Photo-Induced Copper-Catalyzed Alkynylation and Amination of Remote Unactivated C(sp3)−H bond

Zhusong Cao,a Jianye Li,b Youwen Sun,a Hanwen Zhang,a Xueling Mo,a Xin Cao,c,* and Guozhu Zhang,a,b,*

a State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China
b College of Chemistry, Central China Normal University (CCNU), 152 Luoyu Road, Wuhan, Hubei 430079, P. R. China.
c Zhongshan Hospital, Fudan University, Shanghai, China. 180 Fenglin Road, Shanghai 200032, P. R. China.
Content

1. General information ...................................................................................................................2
2. Synthesis and characterizations of substrates ............................................................................2
   1.1 General procedure for the synthesis of tethered alcohols ....................................................2
   2.2 Characterizations of new substrates.....................................................................................2
3. Experimental Details ..................................................................................................................7
   3.1 Optimization of the reaction conditions ...........................................................................7
   3.2 General procedures and characterizations of products ....................................................9
   3.3 Characterization data of products ......................................................................................10
4. Synthetic applications ..............................................................................................................23
   4.1 Stereoselective Synthesis of tetrahydropyran derivative ...................................................23
   4.2 Stereoselective synthesis of pyrano-chromene derivative .................................................23
5. Mechanistic investigations.......................................................................................................24
   5.1 Radical scavengers studies .............................................................................................24
   5.2 Observation of intermediate ............................................................................................24
   5.3 Photophysical study ..........................................................................................................25
   5.4 Quantum yield measurement ...........................................................................................27
6. References ................................................................................................................................28
7. Spectral Data................................................................................................................................29
1. General information

NMR spectra were recorded on Varian Inova (400 MHz), Bruker (400 MHz) or Agilent (400 MHz) spectrometer. The $^1$H NMR were calibrated against the peak of tetramethylsilane at 0 ppm). The $^{13}$C NMR were calibrated against the peak of the CDCl$_3$ at 77.16 ppm. The multiplicities $^1$H NMR spectra are abbreviated as follows: s (singlet) d (doublet) t (triplet) q (quartet) and m (multiplet). GC/MS analysis was performed on GCMS-QP2010 Plus. HRMS analyses were performed on Bruker maXis, Thermo Scientific Q Exactive HF Orbitrap-FTMS and Waters premier GC-TOF MS. All IR spectra was processed on Nicolet 380 and the method is denoted in brackets. UV/Vis absorption spectra were recorded on Varian Cary 100. Fluorescence spectrum was performed on HITACHI F-2700. Materials: Unless stated otherwise, acetonitrile and the substrates were purchased from commercial sources without further purification. Blue LED lamps (40W, Kessil A160WE tuna blue) were used for reactions. Reactions requiring inert conditions were carried out in glove box.

2. Synthesis and characterization of substrates

All the tethered alcohols were prepared by conventional methods.$^1$ Alcohol precursors not commercially available were synthesized from the corresponding aldehydes. Chloro(iodomethyl)diisopropylsilane was prepared according to literature procedure.$^2$

1.1 General procedure for the synthesis of tethered alcohols

$$\text{R}^1 \text{R}' \text{OH} + \text{imidazole} \rightarrow \text{imidazole} \rightarrow \text{R}^1 \text{R}' \text{O} \text{Si} \text{i-Pr} \text{i-Pr} \text{I}$$

Under nitrogen atmosphere, to a 25 mL round bottom flask was added imidazole (272 mg, 4 mmol, 2 equiv) in 5 mL CH$_2$Cl$_2$, Chloro(iodomethyl)diisopropylsilane (640 mg, 2.2 mmol, 1.1 equiv) and corresponding alcohol. The mixture was stirred until completion of the reaction as judged by GC/MS analysis. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography in hexanes.

2.2 Characterizations of new substrates

$((2,7$-dimethyloctan-4-yl)oxy)(iodomethyl)diisopropylsilane

$$\text{1d}$$
**1d** was prepared according to general procedure in 75% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.96-3.88 (m, 1H), 2.08 (s, 2H), 1.75-1.63 (m, 1H), 1.58-1.42 (m, 3H), 1.39-1.30 (m, 2H), 1.27-1.15 (m, 4H), 1.13-1.05 (m, 12H), 0.94-0.83 (m, 12H). $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 71.63, 46.25, 35.11, 33.79, 28.34, 24.61, 23.104, 23.096, 22.79, 22.64, 17.92, 17.89, 17.61, 17.58, 12.79, 12.75. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2953, 2867, 1464, 1367, 1139, 1052, 882, 722, 679. HRMS (EI, 70eV) m/z calcd. for C$_{17}$H$_{37}$IOSi [M]$^+$: 412.1653; found: 412.1657.

(1-cyclopropyl-3-methylbutoxy)(iodomethyl)diisopropylsilane

![Structure](image)

**1i** was prepared according to general procedure in 89% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 3.36-3.29 (m, 1H), 2.10 (s, 2H), 1.90-1.79 (m, 1H), 1.58-1.48 (m, 1H), 1.44-1.36 (m, 1H), 1.28-1.16 (m, 2H), 1.12-1.05 (m, 12H), 0.90 (dd, $J = 6.6, 5.0$ Hz, 5H), 0.50-0.45 (m, 2H), 0.36-0.30 (m, 1H), 0.22-0.16 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 75.76, 48.04, 24.50, 23.46, 23.02, 18.16, 18.11, 17.99, 17.91, 17.80, 13.24, 13.08, 4.05, 2.79. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2952, 2866, 1463, 1382, 1367, 1087, 1060, 1014, 919, 882, 721, 681, 520. HRMS (EI, 70eV) m/z calcd. for C$_{15}$H$_{31}$IOSi [M]$^+$: 382.1183; found: 382.1192.

((4-ethoxybutan-2-yl)oxy)(iodomethyl)diisopropylsilane

![Structure](image)

**1j** was prepared according to general procedure in 78% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.19-4.10 (m, 1H), 3.54-3.41 (m, 4H), 2.07 (d, $J = 0.9$ Hz, 2H), 1.75-1.67 (m, 2H), 1.25-1.15 (m, 8H), 1.10-1.04 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 67.26, 66.65, 66.27, 39.78, 24.34, 17.95, 17.86, 17.61, 17.59, 15.37, 12.71, 12.67. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.88, 136.74, 126.355, 112.59, 72.94, 54.30, 49.42, 23.58, 22.03, 17.08, 16.72, 16.63, 16.47, 11.69, 11.52, -20.66. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2941, 2865, 1462, 1377, 1117, 1051, 1027, 953, 882, 719, 680. HRMS (EI, 70eV) m/z calcd. for C$_{15}$H$_{29}$IO$_2$Si [M]$^+$: 372.0976; found: 372.0978.

(iodomethyl)diisopropyl(pent-4-en-1-yl)oxy)silane
1k was prepared according to general procedure in 85% isolated yield. Colorless oil. 1H NMR (400 MHz, CDCl₃): 5.88-5.77 (m, 1H), 5.05-4.93 (m, 2H), 3.75 (t, J = 6.4 Hz, 2H), 2.17-2.10 (m, 2H), 2.07 (s, 2H), 1.70-1.59 (m, 2H), 1.27-1.16 (m, 2H), 1.10-1.04 (m, 12H). 13C NMR (101 MHz, CDCl₃): δ 138.38, 114.60, 63.14, 31.99, 29.96, 17.68, 17.44, 12.27. IR (neat) cm⁻¹ ʋ: 2940, 2866, 1641, 1462, 1099, 992, 911, 881, 804, 723, 684. HRMS (EI, 70eV) m/z calcd. for C₁₂H₂₅IOSi [M]+: 340.0714; found: 340.0716.

(iodomethyl)diisopropyl(3-phenylpropoxy)silane

11 was prepared according to general procedure in 80% isolated yield. Colorless oil. 1H NMR (400 MHz, CDCl₃): 7.33-7.27 (m, 2H), 7.25-7.17 (m, 3H), 3.80 (t, J = 6.3 Hz, 2H), 2.73 (t, J = 7.7 Hz 2H), 2.10 (s, 2H), 1.95-1.85 (m, 2H), 1.32-1.20 (m, 2H), 1.13-1.07 (m, 12H). 13C NMR (101 MHz, CDCl₃): δ 142.24, 128.60, 128.42, 125.84, 63.15, 34.59, 32.17, 17.83, 17.61, 12.43. IR (neat) cm⁻¹ ʋ: 2941, 2864, 1458, 1381, 1102, 964, 881, 786, 723, 697. HRMS (EI, 70eV) m/z calcd. for C₁₆H₂₇IOSi [M]+: 390.0870; found: 390.0878.

(iodomethyl)diisopropyl(3-methyl-1-phenylbutoxy)silane

1m was prepared according to general procedure in 79% isolated yield. Colorless oil. 1H NMR (400 MHz, CDCl₃): 7.33-7.29 (m, 2H), 7.27-7.21 (m, 3H), 4.86 (t, J = 6.3 Hz, 1H), 1.89 (d, J = 1.6 Hz, 2H), 1.78-1.69 (m, 1H), 1.63-1.54 (m, 1H), 1.52-1.42 (m, 1H), 1.26-1.02 (m, 8H), 1.01-0.86 (m, 1H). 13C NMR (101 MHz, CDCl₃): δ 144.56, 127.28, 126.40, 125.24, 73.41, 49.44, 23.56, 22.13, 22.01, 17.07, 16.71, 16.62, 16.46, 11.69, 11.52, -20.81. IR (neat) cm⁻¹ ʋ: 2952, 2866, 1462, 1366, 1060, 1006, 915, 882,
856, 804, 761, 727, 698, 552. HRMS (ESI) m/z calcd. for C_{18}H_{31}INaOSi [M+Na]^+: 413.0768; found: 413.0788.

(iodomethyl)diisopropyl(1-(4-methoxyphenyl)-3-methylbutoxy)silane

\[ \text{1n} \]

1n was prepared according to general procedure in 85% isolated yield. Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 7.23\ (d, J = 8.6\ Hz, 2H), 6.87\ (d, J = 8.5\ Hz, 2H), 4.82\ (t, J = 6.7\ Hz, 1H), 3.81\ (s, 3H), 1.88\ (d, J = 3.8Hz, 2H), 1.77-1.67\ (m, 1H), 1.60-1.51\ (m, 1H), 1.50-1.41\ (m, 1H), 1.25-1.04\ (m, 8H), 1.02-0.86\ (m, 12H). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\ 157.88, 136.74, 126.35, 112.59, 72.94, 54.30, 49.42, 23.58, 22.03, 17.08, 16.72, 16.63, 16.47, 11.69, 11.52, -20.66. \) IR (neat) cm\(^{-1}\) \(\tilde{\nu}\): 2951, 2866, 1612, 1511, 1463, 1366, 1299, 1246, 1172, 1059, 1003, 882, 859, 831, 725, 683, 555, 520. HRMS (EI, 70eV) m/z calcd. for C_{19}H_{33}IO_{2}Si [M]^+: 448.1289; found: 448.1295.

(iodomethyl)diisopropyl(3-methyl-1-(4-(trifluoromethyl)phenyl)butoxy)silane

\[ \text{1p} \]

1p was prepared according to general procedure in 80% isolated yield. Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 7.58\ (d, J = 8.0\ Hz, 2H), 7.44\ (d, J = 8.0\ Hz, 2H), 4.95\ (t, J = 6.3\ Hz, 1H), 1.92\ (s, 2H), 1.78-1.69\ (m, 1H), 1.60 -1.43(m, 2H), 1.30-1.04 (m, 8H), 1.02– 0.87 (m, 12H). \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\ 148.58, 128.62\ (q, J = 32.3\ Hz), 125.46, 125.39, 124.32\ (q, J = 4.0\ Hz), 123.75\ (q, J = 272.7\ Hz), 109.17, 72.84, 49.41, 23.48, 22.07, 22.04, 16.95, 16.70, 16.57, 16.45, 11.67, 11.53. \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\ -62.37\ (s, 1F). \) IR (neat) cm\(^{-1}\) \(\tilde{\nu}\): 2954, 2868, 1620, 1464, 1323, 1164, 1125, 1063, 1013, 882, 861, 839, 727, 606. HRMS (EI, 70eV) m/z calcd. for C_{19}H_{30}F_{3}IO_{2}Si [M]^+: 486.1057; found: 486.1061.

4-(1-(((iodomethyl)diisopropylsilyl)oxy)-3-methylbutyl)benzonitrile

\[ \text{1o} \]
10 was prepared according to general procedure in 88% isolated yield. Colorless oil. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3]: \delta 7.61 (d, J = 8.2 \text{ Hz, 2H}), 7.43 (d, J = 8.1 \text{ Hz, 2H}), 4.93 (t, J = 6.3 \text{ Hz, 1H}), 1.90 (s, 2H), 1.75-1.64 (m, 1H), 1.57-1.40 (m, 2H), 1.28-1.01 (m, 8H), 1.00-0.84 (m, 12H). \]

\[ ^13C \text{NMR (101 MHz, CDCl}_3]: \delta 150.91, 132.24, 126.86, 118.98, 111.18, 73.71, 50.19, 24.41, 23.05, 23.00, 17.86, 17.65, 17.52, 17.41, 12.60, 12.49. \]

IR (neat) cm\(^{-1}\): 2952, 2866, 2228, 1609, 1503, 1384, 1367, 1081, 1005, 901, 881, 861, 837, 816, 727, 864, 570. HRMS (EI, 70eV) m/z calcd. for C\(_{19}\)H\(_{30}\)NOSi [M]: 443.1136; found: 443.1138.

(iodomethyl)diisopropyl(3-methyl-1-(4-(trifluoromethoxy)phenyl)butoxy)silane

1q was prepared according to general procedure in 87% isolated yield. Colorless oil.

\[ ^1H \text{NMR (400 MHz, CDCl}_3]: \delta 7.35 (d, J = 8.6 \text{ Hz, 2H}), 7.16 (d, J = 8.1 \text{ Hz, 2H}), 4.90 (t, J = 6.6 \text{ Hz, 1H}), 1.92 (s, 2H), 1.78-1.69 (m, 1H), 1.60-1.52 (m, 1H), 1.51-1.42 (m, 1H), 1.25-1.03 (m, 8H), 1.20-0.87 (m, 12H). \]

\[ ^13C \text{NMR (101 MHz, CDCl}_3]: \delta 147.48, 126.54, 119.79, 119.65 (q, J = 272.7 \text{ Hz}), 72.67, 49.44, 23.52, 22.05, 22.02, 16.97, 16.65, 16.57, 16.43, 11.70, 11.56, -21.32. \]

\[ ^19F \text{NMR (376 MHz, CDCl}_3]: \delta -57.94 (s, 1F). \]

IR (neat) cm\(^{-1}\): 2954, 2868, 1508, 1464, 1368, 1255, 1219, 1163, 1081, 1007, 881, 861, 726, 680, 559. HRMS (ESI) m/z calc. for C\(_{19}\)H\(_{30}\)F\(_3\)INaO\(_2\)Si [M+Na]: 525.0920.

(1-(2-bromo-6-fluorophenyl)-3-methylbutoxy)(iodomethyl)diisopropylsilane

1r was prepared according to general procedure in 65% isolated yield. Colorless oil.

\[ ^1H \text{NMR (400 MHz, CDCl}_3]: \delta 7.42 (dd, J = 8.7, 5.3 \text{ Hz, 1H}), 7.28 (d, J = 3.1 \text{ Hz, 1H}), 6.84 (td, J = 8.4, 3.1 \text{ Hz, 1H}), 5.20 (dd, J = 8.3, 3.3 \text{ Hz, 1H}), 1.95 (s, 2H), 1.84-1.73 (m, 1H), 1.61-1.54 (m, 1H), 1.44-1.35 (m, 1H), 1.30-1.06 (m, 8H), 1.03-0.90 (m, 12H). \]

\[ ^13C \text{NMR (101 MHz, CDCl}_3]: \delta 161.43 (d, J = 247.89 \text{ Hz}), 146.49 (d, J = 7.0 \text{ Hz}), 132.70 (d, J = 8.0 \text{ Hz}), 115.02 (d, J = 22.9 \text{ Hz}), 114.19 (d, J = 23.7 \text{ Hz}), 109.16, 71.59, 48.18, 23.60, 23.03, 21.26, 16.99, 16.77, 16.55, 16.38, 11.51, 11.43, -21.62. \]

\[ ^19F \text{NMR (376 MHz, CDCl}_3]: \delta -114.02 (dd, J = 12.7, 7.7 \text{ Hz}). \]

IR (neat) cm\(^{-1}\): 2953, 2867, 1580, 1463, 1407, 1366, 1256, 1154, 1084, 1006, 900, 882, 808, 765, 729, 629,
585, 482. HRMS (EI, 70 eV) m/z calcd. for C_{18}H_{29}BrFiOSi [M]: 514.0194; found: 514.0201.

3. Experimental Details

3.1 Optimization of the reaction conditions

Table S1 Ligand Screening

| Entry | Ligand | yield%b |
|-------|--------|---------|
| 1     | L1     | 62/60c  |
| 2     | L2     | 0       |
| 3     | L3     | 41      |
| 4     | L4     | 0       |

Table S2 Catalyst Screening

| Entry | CuX       | yield%b |
|-------|-----------|---------|
| 1     | CuCl      | 50      |
| 2     | CuBr      | 38      |
| 3     | Cu(MeCN)_4PF_6 | 36 |
| 4     | CuTc      | 52      |
| 5     | Cu(OTf)_2 | 32      |
| 6     | CuCN      | 30      |

Notes:
- a 1a (0.1 mmol), 2a (0.15 mmol), CuI (15 mol %), Ligand (15 mol %) and K_2CO_3 (3 equiv.) in MeCN, under N_2, rt, blue LEDs, 32 h. b Determined by ^1H NMR analysis with internal standard (diethyl phthalate). c Isolated yield.
Table S3 Solvent Screening

| Entry | Solvent | yield%b |
|-------|---------|---------|
| 1     | DMF     | 35      |
| 2     | THF     | Trace   |
| 3     | Et2O    | Trace   |
| 4     | PhH     | 0       |
| 5     | DCM     | 38      |
| 6     | DCE     | 0       |

Table S4 Base Screening

| Entry | Base        | yield%b |
|-------|-------------|---------|
| 1     | Na2CO3      | 0       |
| 2     | Cs2CO3      | 0       |
| 3     | K3PO4       | 39      |
| 4     | KOtBu       | 0       |

Table S4 Temperature Screening

\(7^c\) Pd(OAc)₂ 0

\(1^a\) 1a (0.1 mmol), 2a (0.15 mmol), CuX (15 mol %), L1 (15 mol %) and K₂CO₃ (3 equiv.) in MeCN, under N₂, rt, blue LEDs, 32 h. Determined by ¹H NMR analysis with internal standard (diethyl phthalate). ³ Pd(OAc)₂ (10 mol %), Xanphos (20 mol %) and Cs₂CO₃ (2 equiv.) in PhH, under N₂, rt, blue LEDs, 32 h.
| Entry | Temperature | yield%<sup>b</sup> |
|-------|-------------|------------------|
| 1     | 10 °C       | 20               |

<sup>a</sup> 1a (0.1 mmol), 2a (0.15 mmol), CuI (15 mol %), L1 (15 mol %) and K<sub>2</sub>CO<sub>3</sub> (3 equiv.) in solvent, under N<sub>2</sub>, 10°C, blue LEDs, 32 h. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis with internal standard (diethyl phthalate).

3.2 General procedures and characterizations of products

**General procedure A**

In a dried sealed vial, L1 (0.015 mmol, 15 mol %), CuI (0.015 mmol, 15 mol %), K<sub>2</sub>CO<sub>3</sub> (0.3 mmol, 3.0 equiv.) and terminal alkyne (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous CH<sub>3</sub>CN (2.0 mL) under a N<sub>2</sub> atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 32 h. The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of silica gel, and concentrated under a reduced pressure. The residual oil was purified by column chromatography in hexanes/EtOAc to afford protected products.

**General procedure B**

In a dried sealed vial, L1 (0.015 mmol, 15 mol %), CuI (0.015 mmol, 15 mol %), K<sub>2</sub>CO<sub>3</sub> (0.3 mmol, 3.0 equiv.) and terminal alkyne (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous CH<sub>3</sub>CN (2.0 mL) under a N<sub>2</sub> atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 32 h. The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of silica gel, and concentrated under a reduced pressure. The residue oil was dissolved in THF (1.0 mL), and TBAF (2 mL, 1.0 M THF) was added. After completion (monitored by TLC), the resulting mixture was poured into water with EtOAc. The aqueous layer was extracted with two portions of EtOAc. The combined extract was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue oil was purified by column chromatography in hexanes/EtOAc to afford deprotected products.

**General procedure C**

In a dried sealed vial, L1 (0.015 mmol, 15 mol %), CuI (0.015 mmol, 15 mol %), K<sub>2</sub>CO<sub>3</sub> (0.3 mmol, 3.0 equiv.) and terminal alkyne (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous CH<sub>3</sub>CN (2.0 mL) under a N<sub>2</sub> atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 32 h. The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of Celite, and concentrated under a reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), and montmorillonite K10 (30 mg) and acetyl chloride (71 μL 1.0 mmol) were added.
sequentially. After completion (monitored by TLC), the resulting mixture was passed through a pad of silica gel, and concentrated under reduced pressure. The residue oil was purified by column chromatography in hexanes/EtOAc to afford \( O \)-acetyl alcohols.

**General procedure D**

In a dried sealed vial, \( \text{CuCl} \) (0.015 mmol, 15 mol %), \( \text{LiO}^\text{tBu} \) (0.3 mmol, 3.0 equiv.) and \( 9H \)-carbazole (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous \( \text{CH}_3\text{CN} \) (2.0 mL) under a \( \text{N}_2 \) atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 24h. The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of silica gel, and concentrated under a reduced pressure. The residual oil was purified by column chromatography in hexanes/EtOAc to afford protected products.

**General procedure E**

In a dried sealed vial, \( \text{CuCl} \) (0.015 mmol, 15 mol %), \( \text{LiO}^\text{tBu} \) (0.3 mmol, 3.0 equiv.) and \( 9H \)-carbazole (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous \( \text{CH}_3\text{CN} \) (2.0 mL) under a \( \text{N}_2 \) atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 24h. The vial distance from the lamp was about 2-3 cm. The residue oil was dissolved in THF (1.0 mL), and TBAF (2 mL, 1.0 M THF,) was added. After completion (monitored by TLC), the resulting mixture was poured into water with EtOAc. The aqueous layer was extracted with two portions of EtOAc. The combined extract was washed with brine, dried over \( \text{Na}_2\text{SO}_4 \) and concentrated. The residue oil was purified by column chromatography in hexanes/EtOAc to afford deprotected products.

### 3.3 Characterization data of products

**((4,4-dimethyl-6-(p-tolyl)hex-5-yn-2-yl)oxy)diisopropyl(methyl)silane**

\[ 3a \]

\( 3a \) was prepared according to general procedure A in 60% isolated yield. Colorless oil

\( ^1\text{H NMR (400 MHz, CDCl}_3): \delta \) 7.26 (d, \( J = 7.8 \text{ Hz,} \ 2\text{H}), 7.08 (d, \( J = 7.8 \text{ Hz,} \ 2\text{H}), 4.23-4.14 \text{ (m,} \ 1\text{H),} 2.69(\text{br,} \ 1\text{H),} 2.33 \text{ (s,} \ 1\text{H),} 1.76-1.62 \text{ (m,} \ 2\text{H),} 1.35-1.28 \text{ (m,} \ 9\text{H),} 1.06-0.85 \text{ (m,} \ 14\text{H),} 0.05 \text{ (s,} \ 3\text{H).} ^1\text{C NMR (101 MHz, cdcl}_3): \delta \) 136.47, 130.44,
4,4-dimethyl-6-phenylhex-5-yn-2-ol

3b was prepared according to general procedure B in 60% isolated yield. Colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.41-7.34 (m, 2H), 7.29-7.24 (m, 2H), 4.24-4.15 (m, 1H), 2.86 (br. s, 1H), 1.77 (dd, J = 14.2, 9.1 Hz, 1H), 1.53 (dd, J = 14.2, 1.4 Hz, 1H), 1.35 (d, J = 4.1 Hz, 6H), 1.23 (d, J = 6.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 131.64, 128.38, 128.09, 123.17, 96.64, 82.42, 65.96, 52.02, 31.23, 30.27, 29.12, 24.40. IR (neat) cm⁻¹ v: 3385, 2966, 2926, 1598, 1363, 1293, 1165, 1152, 1119, 1048, 910, 754, 690, 553, 466. HRMS (ESI) m/z calcd. for C22H36OSi [M⁺]: 344.2530; found: 344.2531.

6-([1,1'-biphenyl]-4-yl)-4,4-dimethylhex-5-yn-2-ol

3c was prepared according to general procedure B in 39% isolated yield. White solid. 1H NMR (400 MHz, CDCl3): δ 7.61-7.55 (m, 2H), 7.54-7.49 (m, 2H), 7.47-7.41 (m, 4H), 7.37-7.31 (m, 1H), 4.26-4.17 (m, 1H), 1.78 (dd, J = 14.3, 9.1 Hz, 1H), 1.55 (dd, J = 14.2, 2.1 Hz, 1H), 1.37 (d, J = 4.3 Hz, 6H), 1.25 (d, J = 6.3 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 140.85, 140.54, 132.07, 128.96, 127.70, 127.14, 127.07, 122.15, 97.37, 82.27, 66.02, 52.11, 31.23, 30.40, 29.21, 24.47. IR (neat) cm⁻¹ v: 3240, 2963, 2922, 1485, 1449, 1292, 1148, 1116, 1075, 916, 841, 760, 719, 689. HRMS (ESI) m/z calcd. for C20H23O [M+H]+: 279.1743; found: 279.1743.

6-(4-methoxyphenyl)-4,4-dimethylhex-5-yn-2-ol
3d was prepared according to general procedure B in 64% isolated yield. Colorless oil. 

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\): \delta 7.31 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.23-4.14 (m, 1H), 3.79 (s, 3H), 3.02 (br. s, 1H), 1.75 (dd, J = 14.2, 9.2 Hz, 1H), 1.51 (dd, J = 14.1, 1.7 Hz, 1H), 1.33 (d, J = 3.0 Hz, 6H), 1.22 (d, J = 6.2 Hz, 3H). \[^{13}C\text{ NMR (101 MHz, CDCl}_3\): \delta 158.46, 132.01, 114.26, 112.98, 94.07, 81.26, 64.93, 54.40, 51.07, 30.40, 29.20, 28.10, 23.34. IR (neat) cm\(^{-1}\): 3406, 2965, 2927, 1606, 1508, 1463, 1284, 1245, 1167, 1107, 1031, 945, 911, 831, 764, 618, 531. HRMS (ESI) m/z calcd. for C\(_{15}\)H\(_{21}\)O\(_2\)[M+H]\(^{+}\): 233.1536; found: 233.1537.

6-(4-chlorophenyl)-4,4-dimethylhex-5-yn-2-ol

![Image 3e]

3e was prepared according to general procedure B in 41% isolated yield. Colorless oil. 

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\): \delta 7.30 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 4.23-4.14 (m, 1H), 2.69 (br. s, 1H), 1.76 (dd, J = 14.4, 8.8 Hz, 1H), 1.53 (dd, J = 14.4, 2.0 Hz, 1H), 1.35 (d, J = 4.8 Hz, 6H), 1.23 (d, J = 6.0 Hz, 3H). \[^{13}C\text{ NMR (101 MHz, CDCl}_3\): \delta 134.06, 132.88, 128.71, 121.72, 97.73, 81.28, 66.00, 51.95, 31.06, 30.36, 29.11), 24.47. IR (neat) cm\(^{-1}\): 3405, 2967, 2927, 1490, 1466, 1261, 1089, 1048, 1015, 827, 799, 517. HRMS (EI, 70eV) m/z calcd. for C\(_{14}\)H\(_{17}\)ClO [M]\(^{+}\): 236.0968; found: 236.0960.

6-(4-fluorophenyl)-4,4-dimethylhex-5-yn-2-ol

![Image 3f]

3f was prepared according to general procedure B in 39% isolated yield. Orange oil. 

\[^{1}H\text{ NMR (400 MHz, CDCl}_3\): \delta 7.35 (dd, J = 8.5, 5.5Hz, 2H), 6.97 (t, J = 8.7 Hz, 2H), 4.23-4.14 (m, 1H), 2.79 (br. s, 1H), 1.75 (dd, J = 14.2, 9.1 Hz, 1H), 1.53 (dd, J = 14.2, 2.1Hz, 1H), 1.34 (d, J = 4.4 Hz, 6H), 1.23 (d, J = 6.2 Hz, 3H). \[^{13}C\text{ NMR (101 MHz, CDCl}_3\): \delta 161.42 (d, J = 249.9 Hz), 132.47 (d, J = 8.4 Hz), 118.25 (d, J = 3.5 Hz), 114.62 (d, J = 22.1 Hz), 95.33, 80.33, 64.99, 50.98, 30.16, 29.27, 28.11, 23.44. \[^{19}F\text{ NMR (376 MHz, CDCl}_3\): \delta -111.63--111.70(m, 1F). IR (neat) cm\(^{-1}\): 3418, 2968, 2928, 1601, 1506, 1467, 1230, 1156, 1093, 1049, 835, 525. HRMS (ESI) m/z calcd. for C\(_{14}\)H\(_{18}\)FO [M+H]\(^{+}\): 221.1336; found: 221.1338.

6-(4-(dimethylamino)phenyl)-4,4-dimethylhex-5-yn-2-yl acetate

![Image 3g]
3g was prepared according to general procedure C in 72% isolated yield. Orange oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25 (d, $J$ = 8.2 Hz, 2H), 6.60 (d, $J$ = 8.2 Hz, 2H), 5.31-5.21 (s, 1H), 2.94 (s, 6H), 1.98 (s, 3H), 1.86 (dd, $J$ = 14.2, 8.0 Hz, 1H), 1.63 (dd, $J$ = 14.0, 2.8 Hz, 1H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 170.81, 149.80, 132.63, 112.08, 111.22, 93.84, 81.47, 69.33, 48.89, 40.50, 30.69, 30.59, 29.86, 21.78, 21.75. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2969, 2926, 1734, 1609, 1520, 1445, 1359, 1243, 1163, 1130, 1045, 1017, 946, 817. HRMS (ESI) m/z calcd. for C$_{16}$H$_{24}$NO [$M+H]^+$: 288.1958; found: 288.1957.

4,4-dimethyl-6-(m-tolyl)hex-5-yn-2-ol

3h was prepared according to general procedure B in 55% isolated yield. Orange oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24-7.13 (m, 3H), 7.12-7.06 (m, 1H), 4.27-4.11 (m, 1H), 2.96 (s, 3H), 2.30 (s, 1H), 1.76 (dd, $J$ = 14.2, 9.2 Hz, 1H), 1.52 (dd, $J$ = 14.2, 1.8 Hz, 1H), 1.35 (d, $J$ = 3.7 Hz, 6H), 1.23 (d, $J$ = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.07, 132.23, 128.98, 128.67, 128.28, 122.92, 96.21, 82.59, 65.94, 52.02, 31.28, 30.22, 29.08, 24.37, 21.29. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3395, 2966, 2925, 1734, 1609, 1520, 1445, 1359, 1243, 1163, 1130, 1045, 1017, 946, 817. HRMS (ESI) m/z calcd. for C$_{15}$H$_{21}$O [$M+H]^+$: 217.1587; found: 217.1586.

6-(2-fluorophenyl)-4,4-dimethylhex-5-yn-2-ol

3i was prepared according to general procedure B in 45% isolated yield. Colorless oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.33 (m, 1H), 7.28-7.21 (m, 1H), 7.09-6.99 (m, 2H), 4.27-4.14 (m, 1H), 1.76 (dd, $J$ = 14.2, 9.0 Hz, 1H), 1.54 (dd, $J$ = 14.4, 2.1 Hz, 1H), 1.36 (d, $J$ = 5.4 Hz, 6H), 1.23 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.87 (d, $J$ = 251.4 Hz), 133.42 (d, $J$ = 1.1 Hz), 129.69 (d, $J$ = 8.0 Hz), 123.97 (d, $J$ = 3.7 Hz), 115.49 (d, $J$ = 21.2 Hz), 111.84 (d, $J$ = 15.7 Hz), 102.18 (d, $J$ = 3.4 Hz), 75.59, 65.87, 52.05, 31.06, 30.56, 29.10, 24.46. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -108.57--112.73 (m, 1F). IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3391, 2968, 2928, 1492, 1451, 1264, 1216,
1152, 1102, 1048, 913, 826, 754. HRMS (ESI) m/z calcd. for C_{14}H_{18}FO [M+H]^+: 221.1336; found: 221.1336.

**4,4-dimethyl-6-(pyridin-3-yl)hex-5-yn-2-ol**

![Illustration of 4j](image)

3j was prepared according to general procedure B in 53% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.60 (s, 1H), 8.47 (s, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.23-7.16 (m, 1H), 4.23-4.13 (m, 1H), 2.59 (s, 1H), 1.75 (dd, $J = 14.0, 8.9$ Hz, 1H), 1.56 (d, $J = 14.2$ Hz, 1H), 1.35 (d, $J = 7.7$ Hz, 6H), 1.23 (d, $J = 6.1$ Hz, 3H). 

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 152.28, 148.37, 138.56, 123.04, 120.48, 100.42, 78.84, 65.98, 51.85, 30.72, 30.56, 29.31, 24.65. IR (neat) cm$^{-1}$: 3344.68, 2965.60, 2926.05, 2870.57, 2227.26, 1563.85, 1470.78, 1406.76, 1365.42, 1294.31, 1186.77, 1150.45, 1120.76, 1073.82, 1047.31, 1024.32, 947.14, 910.86, 804.59, 704.02, 628.93, 467.85. HRMS (ESI) m/z calcd. for C$_{14}$H$_{18}$NO [M]$^+$: 204.1383; found: 204.1384.

**3,3-dimethyl-5-phenylpent-4-yn-2-ol**

![Illustration of 4a](image)

4a was prepared according to general procedure B in 30% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43-7.37 (m, 2H), 7.31-7.27 (m, 3H), 3.67-3.60 (m, 1H), 1.82 (s, 1H), 1.32 (s, 3H), 1.28 (d, $J = 6.3$ Hz, 3H), 1.26 (s, 3H). 

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 131.80, 128.36, 128.00, 123.50, 94.36, 82.69, 74.41, 38.30, 25.70, 24.77, 18.31. IR (neat) cm$^{-1}$: 3393, 2972, 2925, 2855, 1670, 1599, 1490, 1444, 1375, 1274, 1076, 1025, 912, 755, 691, 544. HRMS (ESI) m/z calcd. for C$_{13}$H$_{16}$O [M]$^+$: 189.1274; found: 189.1274.

**5,5-dimethyl-7-phenylehept-6-yn-2-ol**

![Illustration of 4b](image)

4b was prepared according to general procedure B in 41% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40-7.35 (m, 2H), 7.30-7.24 (m, 3H), 3.89-3.80 (m, 1H), 1.74-1.59 (m, 3H), 1.54-1.45 (m, 1H), 1.29 (d, $J = 1.6$ Hz, 6H), 1.24 (d, $J = 6.2$ Hz, 3H). 

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 130.69, 127.27, 126.61, 123.07, 96.15,
79.71, 67.65, 38.56, 34.35, 30.58, 28.56, 28.28, 22.75. IR (neat) cm⁻¹ \( \tilde{\nu} \): 3366, 2966, 2930, 2867, 1598, 1490, 1447, 1367, 1261, 1115, 1068, 799, 755, 691. HRMS (ESI) m/z calcd. for C₁₅H₂₁O [M+H]⁺: 217.1587; found: 217.1588.

**2,5,5-trimethyl-7-phenylhept-6-yn-3-ol**

![Structure](image1)

4c was prepared according to general procedure B in 61% isolated yield. Colorless oil. 

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.40-7.35 (m, 2H), 7.31-7.25 (m, 3H), 3.78 (ddd, \( J = 8.9, 4.8, 1.6 \) Hz, 1H), 2.07 (s, 1H), 1.74-1.63 (m, 3H), 1.57 (dd, \( J = 14.2, 1.7 \) Hz, 1H), 1.36 (d, \( J = 13.9 \) Hz, 6H), 0.94 (dd, \( J = 6.8, 2.6 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl₃): \( \delta \) 131.67, 128.36, 128.04, 123.26, 96.93, 82.20, 74.16, 47.38, 34.35, 31.19, 30.39, 29.07, 18.52, 17.47. IR (neat) cm⁻¹ \( \tilde{\nu} \): 3454, 2963, 1598, 1490, 1466, 1364, 1143, 1031, 998, 914, 754, 690. HRMS (ESI) m/z calcd. for C₁₆H₂₃O [M+H]⁺: 231.1743; found: 231.1744.

**3,3,8-trimethyl-1-phenynon-1-yn-5-ol**

![Structure](image2)

4d was prepared according to general procedure B in 60% isolated yield. Colorless oil. 

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.41-7.34 (m, 1H), 7.30-23 (m, 2H), 4.01-3.92 (m, 1H), 1.73 (dd, \( J = 14.2, 9.2 \) Hz, 1H), 1.64-1.11 (m, 12H), 0.90 (dd, \( J = 6.5, 1.3 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl₃): \( \delta \) 131.65, 128.36, 128.07, 123.18, 96.81, 82.35, 70.07, 50.50, 36.19, 34.79, 31.27, 30.30, 29.07, 28.27, 22.81, 22.71. IR (neat) cm⁻¹ \( \tilde{\nu} \): 3425, 2956, 2929, 2869, 1491, 1467, 1384, 1364, 1296, 1164, 1068, 1029, 1010, 913, 755, 691. HRMS (ESI) m/z calcd. for C₁₆H₂₃O [M+H]⁺: 259.2056; found: 259.2056.

**5,5-dimethyl-7-phenylhept-6-yn-3-ol**

![Structure](image3)

4e was prepared according to general procedure B in 64% isolated yield. Colorless oil. 

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 7.39-7.35 (m, 2H), 7.30-7.24 (m, 3H), 4.02-3.95 (m, 1H), 2.83 (s, 1H), 1.72 (dd, \( J = 14.2, 9.1 \) Hz, 1H), 1.55 (d, \( J = 14.4 \) Hz, 1H), 1.48-1.39 (m, 2H), 1.39-1.18 (m, 20H), 0.88 (t, \( J = 6.7 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃): \( \delta \) 131.66, 128.36, 128.06, 123.21, 95.83, 82.33, 69.77, 50.52, 38.40, 32.07, 31.26, 30.33, 29.85, 29.82, 29.80, 29.78, 29.50, 29.11, 25.69, 22.84, 14.27. IR (neat) cm⁻¹ \( \tilde{\nu} \): 3410,
2923, 2853, 1465, 1362, 1295, 754, 690. HRMS (ESI) m/z calcd. for C_{24}H_{39}O [M+H]^+: 343.2995; found: 343.2994.

3,3-dimethyl-5-phenylpent-4-yn-1-ol

4f was prepared according to general procedure B in 31\% isolated yield. Orange oil.

\[ 4f \]

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.39-7.35 (m, 2H), 7.30-7.25 (m, 3H), 3.92 (t, \( J = 6.7 \) Hz, 2H), 1.81 (t, \( J = 6.7 \) Hz, 2H), 1.71 (s, 1H), 1.34 (s, 6H). \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 131.68, 128.35, 127.90, 123.59, 96.65, 81.43, 60.80, 60.80, 45.72, 30.21, 29.90. IR (neat) cm\(^{-1}\) \( \tilde{\nu} \): 3330, 2967, 2927, 1598, 1490, 1444, 1363, 1312, 1063, 1026, 989, 754, 691, 552. HRMS (ESI) m/z calcd. for C\(_{13}\)H\(_{17}\)O [M+H]^+: 189.1274; found: 189.1273.

6-methyl-8-phenyloct-7-yn-4-ol

4g was prepared according to general procedure B in 66\% isolated yield. Colorless oil.

\[ 4g \]

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.43-7.33 (m, 3.8H), 7.29-7.24 (m, 5.7H), 4.03-3.89 (m, 1H), 3.88-3.80(m, 0.9H), 3.00-2.87 (m, 1H), 2.85-2.75 (m, 0.9H), 1.92 (s, 1.8H), 1.77-1.34 (m, 11.4H), 1.29 (d, \( J = 6.9 \) Hz, 5.7H), 0.94 (t, \( J = 6.9 \) Hz, 5.7H). \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 131.68, 131.64, 128.32, 128.30, 127.87, 127.75, 123.85, 123.59, 94.33, 94.02, 81.76, 81.60, 70.69, 69.95, 44.59, 44.57, 40.18, 39.75, 24.17, 23.46, 21.69, 21.41, 19.00, 18.79, 14.22. IR (neat) cm\(^{-1}\) \( \tilde{\nu} \): 3345, 2959, 2931, 2871, 1598, 1489, 1454, 1089, 1022, 946, 843, 754, 690. HRMS (ESI) m/z calcd. for C\(_{15}\)H\(_{21}\)O [M+H]^+: 217.1587; found: 217.1587.

6-methyl-8-phenyl-4-propyloct-7-yn-4-ol

4h was prepared according to general procedure B in 71\% isolated yield. Colorless oil.

\[ 4h \]

\( ^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.40-7.34 (m, 2H), 7.30-7.22 (m, 3H), 2.89-2.74 (m, 1H), 1.79 (dd, \( J = 14.2, 10.8 \) Hz, 1H), 1.67-1.15 (m, 12H), 0.92 (dd, \( J = 15.6, 7.2 \) Hz, 6H). \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 131.48, 128.24, 127.85, 123.35, 94.53, 82.28, 74.59, 45.96, 42.02, 41.57, 22.94, 21.62, 17.29, 16.74, 14.79, 14.74. IR (neat) cm\(^{-1}\) \( \tilde{\nu} \): 3452, 2958, 2931, 2871, 1598, 1490, 1454, 1376, 1137, 1069, 985, 911, 860, 754, 691, 545. HRMS (ESI) m/z calcd. for C\(_{18}\)H\(_{27}\)O [M+H]^+: 259.2056; found: 259.2056.
1-cyclopropyl-3,3-dimethyl-5-phenylpent-4-yn-1-ol

![4i](image)

4i was prepared according to general procedure B in 58% isolated yield. Colorless oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39-7.32 (m, 2H), 7.30-7.23 (m, 3H), 3.25 (t, $J$ = 8.5 Hz, 1H), 2.92-2.52 (br.s, 1H), 1.92-1.97 (m, 1H), 1.35 (d, $J$ = 16.7 Hz, 3H), 1.03-0.91 (m, 1H), 0.60 – 0.36 (m, 3H), 0.26-0.16 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 131.61, 128.34, 127.98, 123.29, 96.87, 82.08, 74.80, 50.31, 30.82, 30.41, 29.28, 18.68, 3.54, 2.45. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3418, 2967, 2927, 1598, 1490, 1443, 1362, 1290, 1069, 1030, 912, 754, 690, 529. HRMS (ESI) m/z calcd. for C$_{16}$H$_{21}$O $[M+H]^+$: 229.1587; found: 229.1586.

4-ethoxy-6-phenylhex-5-yn-2-ol

![4j](image)

4j was prepared according to general procedure B in 71% isolated yield. Colorless oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.41 (m, 4H), 7.36-7.25 (m, 6H), 4.60-4.55 (m, 1H), 4.55-4.45 (m, 1H), 4.37-4.26 (m, 1H), 4.15-4.05 (m, 1H), 4.0-3.87 (m, 1H), 3.59-3.46 (m, 1H), 2.11-1.86 (m, 4H), 1.38-1.12 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 131.83, 131.82, 128.58, 128.55, 128.40, 122.62, 122.56, 87.62, 86.32, 86.00, 69.90, 68.52, 67.25, 65.20, 64.95, 64.80, 44.62, 43.82, 23.57, 23.35, 15.26, 15.24. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3405, 2971, 2927, 2871, 1489, 1443, 1371, 1329, 1080, 952, 755, 690, 594, 527. HRMS (ESI) m/z calcd. for C$_{14}$H$_{18}$NaO$_2$ [M+Na]$^+$: 241.1199; found: 241.1199.

(E)-7-phenylhept-3-en-6-yn-1-ol

![4k](image)

4k was prepared according to general procedure B in 61% isolated yield. Colorless oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.37 (m, 2H), 7.34-7.27 (m, 3H), 5.82-5.72 (m, 1H), 5.68-5.59 (m, 1H), 3.69 (t, $J$ = 6.3 Hz, 2H), 3.17 (d, $J$ = 5.1 Hz, 2H), 2.38-2.30 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 131.54, 128.18, 128.02, 127.73, 127.33, 123.61, 87.05, 82.49, 61.87), 35.67, 22.68. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3341, 2924, 2881, 1490, 1442, 1419, 1260, 1043, 968, 798, 756, 691. HRMS (ESI) m/z calcd. for C$_{13}$H$_{14}$NaO $[M+Na]^+$: 209.0937; found: 209.0939.
((3,5-diphenylpent-4-yn-1-yl)oxy)diisopropyl(methyl)silane

4l was prepared according to general procedure B in 65% isolated yield. Colorless oil. 
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47-7.40 (m, 4H), 7.36-7.21 (m, 6H), 4.09 (t, $J = 7.5$ Hz, 1H), 3.94-3.86 (m, 1H), 3.78-3.70 (m, 1H), 2.05-1.98 (m, 2H), 1.09-0.89 (m, 14H), 0.04 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 142.01, 131.65, 128.54, 128.23, 127.76, 127.58, 123.82, 91.30, 83.31, 60.82, 41.70, 34.55, 17.50, 17.49, 17.45, 13.06, 13.04, -8.61. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2941, 2864, 1599, 1490, 1458, 1384, 1251, 1002, 994, 941, 881, 781, 751, 692, 639, 544. HRMS (EI) m/z calcd. for C$_{24}$H$_{32}$O Si [M$^+$]: 364.2217; found: 364.2223.

3,3-dimethyl-1,5-diphenylpent-4-yn-1-ol

4m was prepared according to general procedure B in 49% isolated yield. Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46-7.37 (m, 4H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.31-7.21 (m, 4H), 5.11 (dd, $J = 9.4$, 1.7 Hz, 1H), 2.06 (dd, $J = 14.3$, 9.4 Hz, 1H), 1.79 (dd, $J = 14.3$, 2.3 Hz, 1H), 1.40 (d, $J = 4.3$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.26 (s), 131.70, 128.57, 128.40, 128.11, 127.46, 125.86, 123.23, 96.56, 82.59, 72.58, 52.76, 31.01, 30.81, 29.30. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 3235, 2966, 2927, 1598, 1491, 1452, 1283, 1053, 1023, 911, 754, 694, 539. HRMS (ESI) m/z calcd. for C$_{19}$H$_{20}$O [M+H]$^+$: 364.2217; found: 364.2223.

1-(4-methoxyphenyl)-3,3-dimethyl-5-phenylpent-4-yn-1-yl acetate

4n was prepared according to general procedure C in 40% isolated yield. Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39-7.35 (m, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 7.28-7.25 (m, 3H), 6.10 (dd, $J = 8.5$, 4.1 Hz, 1H), 3.77 (s, 3H), 2.21 (dd, $J = 14.3$, 8.7 Hz, 1H), 1.98 (s, 3H), 1.90 (dd, $J = 14.4$, 4.0 Hz, 1H), 1.36 (s, 3H), 1.28 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 170.36, 159.34, 134.02, 131.74, 128.27, 128.13, 127.69, 123.94, 113.97, 96.11, 81.47, 73.97, 55.38, 48.99, 30.93, 30.24, 30.10, 21.62. IR (neat) cm$^{-1}$ $\tilde{\nu}$:
2966, 2933, 1735, 1612, 1513, 1369, 1234, 1176, 1028, 831, 757, 693, 608, 544. HRMS (ESI) m/z calcd. for C_{22}H_{24}NaO_{3} [M+Na]^+: 359.1618; found: 359.1620.

1-(4-cyanophenyl)-3,3-dimethyl-5-phenylpent-4-yn-1-yl acetate

\[
\text{\textbf{4o}}
\]

\text{4o} was prepared according to general procedure C in 60% isolated yield. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.38-7.32 (m, 1H), 7.32-7.27 (m, 3H), 6.13 (dd, J = 8.8, 3.5 Hz, 1H), 2.17 (dd, J = 14.5, 8.8 Hz, 1H), 2.03 (s, 1H), 1.88 (dd, J = 14.4, 3.6 Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 170.15, 147.14, 132.56, 131.66, 128.39, 127.97, 127.25, 123.55, 118.75, 111.80, 95.45, 81.97, 73.69, 49.06, 31.12, 30.47, 29.83, 21.36. IR (neat) cm⁻¹: 2969, 2923, 2229, 1739, 1371, 1233, 1031, 1019, 835, 758, 693, 566. HRMS (ESI) m/z calcd. for C_{22}H_{21}NNaO_{2} [M+Na]^+: 354.1465; found: 354.1468.

3,3-dimethyl-5-phenyl-1-(4-(trifluoromethyl)phenyl)pent-4-yn-1-ol

\[
\text{\textbf{4p}}
\]

\text{4p} was prepared according to general procedure B in 55% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, J = 6.6 Hz, 2H), 7.51 (d, J = 6.6 Hz, 2H), 7.45-7.36 (m, 1H), 7.35-7.23 (m, 3H), 5.17 (d, J = 8.8 Hz, 1H), 3.30 (s, 1H), 2.08-1.96 (m, 1H), 1.80-1.73 (m, 1H), 1.43 (dd, J = 6.4, 2.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 149.15, 131.69, 129.62 (q, J = 30.6 Hz), 128.47, 128.30, 126.16, 125.52 (q, J = 3.6 Hz), 122.99, 96.16, 82.98, 72.04, 52.81, 31.04, 30.76, 29.23. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.46 (s, 3F). IR (neat) cm⁻¹: 3297, 2970, 1926, 1619, 1444, 1420, 1321, 1160, 1131, 1105, 1068, 1048, 1015, 842, 756, 692, 605. HRMS (ESI) m/z calcd. for C_{20}H_{20}FO [M+H]^+: 333.1461; found: 333.1460.

3,3-dimethyl-5-phenyl-1-(4-(trifluoromethoxy)phenyl)pent-4-yn-1-ol

\[
\text{\textbf{4q}}
\]

\text{4q} was prepared according to general procedure B in 51% isolated yield. Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.47-7.38 (m, 4H), 7.35-7.28 (m, 3H), 7.24-7.16 (m,
2H), 5.12 (d, J = 9.2 Hz, 1H), 3.24 (br. s, 1H), 2.04 (dd, J = 13.6, 9.0 Hz, 1H), 1.75 (d, J = 14.3 Hz, 1H). 13C NMR (101 MHz, CDCl3): δ 148.47 (d, J = 1.7 Hz), 143.95, 131.69, 128.45, 128.24, 127.26, 123.08, 121.08, 120.64 (q, J = 258.1 Hz), 96.28, 82.88, 71.88 (d, J = 5.9 Hz), 52.83, 31.06, 30.77, 29.25. 19F NMR (377 MHz, CDCl3): δ -57.87 (s, 3F). IR (neat) cm⁻¹ ʋ: 3436, 2969, 1598, 1508, 1255, 1219, 1169, 1016, 854, 755, 690, 544. HRMS (ESI) m/z calcd. for C20H20F3O [M+H]⁺: 333.1461; found: 333.1460.

1-(2-bromo-6-fluorophenyl)-3,3-dimethyl-5-phenylpent-4-yn-1-ol

1H NMR (400 MHz, CDCl3): δ 7.48-7.39 (m, 4H), 7.34-7.28 (m, 3H), 6.90-6.79 (m, 1H), 5.39 (m, 1H), 3.63 (s, 1H), 1.84-1.80 (m, 2H), 1.53 (s, 3H), 1.41 (s, 3H). 13C NMR (101 MHz, CDCl3): δ 162.63 (d, J = 247.8 Hz), 146.19 (d, J = 8.0 Hz), 133.84 (d, J = 7.8 Hz), 131.72, 128.41 (d, J = 13.9 Hz), 122.89, 115.92 (d, J = 22.7 Hz), 115.07 (d, J = 24.2 Hz), 110.13, 96.34, 83.25, 71.20, 50.71, 31.44, 30.78, 28.70. 19F NMR (376 MHz, CDCl3): δ -113.98--114.04 (m, 1F). IR (neat) cm⁻¹ ʋ: 3535, 2968, 2926, 2868, 1646, 1463, 1411, 1259, 1161, 1103, 1067, 1026, 882, 809, 755, 691, 631, 593, 563. HRMS (ESI) m/z calcd. for C19H19BrFO [M+H]⁺: 361.0598; found: 361.0597.

4-(9H-carbazol-9-yl)-4-methylpentan-2-ol

5a was prepared according to general procedure E in 70% isolated yield. White solid. 1H NMR (400 MHz, CDCl3): δ 8.09 (dd, J = 7.7, 0.7 Hz, 2H), 7.85 (d, J = 8.6Hz, 2H), 7.37 (ddd, J = 8.6, 7.1, 1.4 Hz, 2H), 7.21 (t, J = 7.4 Hz, 2H), 3.80-3.70 (m, 1H), 2.51 (dd, J = 15.0, 2.9 Hz, 1H), 2.33 (dd, J = 15.0, 8.3 Hz, 1H), 2.19 (s, 3H), 2.01 (s, 3H), 1.01 (d, J = 6.2 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 140.87, 125.43, 124.61, 120.03, 118.92, 114.00, 65.73, 61.53, 49.24, 31.45, 30.81, 25.19. IR (neat) cm⁻¹ ʋ: 3276, 2967, 2920, 2850, 1646, 1591, 1469, 1443, 1370, 1317, 1289, 1203, 1173, 1155, 1071, 1033, 747, 724, 627. HRMS (ESI) m/z calcd. for C19H21NNaO [M+Na]⁺: 290.1515; found: 290.1515.

9-(4-((diisopropyl(methyl)silyl)oxy)heptan-2-yl)-9H-carbazole
**5b** was prepared according to general procedure D in 70% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.11 (d, $J$ = 7.7 Hz, 4H), 7.58-7.38 (m, 8H), 7.22 (t, $J$ = 7.3 Hz, 4H), 5.05-4.93 (m, 2H), 3.67-3.56 (m, 2H), 2.60 -2.50 (m, 1H), 2.46-2.36 (m, 1H), 2.24-2.15 (m, 1H), 2.14-2.04 (m, 1H), 1.71-1.68 (d, $J$ = 7.0 Hz, 3H), 1.68-1.63 (d, $J$ = 7.0 Hz, 3H), 1.45-1.35 (m, 4H), 1.32-1.22 (m, 2H), 1.21-1.08 (m, 2H), 1.01-0.88 (m, 12H), 0.88-0.78 (m, 4H), 0.79-0.70 (m, 6H), -0.07 (s, 3H), -0.13 (s, 3H). 

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 125.39, 120.41, 118.69, 118.66, 70.63, 69.81, 48.31, 47.55, 42.13, 41.76, 39.84, 39.24, 20.19, 19.57, 18.17, 18.14, 17.78, 17.76, 17.75, 17.69, 17.67, 17.63, 14.27, 13.81, 13.72, 13.67, 13.58, -6.93, -7.45. IR (neat) cm$^{-1}$ ν: 2936, 2864, 1596, 1484, 1453, 1331, 1315, 1222, 1126, 1072, 1040, 995, 908, 882, 782, 746, 721, 641. HRMS (ESI) m/z calcd. for C$_{26}$H$_{40}$NOSi [M+H]$^+$: 410.2874; found: 410.2873.

**9-(3-((diisopropyl(methyl)silyl)oxy)-1-phenylpropyl)-9H-carbazole**

**5c** was prepared according to general procedure D in 62% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.12 (d, $J$ = 7.8 Hz, 2H), 7.45-7.13 (m, 1H), 6.25 (dd, $J$ = 9.6, 5.4 Hz, 1H), 3.62-3.54 (m, 1H), 3.25-3.20 (m, 1H), 2.83-2.72 (m, 2H), 0.97-0.75 (m, 14H), -0.16 (s, 3H). 

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 140.46, 140.37, 128.71, 127.37, 126.89, 125.51, 123.38, 120.27, 119.04, 110.77, 59.51, 53.24, 34.41, 17.53, 17.47, 12.99, 12.97, -8.65. IR (neat) cm$^{-1}$ ν: 3059, 2940, 2843, 1596, 1483, 1451, 1331, 1315, 1222, 1126, 1072, 1040, 995, 908, 882, 782, 746, 721, 644. HRMS (ESI) m/z calcd. for C$_{28}$H$_{36}$NOSi [M+H]$^+$: 430.2561; found: 430.2559.

**4-(2-chloro-9H-carbazol-9-yl)-4-methylpentan-2-ol**

**5d**
**5d** was prepared according to general procedure **E** in 65% isolated yield. White solid. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (d, $J$ = 7.8 Hz, 1H), 7.97 (d, $J$ = 8.3 Hz, 1H), 7.85 (s, 1H), 7.82 (d, $J$ = 9.0 Hz, 1H), 7.37 (t, $J$ = 7.9 Hz, 1H), 7.21 (t, $J$ = 7.4 Hz, 1H), 7.18 (dd, $J$ = 8.3, 0.9 Hz, 1H), 3.81-3.64 (m, 1H), 2.48 (dd, $J$ = 15.1, 2.8 Hz, 1H), 2.29 (dd, $J$ = 15.1, 8.4 Hz, 1H), 2.18 (s, 3H), 1.99 (s, 3H), 1.02 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.30, 141.10, 131.01, 125.68, 124.04, 123.10, 120.61, 119.99, 119.44, 119.36, 114.27, 113.86, 65.64, 61.81, 49.01, 31.38, 30.70, 25.27. IR (neat) cm$^{-1}$: 3250, 2967, 2920, 1589, 1458, 1423, 1318, 1296, 1274, 1216, 1157, 1124, 1081, 999, 931, 808, 762, 744, 722. HRMS (ESI) m/z calcd. for C$_{18}$H$_{20}$ClNNaO $[M+Na]^+$: 324.1126; found: 324.1124.

**4-(2-methoxy-9H-carbazol-9-yl)-4-methylpentan-2-ol**

![5e](image)

**5e** was prepared according to general procedure **E** in 63% isolated yield. Colorless oil. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J$ = 7.7 Hz, 1H), 7.95 (d, $J$ = 8.5 Hz, 1H), 7.79 (d, $J$ = 8.5 Hz, 1H), 7.36 (d, $J$ = 1.9 Hz, 1H), 7.29 (t, $J$ = 7.8 Hz, 1H), 7.18 (t, $J$ = 7.4 Hz, 1H), 6.85 (dd, $J$ = 8.5, 1.9 Hz, 1H), 3.91 (s, 3H), 3.81-3.72 (m, 1H), 2.48 (dd, $J$ = 15.0, 2.8 Hz, 2H), 2.30 (dd, $J$ = 15.0, 8.3 Hz, 1H), 2.17 (s, 3H), 1.99 (s, 3H), 1.02 (d, $J$ = 6.2 Hz, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.33, 142.02, 141.02, 124.76, 124.24, 120.36, 119.21, 119.06, 118.82, 113.86, 106.44, 99.65, 65.70, 61.44, 55.91, 49.07, 31.35, 30.64, 25.16. IR (neat) cm$^{-1}$: 3385, 2964, 2927, 1627, 1596, 1498, 1498, 1348, 1292, 1197, 1156, 1122, 1042, 819, 743, 724. HRMS (ESI) m/z calcd. for C$_{19}$H$_{23}$NNaO $[M+Na]^+$: 320.1621; found: 320.1620.

**4-(2,7-di-tert-butyl-9H-carbazol-9-yl)-4-methylpentan-2-ol**

![5f](image)

**5f** was prepared according to general procedure **E** in 60% isolated yield. White solid. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J$ = 1.7 Hz, 2H), 7.73 (d, $J$ = 8.9 Hz, 2H), 7.39 (dd, $J$ = 8.9, 1.8 Hz, 2H), 3.85-3.76 (m, 1H), 2.45-2.31 (m, 2H), 2.11 (s, 3H), 1.99 (s, 3H), 1.44 (s, 18H), 1.04 (d, $J$ = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.53,
139.24, 124.51, 123.18, 115.85, 113.41, 65.75, 61.11, 49.31, 34.54, 32.02, 31.19, 30.77, 25.11. IR (neat) cm⁻¹ ν: 3392, 2957, 2920, 2851, 1645, 1467, 1391, 1364, 1296, 1261, 1175, 1113, 1036, 878, 801, 653, 619. HRMS (ESI) m/z calcd. for C₂₆H₃₈NO [M+H]^+: 380.2948; found: 380.2947.

4. Synthetic applications

4.1 Stereoselective Synthesis of tetrahydropyran derivative

4.2 Stereoselective synthesis of pyrano-chromene derivative

Experimental procedure: To a magnetically stirred solution of alkynol 3a (21.6 mg 0.1 mmol) in dry CH₂Cl₂ (2 mL) was added dropwise Et₃SiH (16 µL, 0.1 mmol) followed by TMSOTf (36 µL, 0.2 mmol) at 0 °C. After completion, the mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate-petroleum ether (2:98) as eluent to give the product.

cis-2,4,4-trimethyl-6-(p-tolyl)tetrahydro-2H-pyran 75% yield. Colorless oil. cis-single diastereomer (>19 : 1 dr). ¹H NMR (400 MHz, CDCl₃): δ 7.26 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.52 (dd, J = 11.6, 2.4 Hz, 1H), 3.81 (dq, J = 12.2, 6.1, 2.2 Hz, 1H), 2.33 (s, 3H), 1.49 (dt, J = 13.4, 2.3 Hz, 1H), 1.43-1.34 (m, 2H), 1.24 (d, J = 6.1 Hz, 3H), 1.22-1.16 (m, 1H), 1.12 (s, 3H), 0.97 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 140.69, 136.82, 129.05, 126.05, 75.62, 75.59, 69.90, 46.91, 46.51, 33.28, 30.14, 24.90, 22.39, 21.23. IR (neat) cm⁻¹ ν: 2922, 2863, 1515, 1452, 1366, 1304, 1187, 1172, 1148, 1101, 1067, 1050, 1020, 992, 912, 810, 784, 584, 536. HRMS (ESI) m/z calcd. for C₁₅H₂₃O [M+H]^+: 219.1743; found: 219.1744.

Experimental procedure: To a magnetically stirred solution of alkynol 3a (21.6 mg 0.1 mmol), salicylaldehyde (11µL 0.1 mmol) in dry CH₂Cl₂ (2 mL) was added dropwise Et₃SiH (16 µL, 0.1 mmol) followed by TMSOTf (36 µL, 0.2 mmol) at 0 °C. After completion, the mixture was then concentrated under reduced pressure. The residue was purified by column chromatography.
**trans-2,4,4-trimethyl-10a-(p-tolyl)-3,4-dihydro-2H,10aH-pyran[2,3-b]chromene**

White solid. cis-single diastereomer (>19 : 1 dr). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J = 8.2$ Hz, 2H), 7.09 (dd, $J = 7.4$, 1.3 Hz, 1H), 7.03 (d, $J = 8.1$ Hz, 2H), 6.99 (dd, $J = 7.7$, 1.3 Hz, 1H), 6.83 (td, $J = 7.4$ Hz, 0.9 Hz, 1H), 6.70 (d, $J = 7.9$ Hz, 1H), 6.65 (s, 1H), 4.42-4.32 (m, 1H), 2.26 (s, 3H), 1.65-1.48 (m, 2H), 1.37 (d, $J = 6.2$ Hz, 3H), 1.33 (s, 3H), 0.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 152.13, 139.15, 138.16, 137.81, 128.95, 128.75, 126.26, 125.54, 122.91, 121.07, 121.03, 120.98, 116.51, 103.72, 67.68, 47.02, 33.88, 31.66, 29.34, 21.77, 21.26. IR (neat) cm$^{-1}$ $\tilde{\nu}$: 2956, 2922, 2866, 1646, 1484, 1456, 1366, 1275, 1232, 1170, 1136, 1108, 1069, 1045, 974, 925, 903, 857, 818, 796, 738, 721. HRMS (ESI) m/z calcd. for C$_{22}$H$_{25}$O$_2$ [M+H]$^+$: 219.1743; found: 219.1744.

5. Mechanistic investigations

5.1 Radical scavengers study

![Radical scavengers study diagram]

The radical scavenger experiments showed that TEMPO greatly hampered the reaction. This results evidently support radical-involved mechanism.

5.2 Observation of intermediate

The iodine atom transfer intermediate 1a was observed by GC/MS during the reaction. The intermediate remained at a low concentration until it vanished at last. So the intermediate 1a was most probably gradually converted to product.

![Intermediate observation diagram]

To verify the possibility of this process, we explored the reaction with phenylacetylene and intermediate 1a. The intermediate 1a was finally converted to wanted product with 70% isolated yield. So this process was proved to be reasonable.
In a dried sealed vial, \textbf{L1} (0.015 mmol, 15 mol %), CuI (0.015 mmol, 15 mol %), K$_2$CO$_3$ (0.3 mmol, 3.0 equiv.) and phenylacetylene (0.2 mmol, 2 equiv.) were dissolved in anhydrous CH$_3$CN (2.0 mL) under a N$_2$ atmosphere, and the mixture was stirred for 30 min. Then iodide 6 (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 32 h. The vial distance from the lamp was about 2-3 cm. The resulting mixture was passed through a pad of silica gel, and concentrated under a reduced pressure. The residue oil was dissolved in THF (1.0 mL), and TBAF (2 mL, 1.0 M THF,) was added. After completion (monitored by TLC), the resulting mixture was poured into water with EtOAc. The aqueous layer was extracted with two portions of EtOAc. The combined extract was washed with brine, dried over Na$_2$SO$_4$ and concentrated. The residue oil was purified by column chromatography in hexanes/EtOAc to afford deprotected products with 73% isolated yield.

5.3 Photophysical studies

UV-visible Spectroscopic Study of substrates and complexes

Experimental details

The UV-Vis spectra of a single substrate was measured directly in MeCN. A mixture of two or more substrates was stirred for 30 min before its spectra was measured.$^5$

\textbf{Figure S1.} Absorption Spectra of reaction components: CuI (1×10$^{-4}$ M), Ligand (1×10$^{-4}$ M), Phenylacetylene (1×10$^{-4}$ M), CuI (1×10$^{-4}$ M) + Ligand (1×10$^{-4}$ M), CuI (1×10$^{-4}$ M) + Phenylacetylene (1×10$^{-3}$ M) + Base, CuI (1×10$^{-4}$ M) + Ligand (1×10$^{-4}$ M) + Alkyne (1×10$^{-3}$ M) + Base.

In the range of 380-500 nm, copper acetylide and copper acetylide-ligand showed obvious absorption.

Stern-Volmer Experiment

In order to figure out how the excited state of copper acetylide and copper acetylide-
ligand interacts with the tethered alcohols, luminescence quenching experiments were performed.\(^5\)

**Experimental procedure**

In situ generated copper acetylide: phenylacetylene (0.1 mmol, 1.0 equiv), Cul (0.01 mmol, 10 mol %), K\(_2\)CO\(_3\) (0.3 mmol, 3.0 equiv) were added in a dried reaction vessel with 2 mL MeCN and the reaction mixture was stirred at room temperature. After turned yellow, 100\(\mu l\) of the solution diluted with 2 mL MeCN was added tethered alcohol 1a (0.15-2.0 mM). The solution was transferred to the cuvette with 1 cm optical path utilizing an oven-dried glass Pasteur pipette. Fluorescence spectra of in situ generated copper acetylide (0.25 mM) is given in Figure S2.

![Figure S2](image)

**Figure S2.** Fluorescence spectra of in situ generated copper acetylide

In situ generated copper acetylide-ligand phenylacetylene: Cul, L1 and K\(_2\)CO\(_3\) in MeCN: phenylacetylene (0.1 mmol, 1.0 equiv), Cul (0.01 mmol, 10 mol %), L1 (0.01 mmol, 10 mol %), K\(_2\)CO\(_3\) (0.3 mmol, 3.0 equiv) were added in a dried reaction vessel with 2 mL MeCN and the reaction mixture was stirred at room temperature. After turned yellow, 100\(\mu l\) of the solution diluted with 2 mL MeCN was added tethered alcohol 1a (0.15-2.0 mM). Stern-Volmer plot for the emission quenching of in situ generated copper acetylide-ligand (0.25 mM) is given in Figure S3.

![Figure S3](image)

**Figure S3.** Fluorescence spectra of in situ generated copper acetylide-ligand

Stern-Volmer plot for in situ generated copper-ligand and copper acetylide-ligand quenched by tethered alcohol 1a were showed in Figure S4. Based on Stern-Volmer constants, the excited-state copper acetylide cannot be quenched by the quencher. But the excited-state copper acetylide-ligand can be quenched by the tethered alcohol 1a.
5.4 Quantum yield measurement

We conducted the quantum yield measurement of the photoinduced reaction between tethered alcohols and terminal alkyne by an optical power meter. The result was calculated based on the product yield and the photon flux of the light source.

**Experimental procedure**

In a dried sealed vial, L1 (0.015 mmol, 15 mol %), CuI (0.015 mmol, 15 mol %), K₂CO₃ (0.3 mmol, 3.0 equiv.) and terminal alkyne (0.15 mmol, 1.5 equiv.) were dissolved in anhydrous CH₃CN (2.0 mL) under a N₂ atmosphere, and the mixture was stirred for 30 min. Then tethered alcohols (0.1 mmol, 1.0 equiv.) were added. The tube was sealed with Teflon septum, the reaction mixture was stirred under nitrogen at room temperature under Blue LED for 30 min. The vial distance from the lamp was about 3-4 cm. The resulting mixture was passed through a pad of silica gel, and concentrated under a reduced pressure. Diethyl phthalate was internal standard for 1H NMR. The photon flux of the light source was determined by an optical power meter to be 82.2 mW.

\[
p = \frac{88.2 \times 10^{-3}}{602 \times 10^{23} \times 6.63 \times 10^{-34} \times 3 \times 10^8 / 400 \times 10^{-9}} = 2.95 \times 10^{-7}
\]

Thus, the quantum yield can be calculated by the equation (2). f is the fraction of light (f>0.999), and assuming that the light was absorbed by the copper acetylide-ligand, the production of \(4 \times 10^{-6}\) mol product (4 % yield) in 30 min (1800 s) corresponds to a
quantum yield $\Phi = 0.75\%$.

\[
\Phi = \text{mol product} \times \frac{4 \times 10^{-6}}{\text{photon flux} \cdot t \cdot f} = 2.95 \times 10^{-7} \times 1800 \times 1 = 0.75\%
\] (2)

6. References

1 (a) P. Chuentragool, D. Yadagiri, T. Morita, S. Sarkar, M. Parasram, Y. Wang, V. Gevorgyan, Angew. Chem. Int. Ed. 2019, 58, 1794-1798; (b) D. Kurandina, D. Yadagiri, M. Rivas, A. Kavun, P. Chuentragool, K. Hayama, V. Gevorgyan, J. Am. Chem. Soc. 2019, 141, 8104-8109.
2 M. Parasram, V. O. Iaroshenko, V. Gevorgyan, J. Am. Chem. Soc. 2014, 136, 17926-17929.
3 S. J. Gharpure, D. S. Vishwakarma, S. K. Nanda, Org. Lett. 2017, 19, 6534-6537.
4 S. J. Gharpure, S. K. Nanda, Padmaja, Y. G. Shelke, Chem. Eur. J. 2017, 23, 10007-10012.
5 Z. Li, J. Lei, J. Am. Chem. Soc. 2019, 141, 9124-9128.
7. Spectral Data

$^1$H NMR (400 MHz, CDCl$_3$) of 1d

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1d
$^1$H NMR (400 MHz, CDCl$_3$) of 1i

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1i
$^1$H NMR (400 MHz, CDCl$_3$) of 1j

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1j
$^1$H NMR (400 MHz, CDCl$_3$) of 1k

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1k
$^1$H NMR (400 MHz, CDCl$_3$) of II

$^{13}$C NMR (101 MHz, CDCl$_3$) of II
$^1$H NMR (400 MHz, CDCl$_3$) of 1m

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1m
$^1$H NMR (400 MHz, CDCl$_3$) of 1n

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1n
$^1$H NMR (400 MHz, CDCl$_3$) of 10

$^{13}$C NMR (101 MHz, CDCl$_3$) of 10
$^1$H NMR (400 MHz, CDCl$_3$) of 1p

$^{13}$C NMR (101 MHz, CDCl$_3$) of 1p
$^1$F NMR (376 MHz, CDCl$_3$) of $1p$

$^1$H NMR (400 MHz, CDCl$_3$) of $1q$
$^{13}$C NMR (400 MHz, CDCl$_3$) of 1q

$^{19}$F NMR (376 MHz, CDCl$_3$) of 1q
$^{19}$F NMR (376 MHz, CDCl$_3$) of 1r

$^1$H NMR (400 MHz, CDCl$_3$) of 3a
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3a

$^1$H NMR (400 MHz, CDCl$_3$) of 3b
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3a

$^1$H NMR (400 MHz, CDCl$_3$) of 3c
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3c

$^1$H NMR (400 MHz, CDCl$_3$) of 3d
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3d

$^1$H NMR (400 MHz, CDCl$_3$) of 3e
$^1$H NMR (400 MHz, CDCl$_3$) of 3f

$^1$H NMR (400 MHz, CDCl$_3$) of 3f

$^1$C NMR (101 MHz, CDCl$_3$) of 3e
$^{19}$F NMR (376 MHz, CDCl$_3$) of 3f

$^1$H NMR (400 MHz, CDCl$_3$) of 3g
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3g

$^1$H NMR (400 MHz, CDCl$_3$) of 3h
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3h

$^1$H NMR (400 MHz, CDCl$_3$) of 3i
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3i

$^{19}$F NMR (376 MHz, CDCl$_3$) of 3i
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 3j

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 3j
$^1$H NMR (400 MHz, CDCl$_3$) of 4a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4a
$^1$H NMR (400 MHz, CDCl$_3$) of 4b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4b
$^1$H NMR (400 MHz, CDCl$_3$) of 4c

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4c
$^1$H NMR (400 MHz, CDCl$_3$) of 4d

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4d
$^1$H NMR (400 MHz, CDCl$_3$) of 4e

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4e
$^1$H NMR (400 MHz, CDCl$_3$) of 4f

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4f
$^1$H NMR (400 MHz, CDCl$_3$) of 4g

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4g
$^1$H NMR (400 MHz, CDCl$_3$) of 4h

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4h
$^1$H NMR (400 MHz, CDCl$_3$) of 4i

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4i
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 4j

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4j
**1H NMR (400 MHz, CDCl₃) of 4k**

**13C NMR (101 MHz, CDCl₃) of 4k**
$^1$H NMR (400 MHz, CDCl$_3$) of 4l

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4l
$^1$H NMR (400 MHz, CDCl$_3$) of 4m

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4m
$^1$H NMR (400 MHz, CDCl$_3$) of 4n

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4n
$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$ of 4o

$^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}$ of 4o
$^1$H NMR (400 MHz, CDCl$_3$) of $4p$

$^{13}$C NMR (101 MHz, CDCl$_3$) of $4p$
$^{19}$F NMR (376 MHz, CDCl$_3$) of 4p

$^1$H NMR (400 MHz, CDCl$_3$) of 4q
$^{13}$C NMR (101 MHz, CDCl$_3$) of 4q

$^{19}$F NMR (376 MHz, CDCl$_3$) of 4q
$^1$H NMR (400 MHz, CDCl$_3$) of 4r

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4r
$^{19}$F NMR (376 MHz, CDCl$_3$) of 4r

$^1$H NMR (400 MHz, CDCl$_3$) of 5a
$^{13}$C NMR (101 MHz, CDCl$_3$) of 5a

$^1$H NMR (400 MHz, CDCl$_3$) of 5b
$^{13}$C NMR (101 MHz, CDCl$_3$) of 5b

$^1$H NMR (400 MHz, CDCl$_3$) of 5c
$\text{C NMR (101 MHz, CDCl}_3\text{) of } 5c$

$\text{H NMR (400 MHz, CDCl}_3\text{) of } 5d$
$^{13}$C NMR (101 MHz, CDCl$_3$) of 5d

$^1$H NMR (400 MHz, CDCl$_3$) of 5e
$^{13}$C NMR (101 MHz, CDCl$_3$) of 5e

$^1$H NMR (400 MHz, CDCl$_3$) of 5f
$^{13}$C NMR (101 MHz, CDCl$_3$) of 5f

$^1$H NMR (400 MHz, CDCl$_3$) of 7
$^{13}$C NMR (101 MHz, CDCl$_3$) of 7

NOESY of 7
$^1$H NMR (400 MHz, CDCl$_3$) of 8

$^{13}$C NMR (101 MHz, CDCl$_3$) of 8
NOESY of 8