (m, 3H), 7.28 (dt, $J = 13.7$, 6.9 Hz, 1H), 6.35 – 6.19 (m, 1H), 2.02 (dd, $J = 6.9$, 0.9 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.27, 149.48, 133.78, 132.76, 132.72, 130.41, 128.49, 120.03, 90.98, 86.06, 18.37.


3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (1q), colorless oil. Yield = 93%. Prepared
according to the general method by employing benzoyl chloride and 1-ethynyl-4-methoxybenzene. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.30 – 8.16 \text{ (m, 2H)}\), 7.63 (dd, \(J = 14.5, 8.1 \text{ Hz, 3H}\)), 7.52 (t, \(J = 7.6 \text{ Hz, 2H}\)), 6.94 (d, \(J = 8.8 \text{ Hz, 2H}\)), 3.86 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 178.04, 161.72, 137.04, 135.14, 133.88, 129.48, 128.54, 114.41, 111.89, 94.29, 86.86, 55.43.\)

HRMS (ESI): calc. for C\(_{16}\)H\(_{12}\)NaO\(_2\) [M+Na]\(^+\): 259.0730, found: 259.0732.

The \(^1\)H and \(^{13}\)C NMR data are consistent with previous literature.\(^3\)

\[\begin{array}{c}
\text{1-phenyl-3-(m-tolyl)prop-2-yn-1-one (1r), colorless oil. Yield = 80%. Prepared according to the general method by employing benzoyl chloride and 1-ethynyl-3-methylbenzene.}\n\end{array}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.31 – 8.13 \text{ (m, 2H)}\), 7.67 – 7.57 (m, 1H), 7.56 – 7.42 (m, 4H), 7.36 – 7.23 (m, 2H), 2.36 (d, \(J = 3.2 \text{ Hz, 3H}\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 177.92, 138.44, 136.83, 134.01, 133.47, 131.71, 130.16, 129.47, 128.54, 128.52, 119.81, 93.44, 86.61, 21.11.\)


The \(^1\)H and \(^{13}\)C NMR data are consistent with previous literature.\(^9\)

\[\begin{array}{c}
\text{3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one (1s), slightly brown oil. Yield = 40%. Prepared according to the general method by employing benzoyl chloride and 1-ethynyl-4-fluorobenzene.}\n\end{array}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.20 – 8.08 \text{ (m, 2H)}\), 7.60 (ddd, \(J = 26.8, 14.2, 6.4 \text{ Hz, 3H}\)), 7.45 (t, \(J = 7.6 \text{ Hz, 2H}\)), 7.05 (t, \(J = 8.7 \text{ Hz, 2H}\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 177.87, 164.00 \text{ (d, } J = 253.9 \text{ Hz)}, 136.76, 135.34 \text{ (d, } J = 8.9 \text{ Hz)}, 134.17, 129.52, 128.63, 116.23 \text{ (d, } J = 22.4 \text{ Hz)}, 116.22 \text{ (d, } J = 3.6 \text{ Hz), 91.97, 86.79.}\)


The \(^1\)H and \(^{13}\)C NMR data are consistent with previous literature.\(^9\)

\[\begin{array}{c}
\text{1-phenylbut-2-yn-1-one (1t), slightly brown oil. Yield = 45%. Prepared according to the general method by employing benzoyl chloride and prop-1-yne.}\n\end{array}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.18 – 8.07 \text{ (m, 2H)}\), 7.63 – 7.55 (m, 1H), 7.51 – 7.42 (m, 2H), 2.14 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 178.08, 136.64, 133.81, 129.42, 128.36, 92.44, 78.84, 4.17.\)

HRMS (ESI): calc. for C\(_{10}\)H\(_{8}\)NaO [M+Na]\(^+\): 167.0467, found: 167.0466.
1-phenylhept-2-yn-1-one (1u), colorless oil. Yield = 67%. Prepared according to the general method by employing benzoyl chloride and hex-1-yne.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 – 8.07 (m, 2H), 7.59 (ddd, $J = 6.9, 4.6, 1.2$ Hz, 1H), 7.47 (dd, $J = 10.6, 4.7$ Hz, 2H), 2.50 (t, $J = 7.1$ Hz, 2H), 1.73 – 1.43 (m, 4H), 0.96 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.11, 136.80, 133.75, 129.40, 128.37, 96.73, 79.54, 29.71, 21.95, 18.77, 13.40.


The $^1$H and $^{13}$C NMR data are consistent with previous literature.

4,4-dimethyl-1-phenylpent-2-yn-1-one (1v), brown oil. Yield = 90%. Prepared according to the general method by employing benzoyl chloride and 3,3-dimethylbut-1-yne.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 – 8.00 (m, 2H), 7.59 (dd, $J = 10.5, 4.2$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 1.39 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.29, 136.95, 133.75, 129.42, 128.40, 103.89, 78.04, 30.10, 27.97.


The $^1$H and $^{13}$C NMR data are consistent with previous literature.

3-cyclohexyl-1-phenylprop-2-yn-1-one (1x), brown oil. Yield = 73%. Prepared according to the general method by employing benzoyl chloride and ethynylcyclohexane.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 – 8.05 (m, 2H), 7.64 – 7.53 (m, 1H), 7.46 (dd, $J = 10.5, 4.7$ Hz, 2H), 2.69 (ddd, $J = 12.8, 8.8, 3.8$ Hz, 1H), 1.92 (dd, $J = 9.6, 3.5$ Hz, 2H), 1.80 – 1.72 (m, 2H), 1.67 – 1.52 (m, 3H), 1.47 – 1.31 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.23, 136.86, 133.71, 129.37, 128.34, 100.30, 79.41, 31.55, 29.23, 25.51, 24.56.


The $^1$H and $^{13}$C NMR data are consistent with previous literature.

3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1y).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 – 7.87 (m, 2H), 7.72 (d, $J = 15.7$ Hz, 1H), 7.60 – 7.26 (m, 6H), 6.97 – 6.80 (m, 2H), 3.78 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.58, 161.66, 144.69, 138.49, 132.53, 130.21, 128.54, 128.39, 127.60, 119.77, 114.40, 55.40.

3. The photocatalytic cross-coupling reactions of acetenyl ketones.

3.1 General procedure for the photocatalytic cross-coupling reactions

Acetenyl ketone (0.1 mmol), potassium trifluoroborates (0.15 mmol) and Ir[dF(CF$_3$)(ppy)$_2$(dtbbp-
y)PF₆ (2.0 mmol%) were added to a transparent glass tube equipped with a magnetic stir bar. Then the tube was covered with a rubber septum and sealed with a coiled seal film. By evacuating air with N₂ for three times at -78 °C, dried and degassed acetone (1mL) was added. Subsequently, the reaction system was treated under the irradiation of blue LEDs (36 W) at room temperature for 24 hours. Monitored the reaction process with TLC till completed, the reaction mixture was filtered and the residue was washed with acetone (2 mL). The resulting filter liquor was concentrated under reduced pressure and purified by column chromatography to afford propargyl alcohols.

3.2 Characterization of the cross-coupling products.

1,2,4-triphenylbut-3-yn-2-ol (2a), was prepared following the general procedure by the reaction of 1a with benzyl trifluoroborate, and flash column chromatography afforded 2a as colorless oil in 72% yield (21.5 mg).

1H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.7 Hz, 2H), 7.45 – 7.20 (m, 13H), 3.24 (s, 2H), 2.52 (s, 1H);
13C NMR (101 MHz, CDCl₃) δ 144.13, 135.90, 131.64, 131.01, 128.53, 128.29, 128.13, 127.87, 127.76, 127.02, 125.63, 122.52, 91.05, 87.33, 73.63, 51.96.
GC-MS (EI): 298.1, 280.1, 265.1, 202.1, 178.1. 77.1
The 1H and 13C NMR data are consistent with previous literature.¹¹

2-(4-methoxyphenyl)-1,4-diphenylbut-3-yn-2-ol (2b), was prepared following the general procedure by the reaction of 1b with benzyl trifluoroborate, and flash column chromatography afforded 2b as colorless oil in 70% yield (22.9 mg).

1H NMR (400 MHz, CDCl₃) δ 7.51 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.17 (m, 6H), 7.16 – 7.13 (m, 2H), 6.85 – 6.76 (m, 2H), 3.72 (s, 3H), 3.15 (q, J = 13.1 Hz, 2H), 2.49 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ 159.11, 136.28, 136.00, 131.58, 130.98, 128.45, 128.25, 127.79, 126.91, 122.53, 113.37, 91.20, 87.19, 73.33, 55.26, 51.90.
GC-MS (EI): 328.1, 295.1, 279.2, 252.1, 131.1

2-(2-methoxyphenyl)-1,4-diphenylbut-3-yn-2-ol (2c), was prepared following the general
procedure by the reaction of 1c with benzyl trifluoroborate, and flash column chromatography afforded 2c as colorless oil in 64% yield (21.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.37 – 7.30 (m, 2H), 7.23 – 7.16 (m, 4H), 7.14 – 7.09 (m, 3H), 7.04 (dd, $J = 7.0, 2.6$ Hz, 2H), 6.89 – 6.77 (m, 2H), 4.46 (s, 1H), 3.80 (s, 3H), 3.38 (dd, $J = 40.9, 12.9$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.50, 136.53, 131.59, 130.81, 130.43, 129.09, 128.44, 128.22, 128.12, 127.48, 126.51, 122.80, 120.82, 111.45, 90.50, 86.96, 74.87, 55.60, 49.04.

GC-MS (EI): 328.2, 310.3, 295.1, 279.1, 189.1, 77.1


1,4-diphenyl-2-(m-tolyl)but-3-yn-2-ol (2d), was prepared following the general procedure by the reaction of 1d with benzyl trifluoroborate, and flash column chromatography afforded 2d as colorless oil in 56% yield (17.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.16 (ddd, $J = 15.6, 8.5, 4.8$ Hz, 9H), 7.01 (d, $J = 7.5$ Hz, 1H), 3.19 – 3.04 (m, 2H), 2.49 (s, 1H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.05, 137.69, 135.96, 131.58, 130.98, 128.42, 128.21, 127.97, 127.78, 126.93, 126.13, 122.72, 122.52, 91.14, 87.16, 73.50, 51.87, 21.53.

GC-MS (EI): 312.1, 220.1, 192.1, 143.1, 77.1


2-(4-(tert-butyl)phenyl)-1,4-diphenylbut-3-yn-2-ol (2e), was prepared following the general procedure by the reaction of 1e with benzyl trifluoroborate, and flash column chromatography afforded 2e as colorless oil in 71% yield (25.1 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.5$ Hz, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.13 (m, 8H), 3.21 – 3.05 (m, 2H), 2.45 (s, 1H), 1.25 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.69, 141.28, 136.12, 131.60, 131.02, 128.42, 128.23, 127.82, 126.94, 125.27, 125.04, 122.59, 91.16, 87.21, 73.41, 51.81, 34.48, 31.34.


2-(4-chlorophenyl)-1,4-diphenylbut-3-yn-2-ol (2f), was prepared following the general procedure by the reaction of 1f with benzyl trifluoroborate, and flash column chromatography afforded 2f as colorless oil in 53% yield (17.6 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.44 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.16 (m, 8H), 7.16 – 7.10 (m, 2H), 3.12 (s, 2H), 2.52 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.61, 135.46, 133.54, 131.60, 130.95, 128.67, 128.32, 128.18, 127.93, 127.16, 127.12, 122.20, 90.55, 87.51, 73.20, 51.88.


1,4-diphenyl-2-(4-(trifluoromethyl)phenyl)but-3-yn-2-ol (2g), was prepared following the general procedure by the reaction of 1g with benzyl trifluoroborate, and flash column chromatography afforded 2g as colorless oil in 41% yield (15.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, $J$ = 8.2 Hz, 2H), 7.53 (d, $J$ = 8.3 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.19 (m, 6H), 7.19 – 7.13 (m, 2H), 3.14 (s, 2H), 2.56 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.03, 135.26, 131.64, 130.97, 129.93 (q, $J$ = 32.3 Hz), 128.80, 128.37, 128.03, 127.28, 126.09, 125.10 (q, $J$ = 3.7 Hz), 123.95 (q, $J$ = 234.7 Hz), 122.08, 90.28, 87.72, 73.27, 51.90.


HRMS (ESI): calc. for C$_{23}$H$_{17}$F$_3$NaO [M+Na]$^+$: 399.1124, found: 389.1127.

2-(naphthalen-2-yl)-1,4-diphenylbut-3-yn-2-ol, (2h), was prepared following the general procedure by the reaction of 1h with benzyl trifluoroborate, and flash column chromatography afforded 2h as colorless oil in 61% yield (21.2 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J$ = 1.8 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.70 (dd, $J$ = 8.6, 1.8 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.28 – 7.16 (m, 8H), 3.25 (s, 2H), 2.59 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.43, 135.81, 132.96, 132.89, 131.67, 131.02, 128.57, 128.37, 128.31, 127.92, 127.54, 127.05, 126.12, 126.08, 124.36, 123.91, 122.48, 91.05, 87.47, 73.69, 51.73.


2-(naphthalen-1-yl)-1,4-diphenylbut-3-yn-2-ol, (2i), was prepared following the general procedure by the reaction of 1i with benzyl trifluoroborate, and flash column chromatography afforded 2i as colorless oil in 58% yield (20.2 mg).

{\textsuperscript{1}}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.91 (d, \( J = 8.7 \) Hz, 1H), 7.89 – 7.80 (m, 2H), 7.75 (d, \( J = 8.2 \) Hz, 1H), 7.50 (ddd, \( J = 8.5, 6.8, 1.4 \) Hz, 1H), 7.46 – 7.40 (m, 1H), 7.37 – 7.16 (m, 11H), 3.53 (dd, \( J = 64.5, 13.4 \) Hz, 2H), 2.68 (s, 1H); \{\textsuperscript{13}\text{C} NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 138.45, 136.09, 134.66, 131.08, 130.07, 129.21, 129.13, 128.51, 128.25, 127.87, 127.02, 126.10, 125.62, 125.31, 124.88, 124.31, 122.50, 91.69, 88.12, 73.87, 49.16.


2-(furan-2-yl)-1,4-diphenylbut-3-yn-2-ol, (2j), was prepared following the general procedure by the reaction of 1j with benzyl trifluoroborate, and flash column chromatography afforded 2j as colorless oil in 48% yield (13.9 mg).

{\textsuperscript{1}}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.39 (dd, \( J = 1.7, 0.8 \) Hz, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.16 (m, 8H), 6.30 (ddd, \( J = 5.1, 3.2, 1.3 \) Hz, 2H), 3.36 (s, 2H), 2.58 (s, 1H); \{\textsuperscript{13}\text{C} NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 154.81, 142.60, 135.51, 131.75, 130.83, 128.74, 128.33, 127.99, 127.14, 122.22, 110.41, 107.74, 88.79, 86.57, 69.40, 47.64.

GC-MS (EI): 288.1, 270.1, 212.2, 156.1, 128.1, 91.1.


1,4-diphenyl-2-(thiophen-2-yl)but-3-yn-2-ol, (2k), was prepared following the general procedure by the reaction of 1k with benzyl trifluoroborate, and flash column chromatography afforded 2k as colorless oil in 43% yield (13.1 mg).

{\textsuperscript{1}}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.37 – 7.31 (m, 2H), 7.29 – 7.18 (m, 9H), 7.08 (dd, \( J = 3.6, 1.2 \) Hz, 1H), 6.89 (dd, \( J = 5.1, 3.6 \) Hz, 1H), 3.30 (q, \( J = 13.1 \) Hz, 2H), 2.71 (s, 1H); \{\textsuperscript{13}\text{C} NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 148.86, 135.62, 131.64, 130.92, 128.69, 128.30, 127.90, 127.15, 126.54, 125.16, 124.77, 122.18, 90.24, 86.85, 71.40, 51.90.

GC-MS (EI): 304.1, 286.3, 252.2, 239.1, 209.1, 77.1.

HRMS (ESI): calc. for C_{20}H_{16}O_{2} [M+Na]^+: 327.0814, found: 327.0817.
1,4-diphenyl-2-(pyridin-3-yl)but-3-yn-2-ol, (2l), was prepared following the general procedure by the reaction of 1l with benzyl trifluoroborate, and flash column chromatography afforded 2l as colorless oil in 66% yield (20.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.77 (d, $J$ = 1.2 Hz, 1H), 8.37 (d, $J$ = 4.2 Hz, 1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.37 – 7.04 (m, 11H), 4.04 (s, 1H), 3.15 (q, $J$ = 13.1 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.49, 147.40, 140.09, 135.37, 133.80, 131.67, 131.06, 128.76, 128.39, 127.96, 127.18, 122.87, 122.21, 90.37, 87.73, 71.96, 52.01.

GC-MS (EI): 299.1, 281.1, 189.1, 141.1, 115.1, 93.1, 77.1

HRMS (ESI): calc. for C$_{21}$H$_{17}$NNaO $[M+Na]^+$: 322.1202, found: 322.1204.

2-methyl-1,4-diphenylbut-3-yn-2-ol, (2m), was prepared following the general procedure by the reaction of 1m with benzyl trifluoroborate, and flash column chromatography afforded 2m as colorless oil in 36% yield (8.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.19 (m, 10H), 2.98 (dd, $J$ = 29.7, 13.1 Hz, 2H), 2.05 (s, 1H), 1.57 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 136.34, 131.55, 130.77, 128.30, 128.24, 128.13, 127.02, 122.66, 92.37, 84.57, 68.43, 49.75, 29.56.

GC-MS (EI): 236.1, 208.1, 193.1, 159.1, 116.1.


3-benzyl-4,4-dimethyl-1-phenylpent-1-yn-3-ol, (2n), was prepared following the general procedure by the reaction of 1n with benzyl trifluoroborate, and flash column chromatography afforded 2n as colorless oil in 49% yield (13.6 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.30 (m, 2H), 7.24 (dddd, $J$ = 9.5, 7.0, 5.9, 1.7 Hz, 8H), 2.93 (s, 2H), 1.81 (s, 1H), 1.15 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.17, 131.49, 131.28, 128.20, 128.13, 127.94, 126.78, 122.99, 91.21, 86.66, 76.84, 42.17, 38.72, 25.53.

GC-MS (EI): 278.1, 260.1, 217.1, 188.1, 109.1, 91.1.

HRMS (ESI): calc. for C$_{20}$H$_{22}$NaO $[M+Na]^+$: 301.1563, found: 301.1569.
2-cyclopentyl-1,4-diphenylbut-3-yn-2-ol, (2o), was prepared following the general procedure by the reaction of 1o with benzyl trifluoroborate, and flash column chromatography afforded 2o as colorless oil in 54% yield (15.7 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.18 (m, 10H), 2.95 (dd, $J = 67.7, 13.2$ Hz, 2H), 2.15 (dd, $J = 16.7, 8.4$ Hz, 1H), 1.97 (s, 1H), 1.86 – 1.71 (m, 3H), 1.63 (tdd, $J = 8.7, 6.4, 3.1$ Hz, 3H), 1.55 – 1.49 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.38, 131.59, 130.93, 128.23, 128.06, 126.87, 122.86, 90.79, 85.95, 74.67, 49.59, 47.53, 28.86, 27.80, 26.17, 26.13.

GC-MS (EI): 290.1, 238.2, 146.1, 120.1, 105.1, 77.1.

HRMS (ESI): calc. for C$_{21}$H$_{22}$NaO $[M+Na]^+$: 313.1563, found: 313.1560.

3-benzyl-1-phenylhex-4-en-1-yn-3-ol, (2p), was prepared following the general procedure by the reaction of 1p with benzyl trifluoroborate, and flash column chromatography afforded 2p as colorless oil in 24% yield (6.3 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (dt, $J = 13.4, 6.1$ Hz, 5H), 7.26 – 7.19 (m, 5H), 5.99 (dq, $J = 13.2, 6.5$ Hz, 1H), 5.67 – 5.58 (m, 1H), 3.00 (s, 2H), 2.13 (s, 1H), 1.68 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 135.90, 133.61, 131.57, 131.00, 128.36, 128.22, 127.94, 126.94, 126.82, 122.60, 90.21, 86.88, 71.46, 49.18, 17.43.

GC-MS (EI): 262.1, 247.1, 219.1, 204.1, 176.1.


4-(4-methoxyphenyl)-1,2-diphenylbut-3-yn-2-ol, (2q), was prepared following the general procedure by the reaction of 1q with benzyl trifluoroborate, and flash column chromatography afforded 2q as colorless oil in 73% yield (24.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.49 (m, 2H), 7.31 – 7.13 (m, 10H), 6.74 (d, $J = 8.8$ Hz, 2H), 3.69 (s, 3H), 3.14 (d, $J = 3.3$ Hz, 2H), 2.50 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.71, 144.28, 136.00, 133.04, 130.99, 128.05, 127.77, 127.64, 126.90, 125.63, 114.56, 113.89, 89.67, 87.25, 73.62, 55.22, 51.98.

GC-MS (EI): 328.1, 311.2, 295.1, 279.2, 265.1, 239.1.


1,2-diphenyl-4-(m-tolyl)but-3-yn-2-ol, (2r), was prepared following the general procedure by the
reaction of 1r with benzyl trifluoroborate, and flash column chromatography afforded 2r as colorless oil in 44% yield (13.7 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 5.3, 3.3$ Hz, 2H), 7.28 – 7.21 (m, 2H), 7.19 (dt, $J = 5.4, 2.2$ Hz, 1H), 7.17 – 7.03 (m, 8H), 7.01 (d, $J = 7.4$ Hz, 1H), 3.20 – 3.06 (m, 2H), 2.53 (s, 1H), 2.20 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.10, 137.89, 135.88, 132.15, 130.97, 129.34, 128.65, 128.13, 128.04, 127.76, 127.65, 126.90, 125.61, 122.27, 90.69, 87.43, 73.59, 51.90, 21.13.

GC-MS (EI): 312.1, 221.1, 192.2, 143.1, 77.2


4-(4-fluorophenyl)-1,2-diphenylbut-3-yn-2-ol, (2s), was prepared following the general procedure by the reaction of 1s with benzyl trifluoroborate, and flash column chromatography afforded 2s as colorless oil in 68% yield (21.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (dd, $J = 5.3, 3.2$ Hz, 2H), 7.29 – 7.22 (m, 4H), 7.20 (dt, $J = 5.4, 2.2$ Hz, 1H), 7.18 – 7.13 (m, 3H), 7.13 – 7.09 (m, 2H), 6.91 – 6.82 (m, 2H), 3.22 – 2.99 (m, 2H), 2.54 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.56 (d, $J = 249.8$ Hz), 143.96, 135.82, 133.48 (d, $J = 8.4$ Hz), 130.93, 128.09, 127.80, 127.75, 126.97, 125.55, 118.51 (d, $J = 3.5$ Hz), 115.53 (d, $J = 22.1$ Hz), 90.75, 86.21, 73.57, 51.84.

GC-MS (EI): 316.1, 298.1, 226.1, 196.1, 147.1, 105.1.


1,2-diphenylpent-3-yn-2-ol, (2t), was prepared following the general procedure by the reaction of 1t with benzyl trifluoroborate, and flash column chromatography afforded 2t as colorless oil in 39% yield (9.2 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.44 (m, 2H), 7.27 – 7.13 (m, 6H), 7.06 (dd, $J = 6.8, 2.7$ Hz, 2H), 3.04 (s, 2H), 2.33 (s, 1H), 1.78 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.52, 136.02, 130.89, 127.91, 127.69, 127.47, 126.74, 125.56, 83.42, 81.46, 73.14, 51.82, 3.56.

GC-MS (EI): 236.1, 193.1, 176.1, 144.1, 88.1


1,2-diphenyloct-3-yn-2-ol, (2u), was prepared following the general procedure by the reaction of 1u with benzyl trifluoroborate, and flash column chromatography afforded 2u as colorless oil in 45% yield (12.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.43 (m, 2H), 7.29 – 7.12 (m, 6H), 7.06 (dd, $J = 6.7, 2.9$ Hz, 3.56.
5,5-dimethyl-1,2-diphenylhex-3-yn-2-ol, (2v), was prepared following the general procedure by the reaction of 1v with benzyl trifluoroborate, and flash column chromatography afforded 2v as colorless oil in 53% yield (15.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.46 (m, 2H), 7.29 – 7.23 (m, 2H), 7.21 (dd, $J = 4.9$, 3.6 Hz, 1H), 7.19 – 7.15 (m, 3H), 7.09 (dd, $J = 6.7$, 3.0 Hz, 2H), 3.02 (dd, $J = 31.9$, 13.0 Hz, 2H), 2.27 (s, 1H), 1.15 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.79, 136.22, 131.04, 127.93, 127.64, 127.47, 126.75, 125.66, 96.36, 80.56, 73.19, 52.13, 30.82, 27.43.

GC-MS (EI): 278.1, 260.3, 217.1, 188.1, 109.3, 91.2.

HRMS (ESI): calc. for C$_{20}$H$_{22}$NaO [M+Na]$^+$: 301.1563, found: 301.1562.

4-cyclopropyl-1,2-diphenylbut-3-yn-2-ol, (2w), was prepared following the general procedure by the reaction of 1w with benzyl trifluoroborate, and flash column chromatography afforded 2w as colorless oil in 48% yield (12.6 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.43 (m, 2H), 7.33 – 7.12 (m, 6H), 7.05 (dd, $J = 6.6$, 2.9 Hz, 2H), 3.01 (q, $J = 13.1$ Hz, 2H), 2.30 (s, 1H), 1.18 (tt, $J = 8.3$, 5.0 Hz, 1H), 0.80 – 0.46 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.55, 136.11, 130.89, 127.91, 127.64, 127.47, 126.75, 125.66, 91.15, 77.25, 73.15, 51.95, 8.17, 8.12, -0.57.

GC-MS (EI): 262.3, 170.1, 141.1, 115.1, 93.1, 77.1


4-cyclohexyl-1,2-diphenylbut-3-yn-2-ol, (2x), was prepared following the general procedure by the reaction of 1x with benzyl trifluoroborate, and flash column chromatography afforded 2x as colorless oil in 65% yield (20.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.47 (m, 2H), 7.27 – 7.17 (m, 3H), 7.16 – 7.11 (m, 3H), 7.07 (dd, $J = 6.7$, 3.0 Hz, 2H), 3.03 (q, $J = 13.0$ Hz, 2H), 2.35 (dd, $J = 9.7$, 5.8 Hz, 2H), 1.77 – 1.53 (m, 4H), 1.47 – 1.29 (m, 3H), 1.21 (dt, $J = 5.4$, 4.7 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.88, 136.28, 131.10, 128.01, 127.72, 127.56, 126.83, 125.77, 92.27, 82.14, 73.38, 52.16, 32.56, 29.11, 25.94, 24.91.
GC-MS (EI): 304.4, 286.1, 286.1, 213.4, 204.1, 105.1

2,4-diphenyl-1-(p-tolyl)but-3-yne-2-ol, (2y), was prepared following the general procedure by the reaction of 1a with 4-methylbenzyl trifluoroborate, and flash column chromatography afforded 2y as colorless oil in 63% yield (20.0 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J = 5.3, 3.3$ Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 7.06 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 7.9$ Hz, 2H), 3.12 (s, 2H), 2.49 (s, 1H), 2.24 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.28, 136.67, 132.79, 131.72, 130.95, 128.71, 128.56, 128.35, 128.19, 127.78, 125.71, 122.66, 91.28, 87.21, 73.67, 51.65, 21.19.
GC-MS (EI): 312.1, 220.1, 192.2, 143.1, 77.1, 51.1

4-(4-methoxyphenyl)-1,2-diphenylbut-3-en-2-ol, (2z), was prepared following the general procedure by the reaction of 1y with benzyl trifluoroborate, and flash column chromatography afforded 2z as colorless oil in 19% yield (6.3 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 1.4$ Hz, 1H), 7.40 (s, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.20 (d, $J = 1.5$ Hz, 1H), 7.18 (s, 1H), 7.14 (dd, $J = 5.0, 1.9$ Hz, 1H), 6.97 (dd, $J = 6.8, 2.7$ Hz, 1H), 6.80 – 6.73 (m, 1H), 6.43 (d, $J = 3.6$ Hz, 1H), 3.72 (s, 2H), 3.22 (s, 1H), 1.98 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.18, 145.51, 135.93, 133.20, 130.83, 129.57, 128.12, 128.05, 127.68, 126.90, 126.77, 125.66, 113.94, 76.64, 55.27, 49.47.
HRMS (ESI): calc. for C$_{23}$H$_{22}$NaO$_2$ [M+Na]$^+$: 353.1512, found: 353.1517.

4. Mechanistic studies

4.1 Cyclic voltammetry measurement

![Cyclic voltammetry measurement graph]
The cyclic voltammogram was obtained with CHI 620E electrochemical analyzer. The peak at -1.70 V shows the reduction of 1,3-diphenylprop-2-yn-1-one (1a) against SCE. The measurement employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, n-Bu4NPF6 was used as supporting electrolyte, and a scan rate of 100 mV/s. The sample was prepared with 1.0 mM solution in dry, degassed MeCN.

4.2 Stern-Volmer fluorescence quenching experiments

The quenching experiments were carried out in acetone solution of Ir[dF(CF3)(ppy)]2(dtbbpy)PF6 (10^{-4} M), and variable concentrations of benzyl trifluoroborate, 1a, 1a (in the presence of NH4OAc) were added, respectively. \( \lambda_{ex} = 410 \text{ nm}, \lambda_{em} = 473 \text{ nm} \).
Fluorescence quenching experiments of photocatalyst upon addition of benzyl trifluoroborate (A), 1a (B), 1a and NH$_4$OAc (C)

Stern-Volmer fluorescence quenching experiments.
### 4.3 Control experiments.

In the presence of radical trapping agent TEMPO, the cross-coupling reaction was totally repressed and meanwhile afforded alkyl-TEMPO adduct A in 13% yield (eqn 1). Additionally, we also detected the formation of B and C by GC-MS in the standard reaction system (eqn 2). This result provided a useful evidence for the generation of ketyl and benzyl radicals in the Barbier-type reaction process. To exclude the possibility of a benzyl anion-involved pathway, an experiment was carried out by bubbling CO$_2$ to the standard reaction system, in which no carboxylation product was detected (eqn 3).

![Chemical structures](image)

[\[\text{eqn} \, 1\]]

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 – 7.23 (m, 4H), 7.23 – 7.17 (m, 1H), 4.75 (s, 2H), 1.59 – 1.39 (m, 5H), 1.31 – 1.24 (m, 1H), 1.18 (s, 6H), 1.08 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.31, 128.20, 127.44, 127.27, 78.72,

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**1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (A),** was obtained as colorless oil.

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[a] The reaction of eqn 3 was performed referred to previous method$^{12}$ according to the following procedure: 1a (0.1 mmol, 20.7 mg), potassium benzyl trifluoroborates (0.15 mmol, 30.0 mg) and Ir[dF(CF$_3$)(ppy)$_2$(dtbbpy)]PF$_6$ (2.0 mmol%, 2.3 mg) were added to a transparent glass tube equipped with a magnetic stir bar. Then the tube was covered with a rubber septum and sealed with a coiled seal film. By evacuating air with CO$_2$ for three times at -78 °C, dried and degassed acetone (1mL) was added. After that, CO$_2$ (filled in a balloon) was injected into the reaction system via a syringe needle (under the surface of reaction liquid). Subsequently, the reaction system was treated under the irradiation of blue LEDs (36 W) at room temperature for 24 hours. The reaction mixture was filtered and the residue was washed with acetone (2 mL). The resulting filter liquor was concentrated under reduced pressure and purified by column chromatography to afforded 2a in 67% yield but with no product D obtained (as well not detected by GC-MS).
60.00, 39.71, 33.08, 20.29, 17.11.

5. Reference.

6. $^1$H and $^{13}$C spectra