

Supporting Information

Desulphurization strategy for sonogashira couplings by visible light/copper catalysis

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I. General considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. The starting materials were synthesized according to literature procedures. Flash chromatography was performed on silica gel (200~300 mesh). ^1H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in $\text{DMSO-}d_6$ or in CDCl_3 . Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: CHCl_3 ($\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C NMR), $\text{DMSO-}d_6$ ($\delta = 2.50$ and 3.30 for ^1H NMR and $\delta = 39.50$ for ^{13}C NMR). Data are reported as follows: chemical shift δ/ppm , integration (^1H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, assignment.

High Resolution Mass Spectrometry (HRMS): All were recorded on an UPLC-Q/TOF Xevo G2-XS (Waters, MA, USA) with an ESI source.

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer.

Cyclic voltammetry was performed on a CH Instruments electrochemical workstation model CS300H.

The fluorescence emission intensities were recorded on a RF-6000 Fluorescence spectrophotometer.

The power density of the incident light was recorded on CEL-FZ-A radiometer. The reactor was 3.0 cm from a 20W blue LED.

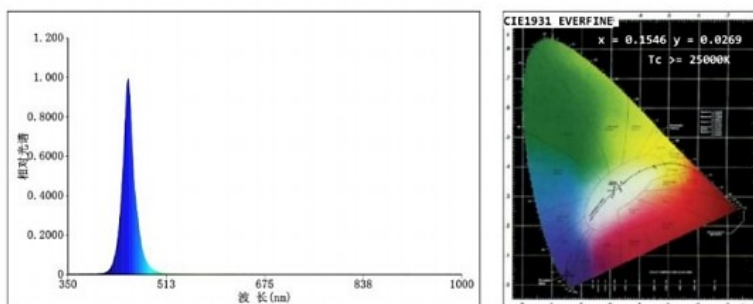
The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED manufactured by Xuzhou Ai Jia Electronic Technology Co., Ltd. without using filters.



Figure S1. The blue light LED

光源光谱测试报告



颜色参数:

色品坐标(2度): $x=0.1546$ $y=0.0269/u'=0.2051$ $v'=0.0804$ $duv=-2.137e-001$
 相关色温: $T_c=100000K$ 主波长: $\lambda_d=454.4nm$ 色纯度: $Purity=98.4\%$
 色比: $R=1.3\%$ $G=13.8\%$ $B=85.0\%$ 峰值波长: $\lambda_p=448.8nm$ 半宽度: $\Delta \lambda_d=18.9nm$
 显色指数: $R_a=-56.8$
 R1 =-1.95 R2 =-44.77 R3 =-159.98 R4 =-101.71 R5 =10.83
 R6 =-52.38 R7 =-59.23 R8 =-44.90 R9 =-242.06 R10=-230.58
 R11=-127.00 R12=-119.15 R13=-20.13 R14=-36.93 R15=14.17
 TM30 参数: $R_f = 0.0$, $R_g:21.9$

Figure S2. The spectrum of our lamp (blue LED)

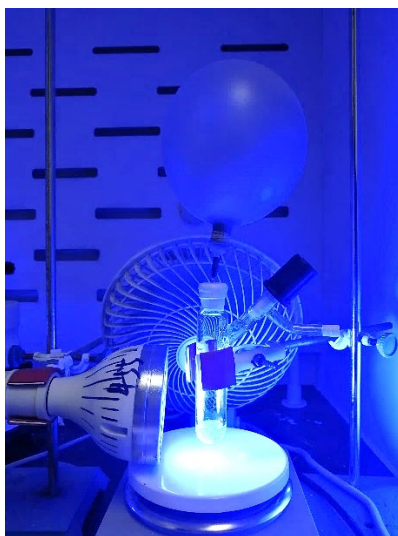
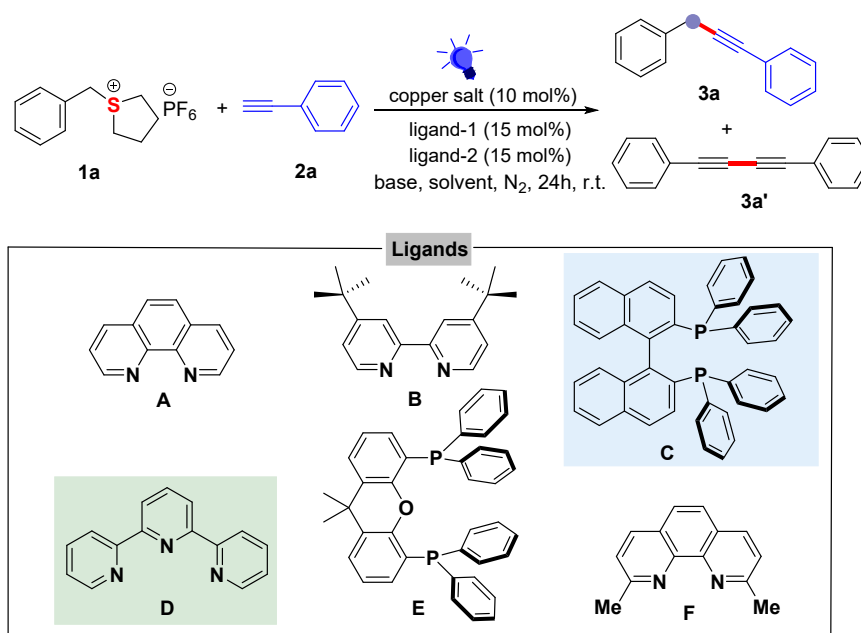


Figure S3. Photograph of the reaction setup

II. Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions^a



Entry	Catalyst	Ligand	Base	Solvent	Yield of 3a(%) ^b	Yield of 3a'(%) ^b
1	CuCl	A	K ₂ CO ₃	DMSO	None	47
2	CuCl	B	K ₂ CO ₃	DMSO	None	36
3	CuCl	C	K ₂ CO ₃	DMSO	46	45
4	CuCl	D	K ₂ CO ₃	DMSO	49	44
5	CuCl	None	K ₂ CO ₃	DMSO	Trace	89
6	CuCl	D	K ₂ CO ₃	DMSO	43 ^c	50 ^c
7	CuCl	D	K ₂ CO ₃	DMSO	33 ^d	61 ^d
8	CuCl	D	K ₂ CO ₃	DMSO	Trace ^e	87 ^e
9	CuCl	D	K ₂ CO ₃	DMSO	46 ^f	47 ^f
10	CuCl	D	K ₂ CO ₃	DMSO	Trace ^g	90 ^g
11	CuCl	D+A	K ₂ CO ₃	DMSO	None	73
12	CuCl	D+B	K ₂ CO ₃	DMSO	46	45
13	CuCl	D+E	K ₂ CO ₃	DMSO	39	52
14	CuCl	D+F	K ₂ CO ₃	DMSO	None	69
15	CuCl	D+C	K ₂ CO ₃	DMSO	88	Trace
16	CuCl	D+C	K ₂ CO ₃	DMSO	None ^h	Trace ^h
17	CuBr	D+C	K ₂ CO ₃	DMSO	26	63
18	CuI	D+C	K ₂ CO ₃	DMSO	42	Trace
19	CuCN	D+C	K ₂ CO ₃	DMSO	86	Trace
20	Cu(CH ₃ CN) ₄ PF ₆	D+C	K ₂ CO ₃	DMSO	59	25
21	Cu(CH ₃ CN) ₄ BF ₄	D+C	K ₂ CO ₃	DMSO	41	22
22	None	D+C	K ₂ CO ₃	DMSO	None	None
23	CuCl	D+C	Cs ₂ CO ₃	DMSO	None	51

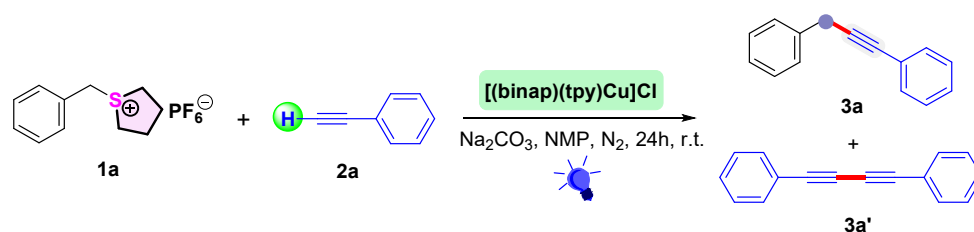
24	CuCl	D+C	Pyridine	DMSO	None	None
25	CuCl	D+C	Et ₃ N	DMSO	40	Trace
26	CuCl	D+C	None	DMSO	None	None
27	CuCl	D+C	Na ₂ CO ₃	DMSO	89	Trace
28	CuCl	D+C	Na ₂ CO ₃	CH ₃ CN	None	None
29	CuCl	D+C	Na₂CO₃	NMP	93	None
30	CuCl	D+C	Na ₂ CO ₃	DCE	None	None
31	CuCl	D+C	Na ₂ CO ₃	DMF	22	Trace
32	CuCl	D+C	Na ₂ CO ₃	Acetone	None	None

^aReaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), catalyst (10 mol%), ligand (15 mol%) respectively, base (0.6 mmol) and DMSO (2 mL) at room temperature under irradiation with a 20 W blue LED (455 nm) for 24 h under a nitrogen atmosphere.

^bIsolated yield. ^c(1a:2a=0.2:0.2). ^d(1a:2a=0.2:0.4). ^e(1a:2a=0.2:0.6). ^f(1a:2a=0.3:0.2).

^g(1a:2a=0.6:0.2). ^hNo LED irradiation.

Table S2. The screening of the amount of [(binap)(tpy)Cu]Cl^a

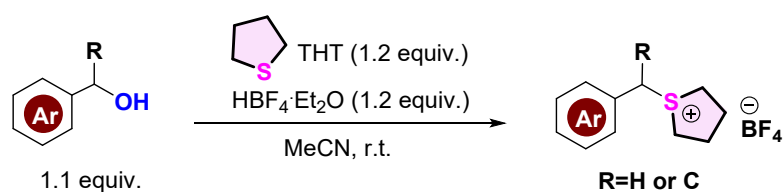


Entry	Copper-complex	Yield of 3a(%) ^b	Yield of 3a'(%) ^b
1	20 mol%	92%	none
2	10 mol%	91%	none
3	5 mol%	91%	none
4	2 mol%	39%	none

^aReaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), [(binap)(tpy)Cu]Cl (xx mol%), Na₂CO₃ (0.6 mmol) and NMP (2 mL) at room temperature under irradiation with a 20 W blue LED (455 nm) for 24 h under a nitrogen atmosphere. ^bIsolated yield.

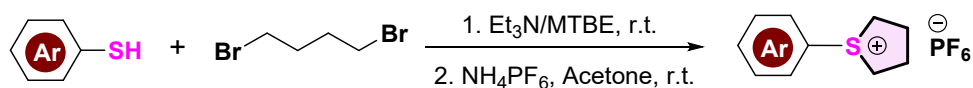
III. Experimental procedures

1. General method for sulfonium salt synthesis: ¹²³

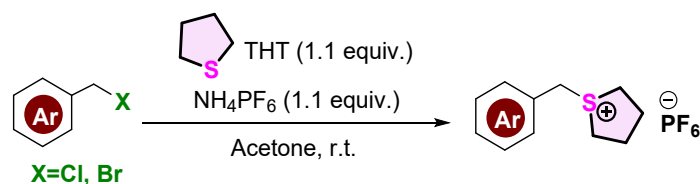


General procedure: A flame-dried round bottom flask with a magnetic stirring bar was charged with the benzyl alcohol (5.5 mmol, 1.1 equiv.), tetrahydrothiophene (THT, 529 μ l, 6.0 mmol, 1.2 equiv.), and acetonitrile (MeCN, [1 M] *with respect to (w.r.t.) the benzyl alcohol*). Thereafter, tetrafluoroboric acid diethyl ether complex

($\text{HBF}_4 \cdot \text{Et}_2\text{O}$, 816.5 μl , 6.0 mmol, 1.2 equiv.) was added dropwise and the reaction was left to stir until full consumption of the alcohol was observed by TLC (1:1 hexanes (Hex)/ethyl acetate (EtOAc)) or for a 12 h period. After the end of the reaction, the reaction liquid was concentrated, and then the desired product was obtained by adding ether to wash and removing the washing liquid.



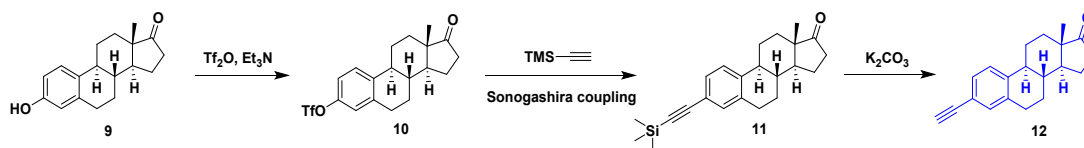
General procedure: Triethylamine (3785 μl , 27.23 mmol, 1.5 equiv.) was slowly added to a 50 mL round-bottom flask containing thiophenol (2.25 g, 18.15 mmol, 1.0 equiv.), 1, 4-dibromobutane (4335 μl , 36.3 mmol, 2.0 equiv.) and Et_2O (20 mL). The reaction mixture was stirred for 30 min then diluted with Et_2O (200 mL) and washed with 1.2 M HCl (2×20 mL) and brine. The organic layer was dried (Na_2SO_4), the solvents were evaporated, and the crude material was dissolved in acetone (30 mL) and treated with NH_4PF_6 (4.44 g, 27.23 mmol). After stirring overnight at room temperature, the reaction mixture was filtered through a medium porosity fritted-glass funnel, the filtrate was concentrated under reduced pressure, and Et_2O (20 mL) was added producing colorless crystals. The crystals were collected on a coarse fritted-glass funnel and washed with water (10 mL), ethanol (10 mL), and Et_2O (10 mL). The product was purified by recrystallization from acetone/ Et_2O to give of analytically pure colorless crystals.



General procedure: Tetrahydrothiophene (485 μl , 5.5 mmol, 1.1 equiv.), benzylbromide or benzylchloride (5.0 mmol, 1.0 equiv.) and NH_4PF_6 (896 mg, 5.5 mmol, 1.1 equiv.) was dissolved in acetone (5.0 mL) and stirred at room temperature for 16 hours. The formed precipitate was filtered and washed with acetone. The filtrate was reduced to half its volume and excess diethyl ether was added. The formed precipitate was filtered and washed with diethyl ether then dried in-vacuo to

get the product.

2. Synthesis of natural product: ⁴

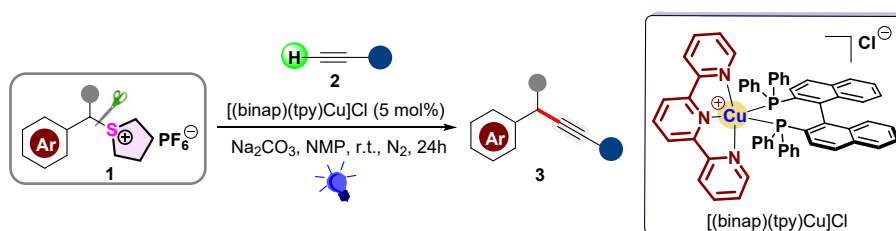


To **9** (486.7 mg, 1.8 mmol) in dry CH_2Cl_2 (15 mL) at 0 °C was added triethylamine (528.2 μl , 3.8 mmol) and trifluoromethanesulfonic anhydride (689.8 μl , 4.1 mmol). The reaction mixture was stirred at 0 °C for 30 min before the addition of water. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases are washed with brine and dried over Na_2SO_4 . The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **10**.

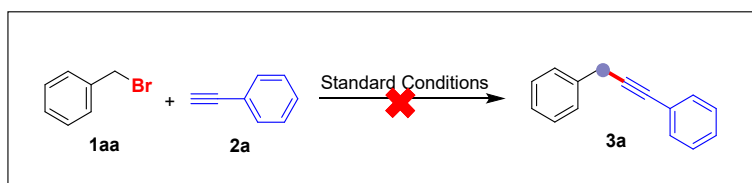
To a mixture of **10** (1.21 g, 3.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (210.6 mg, 0.3 mmol) and CuI (57.1 mg, 0.3 mmol) in DMF (60 mL) was added Et_3N (1.25 mL, 9.0 mmol), and TMSA (2120 μl , 15.0 mmol), then the reaction was stirred at 80°C for 4 hours. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with EtOAc (3×50 mL). The combined organic phases are washed with brine and dried over Na_2SO_4 . The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **11**.

To **11** (385.6 mg, 1.1 mmol) in MeOH (20 mL) was added K_2CO_3 (30.4 mg, 0.22 mmol). The reaction mixture was stirred at room temperature for 4 hours. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with EtOAc (3×20 mL). The combined organic phases are washed with brine and dried over Na_2SO_4 . The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **12**.

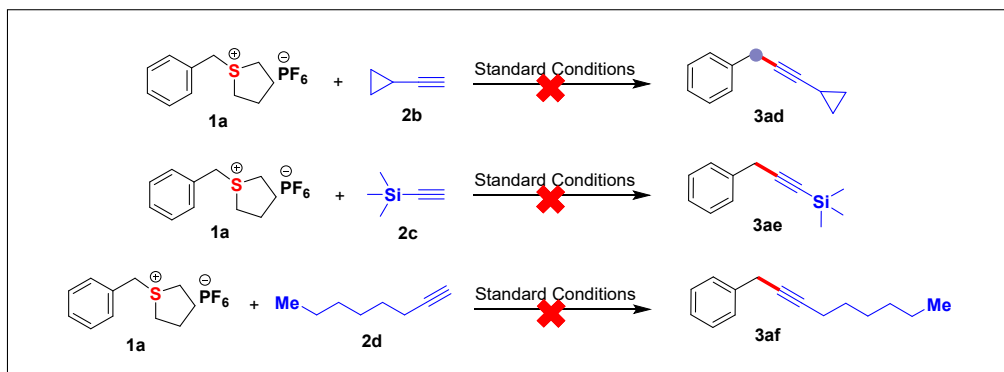
3. General procedure for the synthesis of **3**



General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). **2** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (4 × 5 mL). The combined organic phase was dried over Na₂SO₄. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.

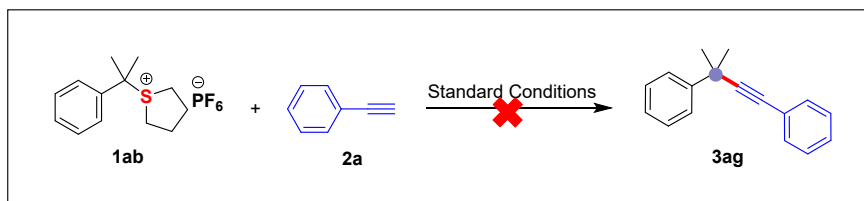


General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added benzyl bromide **1aa** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). **2a** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. No desired product was detected by TLC.

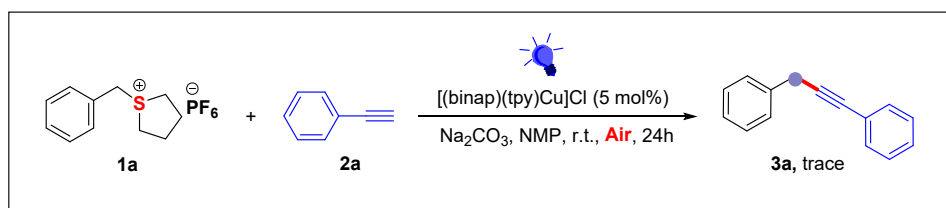


General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1a** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol)

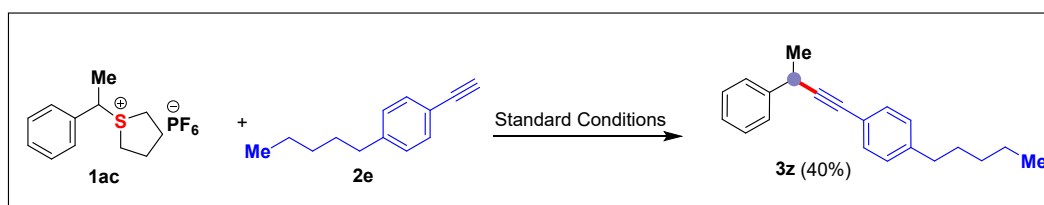
and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). Some of alkyl alkynes such as **2b**, **2c**, **2d** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. No product was detected by TLC.



General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1ab** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). **2a** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. No product was detected by TLC.

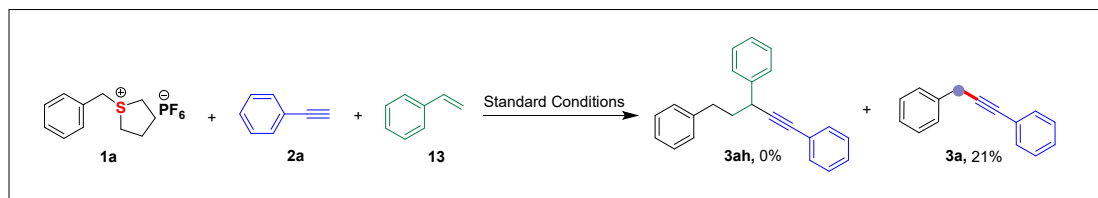


General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1a** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then **2a** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h in air. Only a trace amount of product **3a** was detected by TLC..



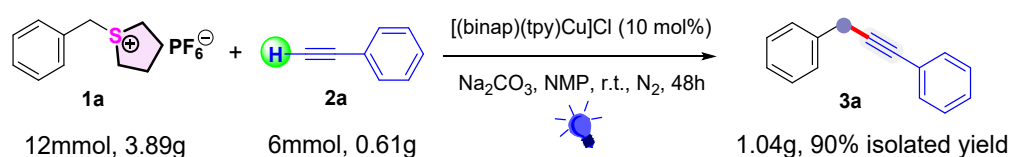
General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1ac** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with

nitrogen (three times). **2e** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (4 × 5 mL). The combined organic phase was dried over Na₂SO₄. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.



General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1a** (0.6 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). **2a** (0.2 mmol) and **13** (0.4 mmol) in degassed NMP (2.0 mL) was added and the mixture was irradiated under 20 W blue LEDs at room temperature for 24 h. The residue was added brine (10 mL) and extracted with ethyl acetate (4 × 5 mL). The combined organic phase was dried over Na₂SO₄. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.

4. Gram scale

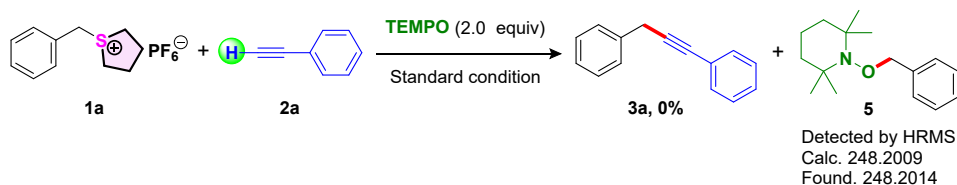


General procedure: To an oven-dried 50 mL Schlenk Tube with a stirring bar was added sulfonium salt **1a** (12.0 mmol), followed by the addition of Na₂CO₃ (3.0 equiv.) and [(binap)(tpy)Cu]Cl (10 mol%). Then, air was withdrawn and backfilled with N₂ (three times). **2a** (6.0 mmol) in degassed NMP (20 mL) was added and the mixture was irradiated under two 20 W blue LEDs at room temperature for 48 h. When the reaction is completed, the reaction mixture was added water and extracted with ethyl acetate, washed with brine, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (Eluent petroleum ether) to afford the

product **3a** (1.04 g, 90%).

IV. Experiments of investigations on the mechanism

1. Investigation on the effect of TEMPO and 1,1-diphenylethylene



General procedure: a mixture **1a** (0.4 mmol), **2a** (0.2 mmol), [(binap)(tpy)Cu]Cl (5 mol%), Na₂CO₃ (0.6 mmol) and 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO, 2.0 equiv.) in degassed NMP (2 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 24 h in N₂.

The radical trapping experiments were conducted with **1a** and **2a** under the standard conditions with a trapping agent 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO, 2.0 equiv.) to capture the radical intermediate expected in our system, and the products were detected by HRMS techniques. Supplementary Figure S4 showed that TEMPO, the most common trapping agent, captured benzyl radical with TEMPO-trapped compound **5** observed. HRMS (ESI): compound **5**, HRMS (ESI) calcd for C₁₆H₂₆NO⁺ [M+H]⁺ : 248.2009, found: 248.2014.

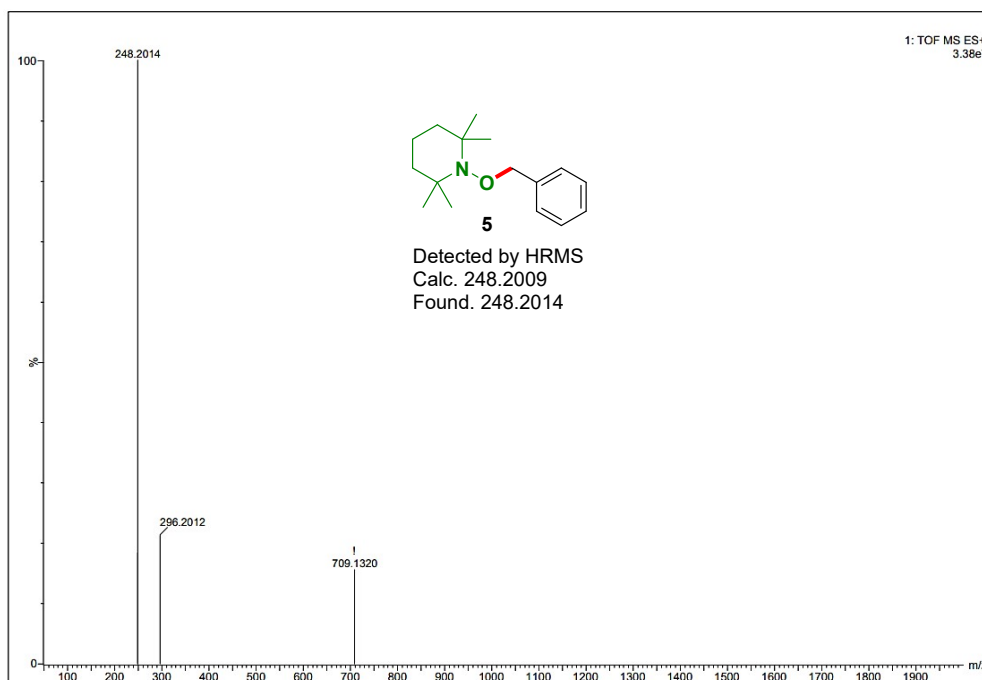
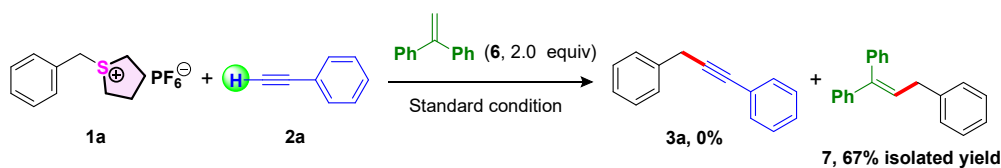


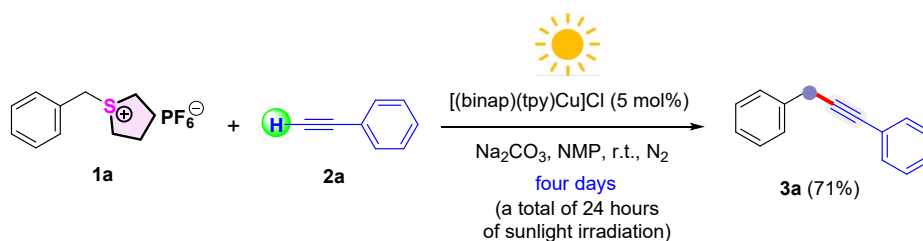
Figure S4. HRMS of TEMPO and the Benzylic Radical Adduct



General procedure: a mixture **1a** (0.4 mmol), **2a** (0.2 mmol), [(binap)(tpy)Cu]Cl (5 mol%), Na₂CO₃ (0.6 mmol) and 1, 1-diphenylethylene (0.4 mmol) in degassed NMP (2 mL) at room temperature under irradiation with 20 W blue LED (455 nm) for 24 h in N₂.

The radical trapping experiments were conducted with **1a** and **2a** under the standard conditions with a trapping agent 1,1-diphenylethylene (**6**, 2.0 equiv.) to capture the radical intermediate expected in our system, and the product **7** (72 mg, 67%) was purified by silica gel column chromatography.

2. Sunlight-driven experiment

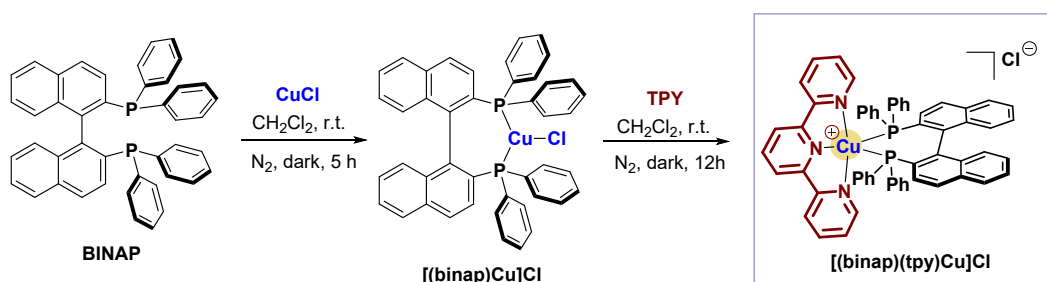


General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salt **1a** (0.4 mmol), followed by the addition of Na₂CO₃ (0.6 mmol) and [(binap)(tpy)Cu]Cl (5 mol%). Then the tube was evacuated and backfilled with nitrogen (three times). **2a** (0.2 mmol) in degassed NMP (2.0 mL) was added and the mixture was stirred under solar light for four days (a total of 24 hours of sunlight irradiation, location: 36°8'54" N, 120°23'3" E). Afterward, the residue was added water (10 mL) and extracted with ethyl acetate (5 mL × 4). The combined organic phase was dried over Na₂SO₄, and the resulting crude residue was purified via column chromatography on silica gel to afford **3a** in 71% yield.

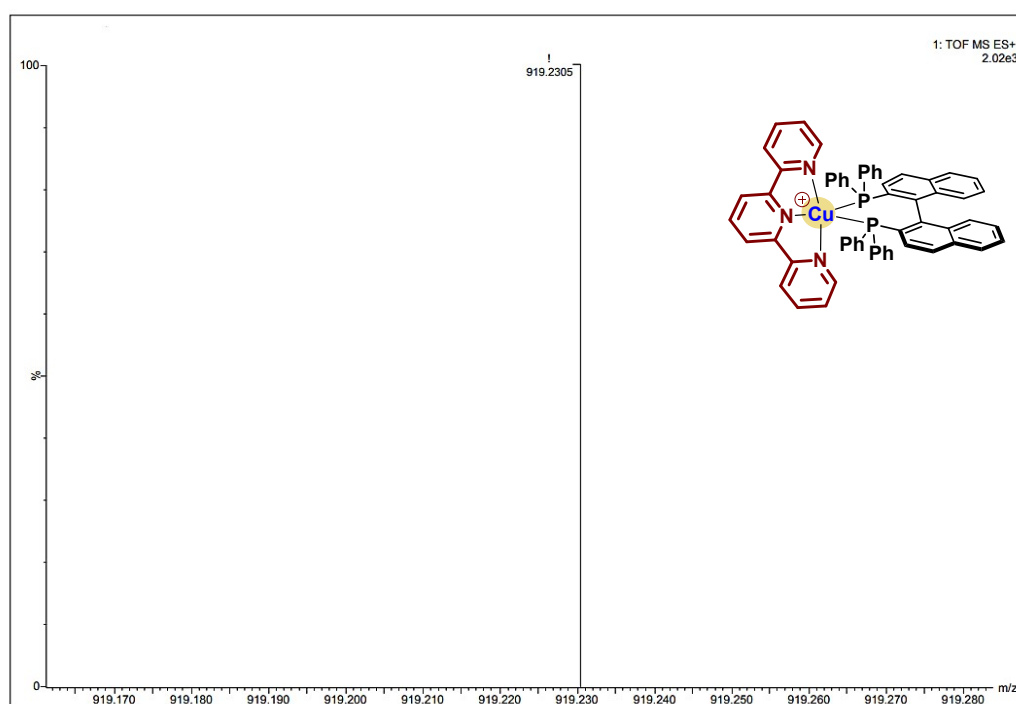
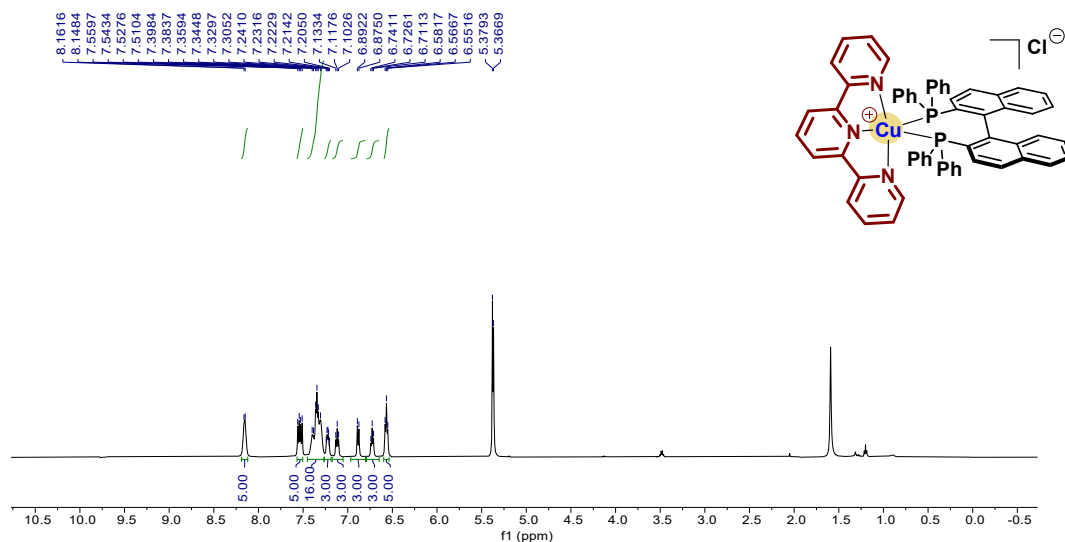


Figure S5. Sunlight-driven experiment

3. Synthesis of Cu-photocatalyzed⁵



To a solution of copper(I) chloride (0.0495 g, 0.5 mmol) in dry dichloromethane (80 mL) was added 1,1'-Binaphthyl-2,2'-diphemyl phosphine (binap, 0.3269 g, 0.52 mmol, 1.05 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 hours. A solution of 2,2':6',2''-Terpyridine (tpy, 0.1125 g, 0.52 mmol, 1.05 equiv.) in dry dichloromethane (3 mL) was then added dropwise under a nitrogen atmosphere and the resulting reaction mixture was stirred for another 12 hours. The reaction mixture was filtered to collect the filtrate. Then the resulting filtrate was then concentrated under reduced pressure to one tenth of the original volume and ether (80 mL) was added to the resulting solution under stirring. The yellow precipitate was collected by filtration and dried under vacuum to give the desired copper complex [(binap)(tpy)Cu]Cl (0.3342 mg, 0.35 mmol, 70%) as a yellow solid; ¹H NMR (CD₂Cl₂, 500 MHz, ppm) δ 8.16 (d, *J* = 6.6 Hz, 5H), 7.57 – 7.50 (m, 5H), 7.45 – 7.27 (m, 16H), 7.26 – 7.19 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 3H), 6.88 (d, *J* = 8.6 Hz, 3H), 6.73 (t, *J* = 7.4 Hz, 3H), 6.57 (t, *J* = 7.5 Hz, 5H). HRMS calcd for C₅₉H₄₄CuN₃P₂⁺ [M+H]: 919.2301; found 919.2305.



4. UV-Vis absorption experiment

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer. The sample was prepared by mixing **1a** (5 mM), **2a** (5 mM), in-situ-generated [(binap)(tpy)Cu]Cl (0.1 mM), [(binap)(tpy)Cu]Cl+Na₂CO₃ (0.1 mM), [(binap)(tpy)Cu]Cl+Na₂CO₃+**2a** (0.1 mM) in NMP. The absorption was collected and the result was listed in Figure S6.

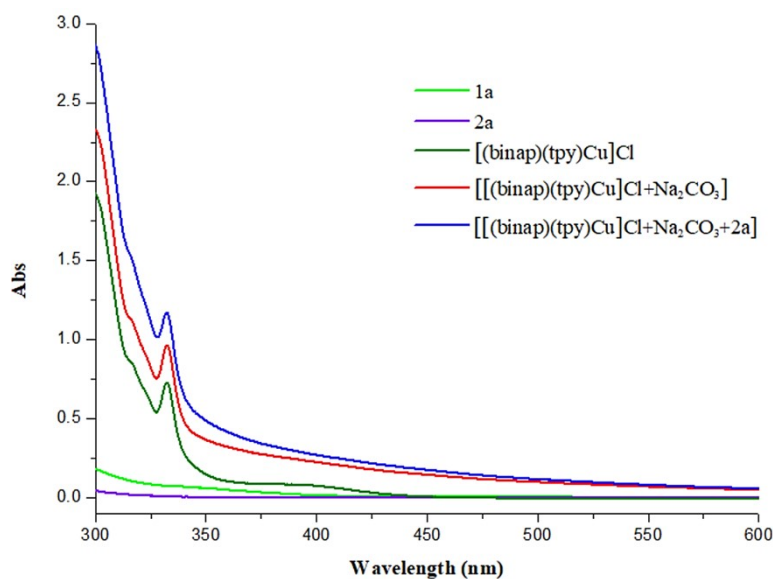


Figure S6. UV-Vis absorption spectra.

5. Cyclic Voltammetry (CV) experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CS300H. A solution of the sample in NMP was tested with 0.3 M Tetrabutylammonium bromide as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and Ag/AgCl as reference electrode. Scan rate = 100 mV/s.

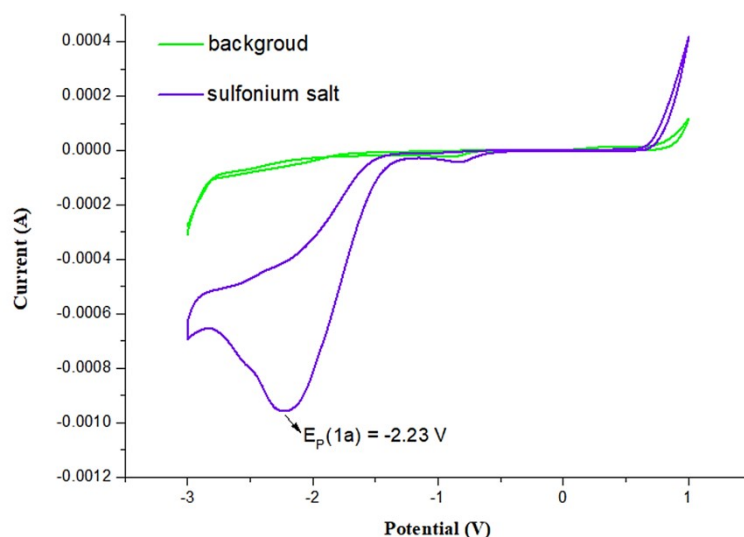


Figure S7. CV spectra of sulfonium salt **1a** (0.2 M) in 0.3 M tetrabutylammonium bromide in NMP.

$$E_p(1a) = -2.23 \text{ V (vs. Ag/AgCl)}$$

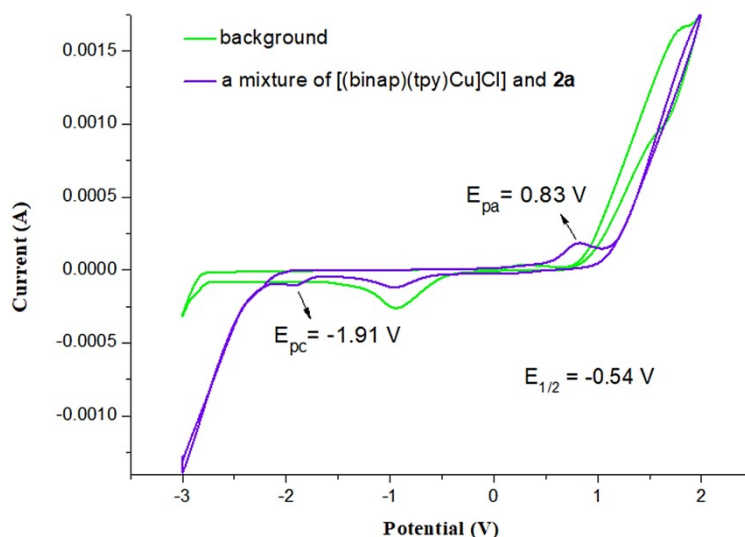


Figure S8. CV spectra of a mixture of [(binap)(tpy)Cu]Cl (5 mM) and phenylacetylene **2a** (5 mM) in 0.3 M tetrabutylammonium bromide in NMP.

$$E_{1/2}(Cu^{II}/Cu^I) = -0.54 \text{ V (vs. Ag/AgCl)} \quad E_{0-0} = 2.60 \text{ V}$$

$$E_{1/2}(Cu^{II}/Cu^{I*}) = E_{1/2}(Cu^{II}/Cu^I) - E_{0-0} = -0.54 - 2.60 = -3.14 \text{ V}$$

6. Fluorescence quenching experiments

The fluorescence emission intensities were recorded on a RF-6000 Fluorescence spectrophotometer. The excitation wavelength was fixed at 381 nm. The samples were prepared by [(binap)(tpy)Cu]Cl (0.1 mM), the in-situ-formed copper complex **A** (a mixture of [(binap)(tpy)Cu]Cl and phenylacetylene **2a**, 0.1 mM) and different amount of quencher **1a** in NMP in a light path quartz fluorescence cuvette. The concentration of quencher **1a** is 10^{-5} M in NMP. For each quenching experiment, 3 μ l of quencher solution was separately titrated to a mixed solution of [(binap)(tpy)Cu]Cl (3.0 mL) and the in-situ-formed copper complex **A** (3.0 mL). Then the emission intensity was collected and the results were presented in Figure S9 and Figure S10.

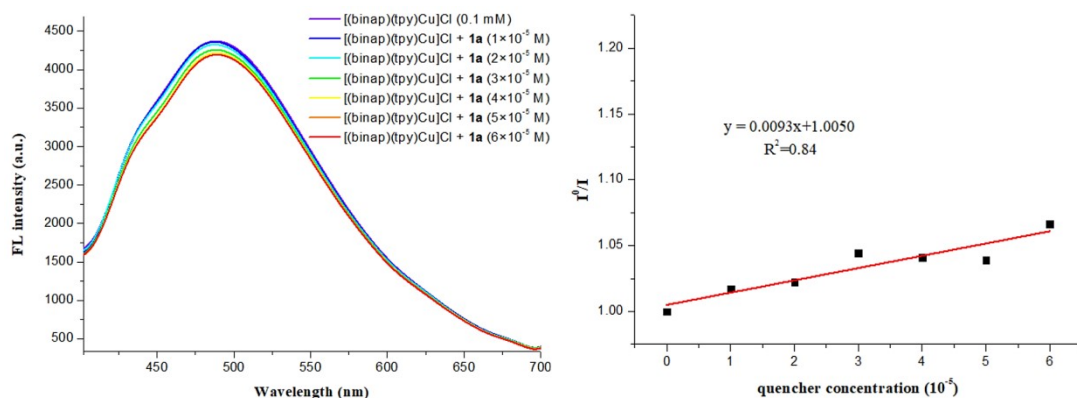


Figure S9. The emission quenching of [(binap)(tpy)Cu]Cl in NMP by various concentrations of quencher **1a**.

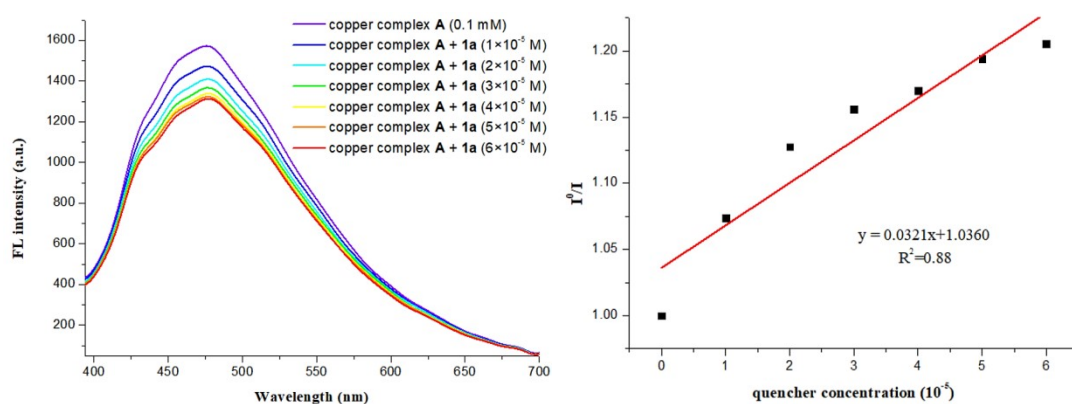


Figure S10. The emission quenching of the in-situ-formed copper complex A (a mixture of [(binap)(tpy)Cu]Cl and phenylacetylene **2a**) in NMP by various concentrations of quencher **1a**.

7. Luminescent decay profile

Luminescent decay profile was done with a FLS1000 transient fluorescence spectrometer (exciting at 381 nm).

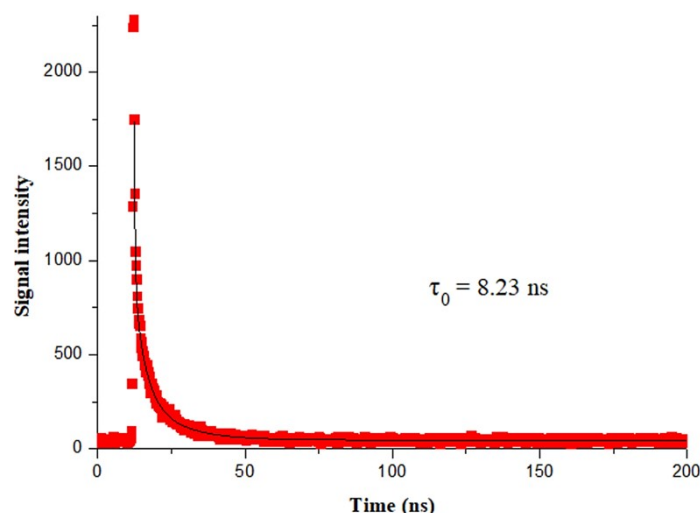


Figure S11. Luminescent decay of [(binap)(tpy)Cu]Cl measured at ambient temperature under argon in NMP (10^{-4} M) and recorded at 477 nm ($\lambda_{\text{exc}} = 381$ nm).

8. Calculation of apparent quantum efficiency (A. Q. E)

The energy of one photon (E_{photon}) with wavelength of λ_{inc} (nm) is calculated using the following equation:

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}}(455\text{nm})} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s} \times 3 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{455 \times 10^{-9} \text{ m}} = 4.37 \times 10^{-19} \text{ J}$$

And the total energy of the incident monochromatic light (E_{total}) is calculated using the following equation:

$$E_{\text{total}} = PSt = 134.69 \times 10^{-3} \text{ W}\cdot\text{cm}^{-2} \times 4.58 \text{ cm}^2 \times 2 \times 3600 \text{ s} = 4.44 \times 10^3 \text{ J}$$

The total number of incident photons can be obtained through the following equation:

$$\text{Number of incident photons} = \frac{E_{\text{total}}}{E_{\text{photon}}} = 1.02 \times 10^{22} = 16.9 \text{ mmol}$$

As a result, the apparent quantum yield (A.Q.Y) is defined as follows:

$$\text{A.Q.Y}(\%) = \frac{\text{Number of product}}{\text{Number of incident photons}} = \frac{0.0384 \text{ mmol}}{16.9 \text{ mmol}} = 0.23\% < 1$$

Where h ($\text{J}\cdot\text{s}$) is Planck's constant, c ($\text{m}\cdot\text{s}^{-1}$) is the speed of light and λ_{inc} (m) is the wavelength of the incident light. P ($\text{W}\cdot\text{cm}^{-2}$) is the power density of the incident light, S (cm^2) is the irradiation area and t (s) is the photoreaction time. The A.Q.Y(%) result indicated that our reaction not involved radical chain pathway.

9. Effect of visible light irradiation

The reaction between **1a** and **2a** was conducted under the standard conditions on a 0.2 mmol scale. The mixture was subjected to sequential periods of stirring under visible light irradiation (20 W blue LED) followed by stirring in the absence of light. At each time point, one reaction system was suspended, which was then purified with chromatography column on silica gel (Eluent petroleum ether) to give the corresponding products **3a**. The yield of **3a** was measured by weight of the product.

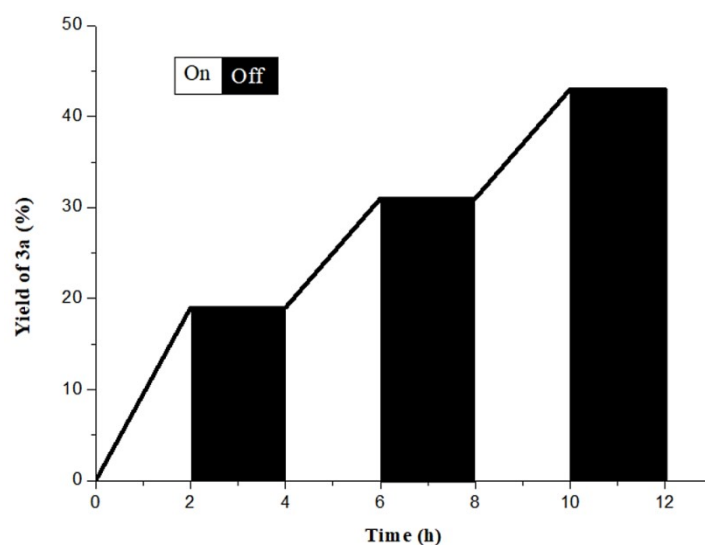


Figure S12. Visible Light Irradiation on/off experiment

10. EPR experiments

Free radical trapping investigation by Electron Paramagnetic Resonance Spectroscopy (EPR):

To an oven-dried Schlenk tube equipped with a stir bar was loaded with [(binap)(tpy)Cu]Cl (0.01 mmol) and phenylacetylene(**2a**, 0.2 mmol) after uniform mixing, then add sulfonium salt (**1a**, 0.4 mmol) and 5,5-dimethyl-1-pyrroline *N*-oxide (**DMPO**, 2.0 equiv.) in NMP (2.0 mL) under N₂. The solution sample was taken out into a capillary tube, after that the capillary tube was transferred to a EPR tube and measured. Subsequently, the reaction solution was irradiated with 20 W blue LED (455 nm) for 5 min, then analyzed by EPR again, as is shown by the orange line. EPR spectrum was recorded at 300 K on EPR spectrometer operated at 9.221 GHz, scan

width 10 mT, center field 329.3 mT, time constant 0.1s, scan time 1min, modulation width 0.1 mT, gain 500, power 1mW.

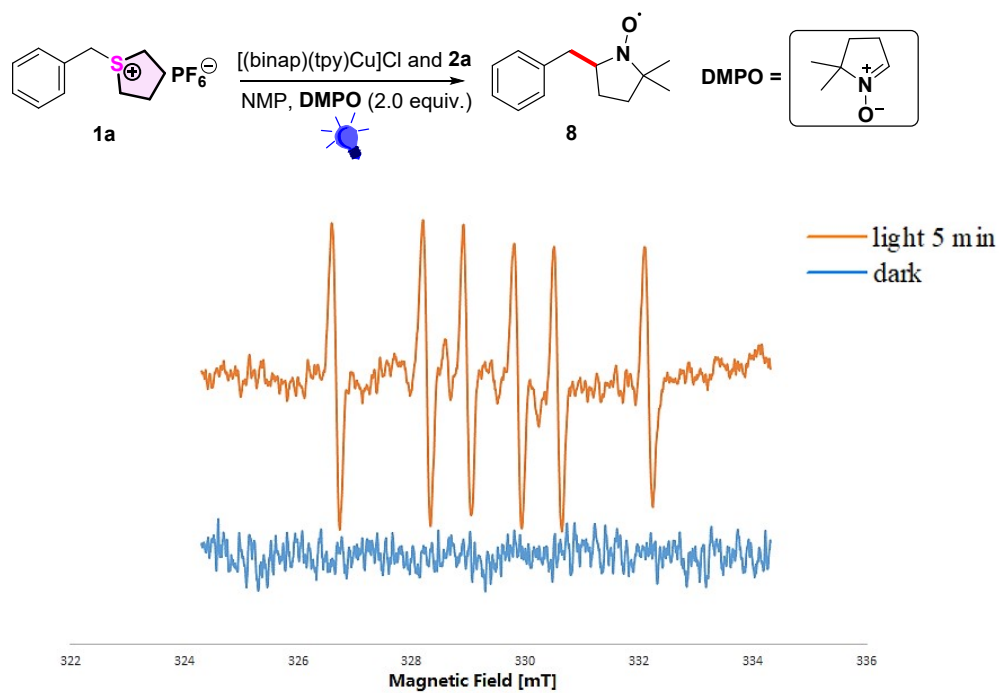
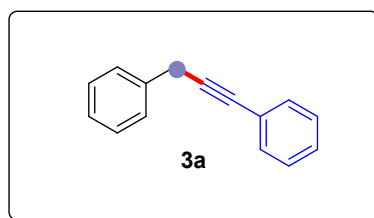


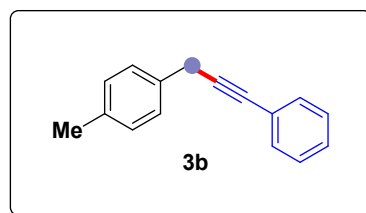
Figure S13. EPR Spectra of the DMPO-Radical Adduct

V. Characterization of products

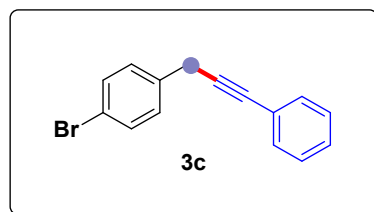
Characterization data of compounds 3a-9



Prop-1-yne-1,3-diyl dibenzene (3a)⁶. Eluent petroleum ether. Pale yellow oil, 35 mg, 91% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.46 – 7.40 (m, 4H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 5.2, 2.0 Hz, 4H), 7.26 – 7.23 (m, 1H), 3.83 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 136.80, 131.68, 128.58, 128.26, 128.00, 127.84, 126.67, 123.72, 87.55, 82.69, 25.76. HRMS calcd for C₁₅H₁₃⁺ [M+H]⁺: 193.1012; found 193.1017.

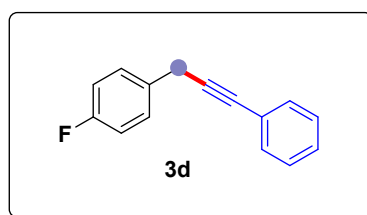


1-Methyl-4-(3-phenylprop-2-yn-1-yl)benzene (3b)⁶. Eluent petroleum ether. Yellow oil, 33 mg, 81% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.43 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 2H), 3.78 (s, 2H), 2.33 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 136.22, 133.76, 131.68, 129.27, 128.25, 127.89, 127.80, 123.81, 87.90, 82.48, 25.36, 21.06. HRMS calcd for C₁₆H₁₅⁺ [M+H]⁺: 207.1169; found 207.1174.

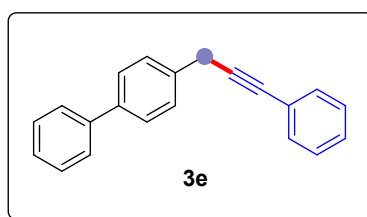


1-Bromo-4-(3-phenylprop-2-yn-1-yl)benzene (3c)⁷. Eluent petroleum ether. Yellow oil, 28 mg, 52% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.53 – 7.44 (m, 4H), 7.38 – 7.29 (m, 5H), 3.82 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 135.81, 131.66,

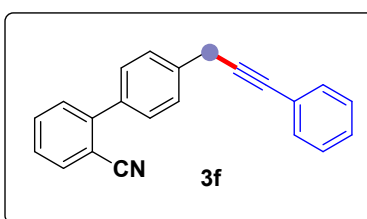
131.62, 129.73, 128.30, 128.01, 123.43, 120.49, 86.76, 83.07, 25.28. HRMS calcd for $C_{15}H_{12}Br^+$ $[M+H]^+$: 271.0117; found 271.0120.



1-Fluoro-4-(3-phenylprop-2-yn-1-yl)benzene (3d)⁶. Eluent petroleum ether. Pale yellow oil, 29 mg, 70% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.43 (dd, $J = 6.7, 3.1$ Hz, 2H), 7.36 (dd, $J = 8.5, 5.4$ Hz, 2H), 7.31 – 7.27 (m, 3H), 7.02 (t, $J = 8.7$ Hz, 2H), 3.79 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 162.73, 160.79, 132.41, 131.65, 129.44, 129.38, 128.28, 127.95, 123.52, 115.42, 115.25, 87.27, 82.84, 25.01. HRMS calcd for $C_{15}H_{12}F^+$ $[M+H]^+$: 211.0918; found 211.0925.

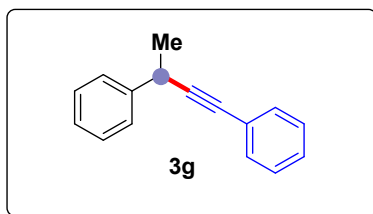


4-(3-Phenylprop-2-yn-1-yl)-1,1'-biphenyl (3e)⁸. Eluent petroleum ether. Colorless oil, 25 mg, 46% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.58 (t, $J = 8.1$ Hz, 4H), 7.52 – 7.46 (m, 4H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.28 (m, 4H), 3.88 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 140.94, 139.73, 135.88, 131.69, 128.79, 128.42, 128.28, 127.88, 127.34, 127.23, 127.09, 123.69, 87.46, 82.77, 25.46. HRMS calcd for $C_{21}H_{17}^+$ $[M+H]^+$: 269.1325; found 269.1335.

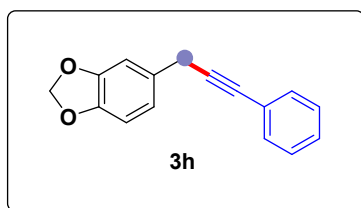


4'-(3-Phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-2-carbonitrile (3f). Eluent petroleum ether/ethyl acetate (10:1). Colorless oil, 48 mg, 81% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.75 (d, $J = 7.8$ Hz, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.54 (s, 4H), 7.53 – 7.46 (m, 4H), 7.50 – 7.44 (m, 3H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.32 – 7.28 (m, 3H), 3.90

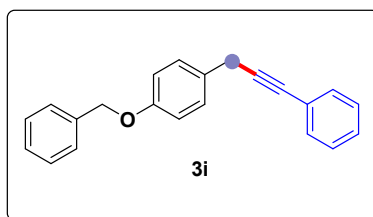
(s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 145.25, 137.51, 136.61, 133.78, 132.86, 131.71, 130.05, 129.18, 128.98, 128.41, 128.30, 127.95, 127.53, 123.57, 118.79, 111.27, 87.03, 83.04, 25.57. HRMS calcd for $\text{C}_{22}\text{H}_{14}\text{N}^+$ $[\text{M}+\text{H}]^+$: 294.1227; found 294.1284.



But-1-yne-1,3-diylidibenzene (3g)⁸. Eluent petroleum ether. Colorless oil, 17 mg, 42% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.48 – 7.41 (m, 4H), 7.34 (t, J = 7.7 Hz, 2H), 7.29 (dd, J = 5.2, 2.0 Hz, 3H), 7.25 (t, J = 3.7 Hz, 1H), 3.98 (q, J = 7.2 Hz, 1H), 1.58 (d, J = 7.1 Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 143.35, 131.64, 128.56, 128.20, 127.75, 126.94, 126.67, 123.76, 92.61, 82.45, 32.48, 24.49. HRMS calcd for $\text{C}_{16}\text{H}_{15}^+$ $[\text{M}+\text{H}]^+$: 207.1169; found 207.1171.

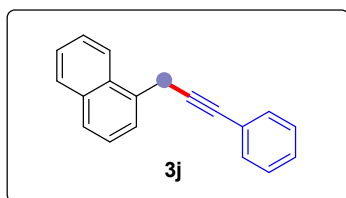


5-(3-Phenylprop-2-yn-1-yl)benzo[d][1,3]dioxole (3h)⁹. Eluent petroleum ether. Yellow oil, 31 mg, 66% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.47 – 7.42 (m, 2H), 7.30 (d, J = 4.3 Hz, 3H), 6.93 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 3.75 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 147.83, 146.34, 131.65, 130.54, 128.24, 127.85, 123.63, 120.83, 108.62, 108.23, 100.99, 87.64, 82.63, 25.44. HRMS calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 237.0910; found 237.0904.

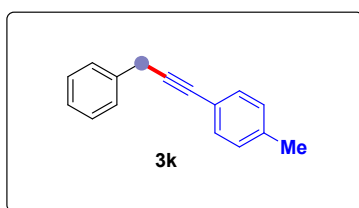


1-(Benzyloxy)-4-(3-phenylprop-2-yn-1-yl)benzene (3i)¹⁰. Eluent petroleum ether. Yellow oil, 36 mg, 60% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.52 – 7.47 (m,

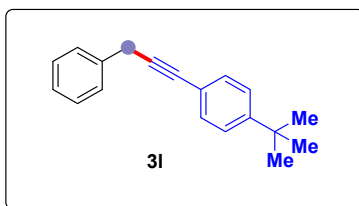
4H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.40 – 7.32 (m, 6H), 7.01 (d, $J = 8.6$ Hz, 2H), 5.11 (s, 2H), 3.82 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 157.66, 137.14, 131.67, 129.13, 128.99, 128.61, 128.26, 127.96, 127.81, 127.48, 123.77, 115.01, 87.97, 82.48, 70.13, 24.93. HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{O}^+$ $[\text{M}+\text{H}]^+$: 299.1431; found 299.1440.



1-(3-Phenylprop-2-yn-1-yl)naphthalene (3j)¹¹. Eluent petroleum ether. Yellow solid, 29 mg, 59% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.12 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.73 (d, $J = 7.1$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.55 – 7.51 (m, 1H), 7.50 – 7.45 (m, 3H), 7.33 – 7.28 (m, 3H), 4.25 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 133.77, 132.54, 131.69, 128.78, 128.27, 127.87, 127.64, 126.22, 125.78, 125.65, 123.71, 123.43, 87.28, 83.60, 23.71. HRMS calcd for $\text{C}_{19}\text{H}_{15}^+$ $[\text{M}+\text{H}]^+$: 243.1169; found 243.1179.

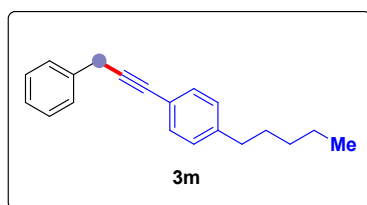


1-Methyl-4-(3-phenylprop-1-yn-1-yl)benzene (3k)⁶. Eluent petroleum ether. Yellow oil, 40 mg, 96% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 8.9$ Hz, 4H), 7.27 (d, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 2H), 3.85 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 137.86, 136.95, 131.55, 129.03, 128.56, 128.00, 126.63, 120.64, 86.75, 82.76, 25.78, 21.45. HRMS calcd for $\text{C}_{16}\text{H}_{15}^+$ $[\text{M}+\text{H}]^+$: 207.1169; found 207.1179.

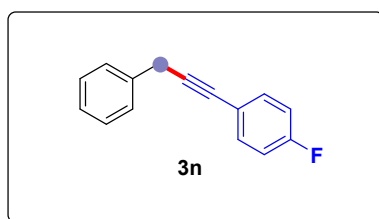


1-(tert-Butyl)-4-(3-phenylprop-1-yn-1-yl)benzene (3l)⁶. Eluent petroleum ether.

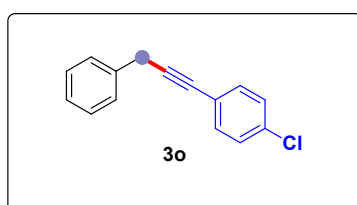
Colorless oil, 44 mg, 89% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.40 (dd, $J = 12.0, 8.1$ Hz, 4H), 7.34 – 7.29 (m, 4H), 7.23 (t, $J = 8.0$ Hz, 1H), 3.82 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 151.05, 136.97, 131.40, 128.55, 128.00, 126.62, 125.27, 120.72, 86.76, 82.78, 34.73, 31.23, 25.79. HRMS calcd for $\text{C}_{19}\text{H}_{21}^+$ $[\text{M}+\text{H}]^+$: 249.1565; found 249.1571.



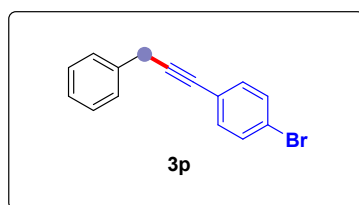
1-Pentyl-4-(3-phenylprop-1-yn-1-yl)benzene (3m)⁷. Eluent petroleum ether. Colorless oil, 30 mg, 58% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.46 (d, $J = 7.1$ Hz, 2H), 7.42 – 7.34 (m, 4H), 7.30 – 7.27 (m, 1H), 7.15 (d, $J = 8.1$ Hz, 2H), 3.87 (s, 2H), 2.63 (t, $J = 7.7$ Hz, 2H), 1.64 (t, $J = 7.5$ Hz, 2H), 1.39 – 1.32 (m, 4H), 0.93 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 142.91, 136.96, 131.54, 128.53, 128.36, 127.98, 126.59, 120.82, 86.70, 82.79, 35.81, 31.43, 30.95, 25.76, 22.52, 14.00. HRMS calcd for $\text{C}_{20}\text{H}_{23}^+$ $[\text{M}+\text{H}]^+$: 263.1795; found 263.1800.



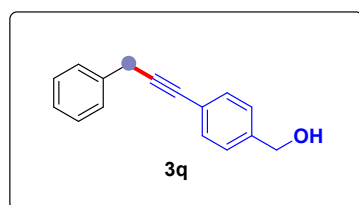
1-Fluoro-4-(3-phenylprop-1-yn-1-yl)benzene (3n)⁶. Eluent petroleum ether. Pale yellow oil, 32 mg, 75% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.46 – 7.40 (m, 4H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.29 – 7.25 (m, 1H), 7.00 (t, $J = 8.7$ Hz, 2H), 3.83 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 163.26, 161.28, 136.69, 133.50, 133.44, 128.60, 127.97, 126.72, 119.77, 115.56, 115.39, 87.23, 81.59, 25.69. HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{F}^+$ $[\text{M}+\text{H}]^+$: 211.0918; found 211.0925.



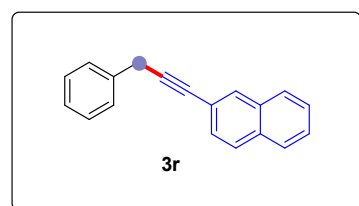
1-Chloro-4-(3-phenylprop-1-yn-1-yl)benzene (3o)⁶. Eluent petroleum ether. Pale yellow oil, 43 mg, 95% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.44 – 7.34 (m, 6H), 7.29 (d, *J* = 8.5 Hz, 3H), 3.84 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 136.53, 133.82, 132.91, 128.64, 128.59, 127.98, 126.77, 122.22, 88.68, 81.59, 25.76. HRMS calcd for C₁₅H₁₂Cl⁺ [M+H]⁺: 227.0622; found 227.0614.



1-Bromo-4-(3-phenylprop-1-yn-1-yl)benzene (3p)⁸. Eluent petroleum ether. Yellow oil, 30 mg, 56% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.46 (dd, *J* = 14.3, 7.8 Hz, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.29 (m, 1H), 3.86 (s, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 136.47, 133.13, 131.50, 128.62, 127.97, 126.76, 122.67, 121.99, 88.87, 81.63, 25.78. HRMS calcd for C₁₅H₁₂Br⁺ [M+H]⁺: 271.0117; found 271.0114.

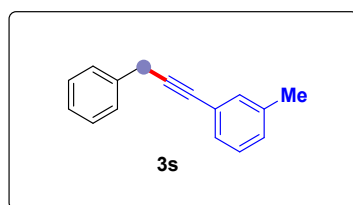


(4-(3-Phenylprop-1-yn-1-yl)phenyl)methanol (3q). Eluent petroleum ether/ethyl acetate (5:1). Pale yellow oil, 36 mg, 82% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.45 – 7.38 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 3H), 4.65 (s, 2H), 3.82 (s, 2H), 1.87 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 140.56, 136.75, 131.83, 128.59, 127.99, 126.79, 126.68, 122.95, 87.66, 82.47, 64.95, 25.76. HRMS calcd for C₁₆H₁₄O⁺ [M+H]⁺: 223.1118; found 223.1108.

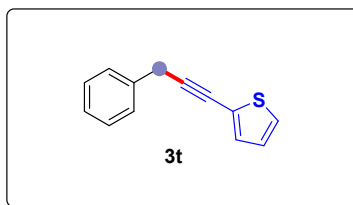


2-(3-Phenylprop-1-yn-1-yl)naphthalene (3r). Eluent petroleum ether. Colorless oil,

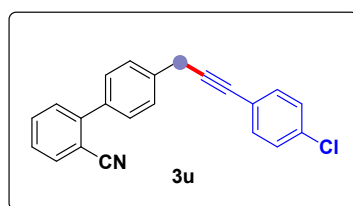
15 mg, 31% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.00 (s, 1H), 7.85 – 7.79 (m, 3H), 7.56 – 7.48 (m, 5H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.31 (d, $J = 7.4$ Hz, 1H), 3.93 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 136.77, 133.05, 132.63, 131.28, 128.68, 128.60, 128.02, 127.87, 127.73, 127.65, 126.69, 126.42, 121.01, 82.99, 25.86. HRMS calcd for $\text{C}_{19}\text{H}_{15}^+$ $[\text{M}+\text{H}]^+$: 243.1169; found 243.1167.



1-Methyl-3-(3-phenylprop-1-yn-1-yl)benzene (3s)⁷. Eluent petroleum ether. Colorless oil, 19 mg, 45% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.46 (d, $J = 7.6$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.33 – 7.28 (m, 3H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 3.87 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 137.90, 136.85, 132.27, 128.71, 128.55, 128.15, 127.97, 126.62, 123.49, 87.12, 82.81, 25.74, 21.20. HRMS calcd for $\text{C}_{16}\text{H}_{15}^+$ $[\text{M}+\text{H}]^+$: 207.1169; found 207.1160.

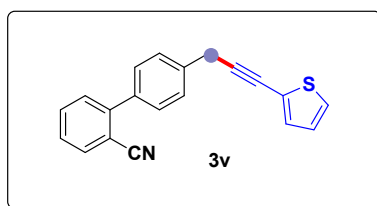


2-(3-Phenylprop-1-yn-1-yl)thiophene (3t)⁷. Eluent petroleum ether. Yellow solid, 18 mg, 45% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.43 (d, $J = 7.5$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.29 (s, 1H), 7.24 (d, $J = 5.3$ Hz, 1H), 7.22 (d, $J = 3.2$ Hz, 1H), 6.99 (dd, $J = 5.2, 3.6$ Hz, 1H), 3.89 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 136.37, 131.40, 128.61, 128.00, 126.83, 126.75, 126.31, 123.76, 91.58, 75.77, 26.01. HRMS calcd for $\text{C}_{13}\text{H}_{11}\text{S}^+$ $[\text{M}+\text{H}]^+$: 199.0576; found 199.0570.

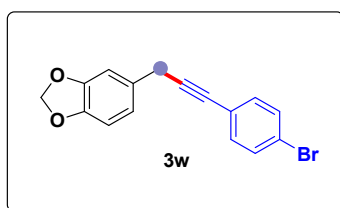


4'-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-[1,1'-biphenyl]-2-carbonitrile (3u). Eluent

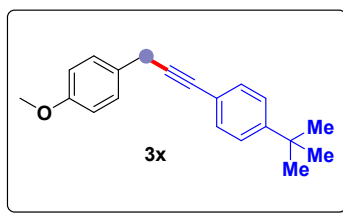
petroleum ether/ethyl acetate (10:1). Pale yellow oil, 49 mg, 75% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.66 – 7.62 (m, 1H), 7.56 – 7.51 (m, 5H), 7.45 – 7.42 (m, 1H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 145.19, 137.22, 136.70, 133.92, 133.79, 132.94, 132.87, 130.04, 129.02, 128.60, 128.39, 127.56, 122.06, 118.77, 118.60, 111.27, 88.14, 81.92, 25.55. HRMS calcd for $\text{C}_{22}\text{H}_{15}\text{ClN}^+$ $[\text{M}+\text{H}]^+$: 328.0888; found 328.0888.



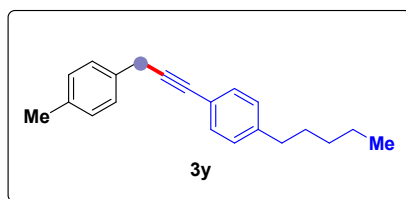
4'-(3-(Thiophen-2-yl)prop-2-yn-1-yl)-[1,1'-biphenyl]-2-carbonitrile (3v). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 38 mg, 63% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.75 (d, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.52 (t, $J = 5.1$ Hz, 5H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.22 – 7.19 (m, 2H), 6.98 – 6.95 (m, 1H), 3.91 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 145.20, 137.08, 136.70, 133.77, 132.85, 131.57, 130.04, 129.02, 128.42, 127.54, 126.88, 126.46, 123.60, 118.77, 111.27, 91.06, 76.17, 25.82. HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{NS}^+$ $[\text{M}+\text{H}]^+$: 300.0842; found 300.0842.



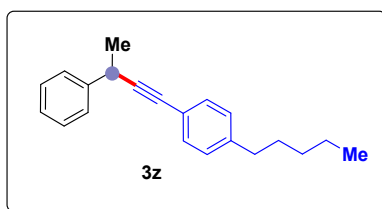
5-(3-(4-Bromophenyl)prop-2-yn-1-yl)benzo[d][1,3]dioxole (3w). Eluent petroleum ether. Yellow oil, 37 mg, 59% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.46 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 6.93 (s, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 5.98 (s, 2H), 3.76 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 147.87, 146.41, 133.11, 131.49, 130.19, 122.59, 122.01, 120.84, 108.58, 108.27, 101.03, 88.98, 81.58, 25.46. HRMS calcd for $\text{C}_{16}\text{H}_{12}\text{BrO}_2^+$ $[\text{M}+\text{H}]^+$: 315.0015; found 315.0023.



1-(*tert*-Butyl)-4-(3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (3x). Eluent petroleum ether. Yellow oil, 17 mg, 31% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.30 (m, 4H), 6.87 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 3.76 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 158.37, 150.97, 131.34, 128.99, 128.92, 125.21, 113.94, 87.17, 82.47, 55.32, 34.69, 31.19, 24.90. HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{O}^+$ $[\text{M}+\text{H}]^+$: 279.1744; found 279.1747.

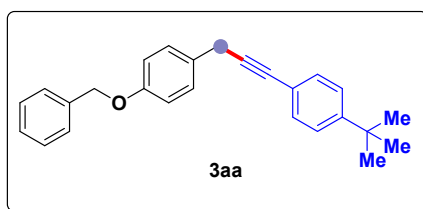


1-Methyl-4-(3-(4-pentylphenyl)prop-2-yn-1-yl)benzene (3y). Eluent petroleum ether. Pale yellow oil, 42 mg, 76% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.38 (d, $J = 6.3$ Hz, 2H), 7.32 (d, $J = 7.2$ Hz, 2H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.13 (d, $J = 6.4$ Hz, 2H), 3.80 (s, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 2.36 (s, 3H), 1.62 (t, $J = 7.5$ Hz, 2H), 1.37 – 1.30 (m, 4H), 0.91 (t, $J = 6.2$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 142.84, 136.13, 133.92, 131.55, 129.22, 128.35, 127.87, 120.93, 87.06, 82.60, 35.83, 31.45, 30.97, 25.37, 22.54, 21.04, 14.03. HRMS calcd for $\text{C}_{21}\text{H}_{25}^+$ $[\text{M}+\text{H}]^+$: 277.1951; found 277.1941.

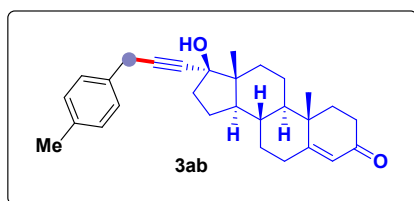


1-Pentyl-4-(3-phenylbut-1-yn-1-yl)benzene (3z)⁷. Eluent petroleum ether. Pale yellow oil, 22 mg, 40% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.45 (d, $J = 7.4$ Hz, 2H), 7.37 – 7.30 (m, 4H), 7.24 (t, 1H), 7.10 (d, $J = 7.9$ Hz, 2H), 3.97 (q, $J = 7.1$ Hz, 1H), 2.58 (t, $J = 7.7$ Hz, 2H), 1.61 – 1.55 (m, 5H), 1.33 – 1.27 (m, 4H), 0.88 (t, $J = 6.9$

Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 143.49, 142.81, 131.52, 128.53, 128.32, 126.95, 126.61, 120.86, 91.82, 82.55, 35.80, 32.48, 31.41, 30.97, 24.59, 22.52, 14.01. HRMS calcd for C₂₁H₂₅⁺ [M+H]⁺: 277.1951; found 277.1958.

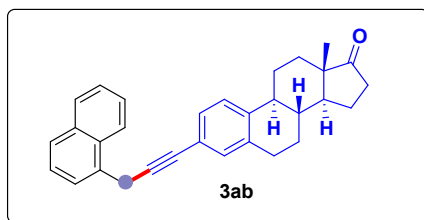


1-(Benzyloxy)-4-(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)benzene (3aa). Eluent petroleum ether. Yellow oil, 18 mg, 26% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.40 (m, 4H), 7.37 – 7.33 (m, 5H), 6.98 (d, *J* = 8.6 Hz, 2H), 5.10 (s, 2H), 3.80 (s, 2H), 1.34 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 157.59, 150.98, 137.13, 131.34, 129.28, 128.95, 128.59, 127.93, 127.46, 125.22, 120.70, 114.95, 87.12, 82.50, 70.11, 34.69, 31.19, 24.92. HRMS calcd for C₁₅H₁₃⁺ [M+H]⁺: 193.1012; found 193.1017. HRMS calcd for C₂₆H₂₇O⁺ [M+H]⁺: 355.2057; found 355.2059.

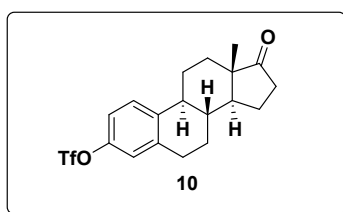


(8*S*,9*R*,10*S*,13*R*,14*R*,17*R*)-17-Hydroxy-10,13-dimethyl-17-(3-(*p*-tolyl)prop-1-yn-1-yl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one (3ab). Eluent petroleum ether/ethyl acetate (5:1). Colorless oil, 40 mg, 48% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.20 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.73 (s, 1H), 3.60 (s, 2H), 2.41 – 2.36 (m, 2H), 2.31 (s, 3H), 2.27 (d, *J* = 9.9 Hz, 2H), 2.06 – 1.97 (m, 3H), 1.84 (d, *J* = 12.9 Hz, 1H), 1.70 (t, *J* = 11.6 Hz, 3H), 1.62 (d, *J* = 10.0 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.41 (d, *J* = 9.3 Hz, 1H), 1.35 – 1.31 (m, 1H), 1.28 – 1.23 (m, 1H), 1.19 (s, 3H), 1.03 (d, *J* = 15.5 Hz, 1H), 0.93 (d, *J* = 10.5 Hz, 1H), 0.89 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 199.64, 171.37, 136.17, 133.75, 129.17, 127.70, 123.85, 85.63, 84.19, 79.86, 53.57,

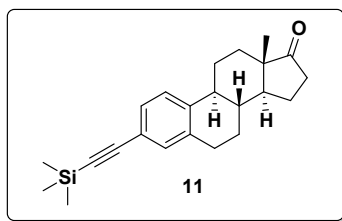
49.94, 46.85, 39.04, 38.65, 36.26, 35.72, 33.96, 32.81, 32.60, 31.57, 24.74, 23.07, 21.00, 20.76, 17.44, 12.82. HRMS calcd for $C_{29}H_{37}O_2^+$ $[M+H]^+$: 417.2788; found 417.2781.



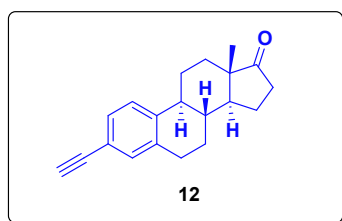
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(3-(naphthalen-1-yl)prop-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3ac). Eluent petroleum ether/ethyl acetate (20:1). Colorless oil, 28 mg, 34% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 8.09 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.51 (t, *J* = 6.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.25 – 7.19 (m, 3H), 4.22 (s, 2H), 2.90 – 2.84 (m, 2H), 2.54 – 2.47 (m, 1H), 2.43 – 2.37 (m, 1H), 2.31 – 2.26 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 1.97 (m, 3H), 1.60 – 1.45 (m, 6H), 0.91 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 220.79, 136.49, 132.11, 131.50, 128.98, 128.73, 127.56, 126.17, 125.73, 125.61, 125.29, 123.41, 86.50, 83.56, 50.52, 47.96, 44.42, 38.01, 35.84, 31.56, 29.08, 26.36, 25.60, 23.69, 21.58, 13.84. HRMS calcd for $C_{31}H_{31}O^+$ $[M+H]^+$: 419.2370; found 419.2363.



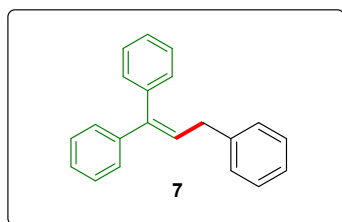
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (10)¹³. Eluent petroleum ether/ethyl acetate (10:1). White solid. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.37 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 7.03 (s, 1H), 2.99 – 2.95 (m, 2H), 2.58 – 2.52 (m, 1H), 2.46 – 2.41 (m, 1H), 2.36 – 2.30 (m, 1H), 2.22 – 2.15 (m, 1H), 2.12 – 2.05 (m, 2H), 2.03 – 1.99 (m, 1H), 1.67 – 1.50 (m, 6H), 0.95 (s, 3H).



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((trimethylsilyl)ethynyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (11)¹⁴. Eluent petroleum ether/ethyl acetate (10:1). Pale yellow solid. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.29 – 7.23 (m, 3H), 2.93 – 2.88 (m, 2H), 2.57 – 2.50 (m, 1H), 2.46 – 2.40 (m, 1H), 2.35 – 2.29 (m, 1H), 2.21 – 2.14 (m, 1H), 2.12 – 1.98 (m, 3H), 1.64 – 1.46 (m, 6H), 0.94 (s, 3H), 0.27 (s, 9H).



(8*R*,9*S*,13*S*,14*S*)-3-Ethynyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (12)¹³. Eluent petroleum ether/ethyl acetate (10:1). Pale yellow solid. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.30 – 7.26 (m, 3H), 3.05 (s, 1H), 2.94 – 2.90 (m, 2H), 2.57 – 2.51 (m, 1H), 2.46 – 2.42 (m, 1H), 2.33 (t, *J* = 10.9 Hz, 1H), 2.22 – 2.14 (m, 1H), 2.11 – 2.04 (m, 2H), 2.02 – 1.98 (m, 1H), 1.65 – 1.49 (m, 6H), 0.94 (s, 3H).



Prop-1-ene-1,1,3-triyltribenzene (7)¹². Eluent petroleum ether. Colorless oil, 72 mg, 67% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.31 (m, 10H), 7.29 (d, *J* = 7.5 Hz, 3H), 6.37 (t, *J* = 7.6 Hz, 1H), 3.57 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 142.56, 142.52, 141.03, 139.91, 130.01, 128.56, 128.48, 128.37, 128.19, 127.83, 127.41, 127.21, 127.13, 126.07, 36.00. HRMS calcd for C₂₁H₁₉⁺ [M+H]⁺: 271.1482; found 271.1485.

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VII. NMR spectra of the products

