Supporting Information for

Stereoselective Synthesis of Enynones via Base-catalyzed Isomerization of 1,5-Disubstituted-2,4-pentadiynyl Silyl Ethers or Their Alcohol Derivatives

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Experimental section

General Methods. All reactions were carried out using standard Schlenk techniques under argon. THF was distilled from sodium and benzophenone. $^1$H NMR spectra was recorded at 300 or 400 MHz, $^{13}$C NMR spectra was recorded at 75 or 100 MHz, and in CDCl$_3$ (containing 0.03% TMS) solutions. $^1$H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) or chloroform ($\delta = 7.26$ ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl$_3$ ($\delta = 77.00$ ppm) as internal reference. NNR yields were determined using dibromomethane as an internal standard. 1,5-disubstituted-2,4-pentadiynyl silyl ethers 1$^1$ and its alcohol derivatives 7$^{2,3}$ were prepared according to the published methods. The characterization data of 1a$^1$, 2h$^4$, 2j$^5$, 3h$^4$, 3i$^6$, 3j$^6$, 7j$^7$, 7l$^7$ are consistent with that

S1
previous reported one. 1,4-bis(TMS)-1,3-diyne and 1,4-bis(TBS)-1,3-diyne were synthesized by modified procedures according to published method.\textsuperscript{8}

**Typical procedure for the preparation of 1,5-disubstituted-2,4-pentadiynyl silyl ethers 1a-1f and 1k\textsuperscript{1}.** To a stirred solution of 1,4-bis(\textit{tert}-butyldimethylsilyl)buta-1,3-diyne (2 mmol, 556 mg) and Ti(O\textit{i}Pr)\textsubscript{4} (2.5 mmol, 0.76 mL) in THF (20 mL) was added n-BuLi (5 mmol, 3.1 mL, 1.6 M solution in hexane) dropwise at -78 °C under argon. The solution was warmed to room temperature and stirred for 1 h. Benzaldehyde (2 mmol, 0.21 mL) was added and stirred for 15 min. Then, I\textsubscript{2} (2.6 mmol, 660 mg) was added to the mixture. After 30 min of stirring, the reaction mixture was quenched with saturated Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, and extracted with EtOAc. Combined organic extracts were washed with brine, dried over MgSO\textsubscript{4}, and concentrated. Column chromatography on silica gel afforded the corresponding enyne 1a in 76% yield.

**\textit{tert}-Butyl(5-\textit{tert}-butyldimethylsilyl)-1-phenylpenta-2,4-diynyloxydimethylsilane (1a)\textsuperscript{1}**. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a white solid in 76% yield. mp 49-50 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 300 MHz) δ 0.16 (s, 9H), 0.22 (s, 3H), 0.97 (s, 9H), 0.98 (s, 9H), 5.55 (s, 1H), 7.32-7.41 (m, 3H), 7.47-7.50 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 75 MHz) δ -5.0, -4.9, -4.6, 16.7, 18.3, 25.7, 26.0, 65.1, 70.6, 77.6, 86.4, 88.1, 126.0, 128.0, 128.4, 140.7.

**\textit{tert}-Butyl(5-\textit{tert}-butyldimethylsilyl)-1-(4-chlorophenyl)penta-2,4-diynyloxydimethylsilane (1b)**. Purification of the crude product by flash chromatography on silica gel (eluent:
petroleum ether) afforded the title compound as a pale yellow oil in 83% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.13 (s, 9H), 0.19 (s, 3H), 0.93 (s, 9H), 0.95 (s, 9H), 5.49 (s, 1H), 7.33 (d, \(J = 8.4\) Hz, 2H), 7.39 (d, \(J = 8.8\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -5.0, -4.9, -4.6, 16.7, 18.2, 25.7, 26.0, 64.6, 70.9, 77.0, 86.9, 87.8, 127.4, 128.6, 133.8, 139.3. IR (neat) 2954, 2930, 2886, 2858, 2221, 2106, 1490, 1470, 1253, 1090, 839, 778, 680 cm\(^{-1}\). HRMS (EI) for C\(_{23}\)H\(_{35}\)OSi\(_2\)Cl [M]\(^+\): calcd 418.1915, found 418.1913.

**tert-Butyl(5-(tert-butyldimethylsilyl)-1-(4-methoxyphenyl)penta-2,4-diynyloxy)dimethylsilane (1c).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 74% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 300 MHz) \(\delta\) 0.13 (s, 3H), 0.15 (s, 6H), 0.19 (s, 3H), 0.94-0.96 (m, 18H), 3.81 (s, 3H), 6.90 (d, \(J = 8.4\) Hz, 2H), 7.39 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 75 MHz) \(\delta\) -5.0, -4.9, -4.6, 16.7, 18.2, 25.8, 26.0, 55.2, 64.8, 70.4, 77.8, 86.3, 88.1, 113.7, 127.4, 133.0, 159.3. IR (neat) 2954, 2930, 2858, 2214, 2105, 1611, 1511, 1250, 1066, 838, 777 cm\(^{-1}\). HRMS (EI) for C\(_{24}\)H\(_{38}\)O\(_2\)Si\(_2\) [M]\(^+\): calcd 414.2410, found 414.2412.

**tert-Butyl(5-(tert-butyldimethylsilyl)-1-(thien-2-yl)penta-2,4-diynyloxy)dimethylsilane (1d).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 77% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.11 (s, 6H), 0.12 (s, 3H), 0.15 (s, 3H), 0.90 (s, 9H), 0.92 (s, 9H), 5.71 (s, 1H), 6.90-6.92 (m, 1H), 7.03-7.04 (m, 1H), 7.21-7.22 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -5.1, -4.9, -4.6, 16.7, 18.3, 25.7, 26.0, 61.5, 70.4, 76.4, 87.0,
87.9, 124.40, 125.4, 126.5, 144.9. IR (neat) 2954, 2930, 2858, 2107, 1471, 1252, 1063, 839, 778, 699 cm⁻¹. HRMS (EI) for C₂₁H₃₄OSi₂ [M]⁺: calcd 390.1869, found 390.1870.

**tert-Butyl(5-(tert-butyldimethylsilyl)-1-(furan-2-yl)penta-2,4-diynloxy)dimethylsilane (1e).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 74% yield. ¹H NMR (CDCl₃, Me₄Si, 400 MHz) δ 0.13-0.15 (m, 12H), 0.91 (s, 9H), 0.95 (s, 9H), 5.54 (s, 1H), 6.33-6.34 (m, 1H), 6.40-6.41 (m, 1H), 7.38-7.39 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz) δ -5.0, -4.9, -4.8, 16.7, 18.3, 25.7, 26.0, 59.4, 70.0, 74.9, 86.5, 87.9, 107.6, 110.4, 142.6, 152.5. IR (neat) 2955, 2930, 2858, 2107, 1471, 1253, 1062, 839, 778, 738 cm⁻¹. HRMS (EI) for C₂₁H₃₄O₂Si₂ [M]⁺: calcd 374.2097, found 374.2095.

**Ph**

(E)-**tert-Butyl(7-(tert-butyldimethylsilyl)-1-phenylhepta-1-en-4,6-diyn-3-ylloxy)dimethylsilane (1f).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 68% yield. ¹H NMR (CDCl₃, Me₄Si, 400 MHz) δ 0.14-0.15 (m, 6H), 0.17 (s, 3H), 0.19 (s, 3H), 0.95 (s, 9H), 0.96 (s, 9H), 5.11 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 6.20 (dd, J = 16.0 Hz, 6.0 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 7.24-7.28 (m, 1H), 7.32-7.35 (m, 2H), 7.39-7.41 (m, 2H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz) δ -4.9, -4.8, -4.5, 16.7, 18.3, 25.8, 26.0, 63.9, 70.5, 76.6, 86.4, 88.1, 126.7, 128.0, 128.0, 128.5, 130.9, 136.2. IR (neat) 2954, 2930, 2858, 2220, 2105, 1471, 1252, 1054, 838, 777, 691 cm⁻¹. HRMS (EI) for C₂₅H₃₈OSi₂ [M]⁺: calcd 410.2461, found 410.2455.
TBS
\begin{align*}
\text{TBS} & \quad \equiv \equiv \\
\text{Pr} & \quad \text{OTBS}
\end{align*}

**1k**

*tert*-Butyl(8-(*tert*-butyldimethylsilyl)octa-5,7-diyn-4-yl oxy)dimethylsilane (1k).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a colorless oil in 50% yield. \( ^1 \text{H NMR (CDCl}_3, \text{Me}_4\text{Si,} \) 400 MHz) \( \delta \) 0.10 (s, 3H), 0.13 (s, 6H), 0.14 (s, 3H), 0.90 (s, 9H), 0.92 (t, \( J = 7.6 \text{ Hz,} \) 3H), 0.94 (s, 9H), 1.39-1.51 (m, 2H), 1.59-1.72 (m, 2H), 4.39 (t, \( J = 6.4 \text{ Hz,} \) 1H); \( ^{13}\text{C NMR (CDCl}_3, \text{Me}_4\text{Si,} \) 100 MHz) \( \delta \) -5.1, -4.8, -4.6, 13.7, 16.7, 18.2, 18.4, 25.8, 26.0, 40.5, 63.0, 69.1, 79.1, 85.1, 88.2. IR (neat) 2956, 2931, 2859, 2215, 2106, 1471, 1463, 1362, 1252, 1112, 1080, 838, 811, 777, 680 cm\(^{-1}\)). HRMS (EI) for C\(_{20}\)H\(_{38}\)O\(_2\)S\(_2\) [M]: calcd 350.2461, found 350.2464.

**Typical procedure for the preparation of 1,5-disubstituted-2,4-pentadiynyl silyl ethers 1g-1j.** To a stirred solution of 5-(*tert*-Butyldiphenylsilyl)-1-phenylpenta-2,4-diyn-1-ol 7q (2 mmol, 789 mg) and imidazole (5 mmol, 340 mg) in dry DCM (5 mL) was added TBSCl (4 mmol, 603 mg) at room temperature and stirred for 1 h. The reaction mixture was washed with H\(_2\)O, and extracted with EtOAc. Combined organic extracts were washed with brine, dried over MgSO\(_4\), and concentrated. Column chromatography on silica gel afforded the corresponding enyne 1g in 92% yield.

TBDPS
\begin{align*}
\text{TBDPS} & \quad \equiv \equiv \\
\text{Ph} & \quad \text{OTBS}
\end{align*}

**1g**

*tert*-Butyl(5-(*tert*-butyldimethylsilyloxy)-5-phenylpenta-1,3-diynyl)diphenylsilane (1g).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 92% yield. \( ^1\text{H NMR (CDCl}_3, \text{Me}_4\text{Si,} \) 400 MHz) \( \delta \) 0.22 (s, 3H), 0.29 (s, 3H), 1.02 (s, 9H), 1.17 (s, 9H), 5.64 (s, 1H), 7.37-7.57 (m, 11H), 7.82-7.84 (m, 4H); \( ^{13}\text{C NMR (CDCl}_3, \text{Me}_4\text{Si,} \) 100 MHz) \( \delta \) -4.9, -4.7, 18.3, 18.8, 25.8, 27.0, 65.3, 70.7, 78.6, 83.3, 91.2, 126.1, 127.8, 128.1, 128.5, 129.7, 132.4,
135.6, 140.5. IR (neat) 3071, 2956, 2930, 2858, 2105, 1694, 1471, 1429, 1256, 1111, 842, 698, 507 cm$^{-1}$. HRMS (EI) for C$_{33}$H$_{40}$OSi$_{2}$ [M]$^{+}$: calcd 508.2618, found 508.2632.

1h

*tert*-Butyldimethyl(1-phenyl-5-(trimethylsilyl)penta-2,4-diynyl)oxy)silane (1h).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 91% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 0.17 (s, 3H), 0.23 (s, 12H), 0.97 (s, 9H), 5.56 (s, 1H), 7.30-7.40 (m, 3H), 7.48-7.49 (m, 2H). $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -5.0, -4.5, -0.4, 18.3, 25.8, 65.1, 70.5, 78.2, 87.5, 87.7, 126.1, 128.0, 128.4, 140.7. IR (neat) 3065, 3031, 2957, 2930, 2858, 2220, 2107, 1472, 1252, 1085, 1065, 845, 778, 761, 696 cm$^{-1}$. HRMS (EI) for C$_{20}$H$_{30}$OSi$_{2}$ [M]$^{+}$: calcd 342.1835, found 342.1838.

Bu

1i

*tert*-Butyldimethyl(1-phenylnona-2,4-diynyl)oxy)silane (1i). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether) afforded the title compound as a pale yellow oil in 82% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 0.13 (s, 3H), 0.18 (s, 3H), 0.90 (t, $J$ = 7.2 Hz, 3H), 0.93 (s, 9H), 1.36-1.54 (m, 4H), 2.27 (t, $J$ = 6.8, 2H), 5.51 (s, 1H), 7.25-7.36 (m, 3H), 7.45-7.47 (m, 2H). $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -5.0, -4.5, 13.5, 18.3, 19.0, 21.9, 25.8, 30.2, 64.6, 65.2, 70.7, 76.0, 81.9, 126.0, 127.8, 128.3, 141.1. IR (neat) 3064, 3030, 2957, 2932, 2252, 1471, 1253, 1088, 1065, 842, 779, 698 cm$^{-1}$. HRMS (EI) for C$_{21}$H$_{30}$OSi [M]$^{+}$: calcd 326.2066, found 326.2070.

Ph

1j

*tert*-Butyl(1,5-diphenylpenta-2,4-diynyl)dimethylsilane (1j). Purification of the
crude product by flash chromatography on silica gel (eluent: petroleum ether) afford the title compound in 92% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.17 (s, 3H), 0.23 (s, 3H), 0.96 (s, 9H), 5.62 (s, 1H), 7.31-7.38 (m, 6H), 7.48-7.52 (m, 4H). \(^1\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -4.9, -4.5, 18.3, 25.8, 65.3, 70.2, 73.5, 78.8, 83.0, 121.6, 126.1, 128.0, 128.4, 128.5, 129.2, 132.5, 140.8. HRMS (EI) for C\(_{23}\)H\(_{26}\)OSi \([M]^+\): calcd 346.1753, found 346.1754.

Typical procedure for the preparation of penta-2, 4-diyne-1-ol 7a-7g, 7p, 7q. To a stirred solution of 1,4-bis(tert-butyldimethylsilyl)buta-1,3-diyne (2 mmol, 556 mg) in dry THF (5 mL) was added MeLi-LiBr (2.2 mmol, 1.5 M in Et\(_2\)O) dropwise at 0 °C, the solution was warmed to room temperature and stirred at the same temperature for 2 h. Benzaldehyde (2 mmol, 0.21 mL) was added and stirred for 2 h. The reaction mixture was quenched with 3 N HCl and extracted with EtOAc. Combined organic extracts were washed with brine, dried over MgSO\(_4\), and concentrated. Column chromatography on silica gel afforded the product 7a in 82% yield.

\[
\text{TBS} \begin{array}{c} \equiv \equiv \equiv \end{array} \text{Ph} \quad \text{OH} \\
7a
\]

5-(tert-Butyldimethylsilyl)-1-phenylpenta-2,4-diyne-1-ol (7a). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) afforded the title compound as a white solid in 82% yield. mp 101-102 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 300 MHz) \(\delta\) 0.16 (s, 6H), 0.97 (s, 9H), 2.63 (d, \(J = 6.0\) Hz, 1H), 5.49 (d, \(J = 6.0\) Hz, 1H), 7.34-7.42 (m, 3H), 7.49-7.52 (m, 2H); \(^1\)C NMR (CDCl\(_3\), Me\(_4\)Si, 75 MHz) \(\delta\) -5.0, 16.7, 26.0, 64.8, 71.5, 76.3, 87.2, 87.7, 126.6, 128.6, 128.7, 139.4. IR (neat) 3353, 3065, 2954, 2858, 2206, 2106, 1470, 1462, 1391, 1252, 1006, 839, 824, 777, 697 cm\(^{-1}\). HRMS (EI) for C\(_{17}\)H\(_{22}\)OSi \([M]^+\): calcd 270.1440, found 270.1441. Anal. Calc. for C\(_{17}\)H\(_{22}\)OSi: C, 75.50; H, 8.20. found: C, 75.70, H, 8.35.
5-(tert-Butyldimethylsilyl)-1-(4-chlorophenyl)penta-2,4-diyn-1-ol (7b). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow solid in 77% yield. mp 86-89 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.14 (s, 6H), 0.95 (s, 9H), 2.45 (d, $J = 5.2$ Hz, 1H), 5.48 (d, $J = 5.6$ Hz, 1H), 7.34-7.37 (m, 2H), 7.44 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -5.0, 16.7, 26.0, 64.2, 71.9, 75.8, 87.4, 87.8, 128.0, 128.1, 134.5, 137.9. IR (neat) 3359, 2954, 2930, 2858, 2200, 2106, 1643, 1589, 1491, 1470, 1252, 1092, 1014, 839, 778, 680 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{21}$OClSi [M]$^+$: calcd 304.1050, found 304.1048.

5-(tert-Butyldimethylsilyl)-1-(4-methoxyphenyl)penta-2,4-diyn-1-ol (7c). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) afforded the title compound as a pale yellow oil in 71% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.14 (s, 6H), 0.95 (s, 9H), 2.51 (bs, 1H), 3.80 (s, 3H), 5.44 (d, $J = 6.0$ Hz, 1H), 6.88-6.91 (m, 2H), 7.41-7.44 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -5.0, 16.7, 26.0, 55.3, 64.5, 71.4, 76.6, 87.1, 87.8, 114.0, 128.1, 131.9, 159.8. IR (neat) 3398, 2954, 2930, 2858, 2200, 2106, 1643, 1589, 1491, 1470, 1252, 1092, 1014, 839, 778, 680 cm$^{-1}$. HRMS (EI) for C$_{18}$H$_{24}$O$_2$Si [M]$^+$: calcd 300.1546, found 300.1546.

5-(tert-Butyldimethylsilyl)-1-(thien-2-yl)penta-2,4-diyn-1-ol (7d). Purification of the
crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow solid in 63% yield. mp 45-46 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.15 (s, 6H), 0.96 (s, 9H), 2.68 (d, \(J = 6.4 \text{ Hz}, 1H\)), 5.70 (d, \(J = 6.4 \text{ Hz}, 1H\)), 6.97-6.99 (m, 1H), 7.17-7.18 (m, 1H), 7.31-7.32 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -5.0, 16.7, 26.0, 60.5, 71.1, 75.4, 87.5, 87.8, 125.9, 126.4, 126.8, 143.1. IR (neat) 3381, 2954, 2929, 2858, 2227, 2106, 1470, 1252, 1006, 829, 778, 702 cm\(^{-1}\). HRMS (EI) for C\(_{15}\)H\(_{20}\)OSSi [M]+: calcd 276.1004, found 276.0999.

5-\((\text{tert-Butyldimethylsilyl})\)-1-\((\text{furan-2-yl})\)penta-2,4-diyn-1-ol (7e). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow oil in 72% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.14 (s, 6H), 0.95 (s, 9H), 2.61(d, \(J = 6.0 \text{ Hz}, 1H\)), 5.50 (d, \(J = 6.0 \text{ Hz}, 1H\)), 6.35-6.36 (m, 1H), 6.46-6.47 (m, 1H), 7.40-7.41 (m, 1H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -5.0, 16.7, 26.0, 58.4, 70.8, 73.7, 87.5, 87.5, 108.2, 110.5, 143.2, 151.7. IR (neat) 3366, 2954, 2930, 2858, 2221, 2107, 1471, 1252, 1142, 1009, 841, 778, 740 cm\(^{-1}\). HRMS (EI) for C\(_{15}\)H\(_{20}\)O\(_2\)Si [M]+: calcd 260.1233, found 260.1234.

(E)-7-\((\text{tert-Butyldimethylsilyl})\)-1-\((\text{phenylhepta-1-en-4,6-diyn-3-ol})\) (7f). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow oil in 67% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.16 (s, 6H), 0.97 (s, 9H), 2.33 (d, \(J = 6.4 \text{ Hz}, 1H\)), 5.11 (td, \(J = 6.0 \text{ Hz}, 0.8 \text{ Hz}, 1H\)), 6.26 (dd, \(J = 16.0 \text{ Hz}, 6.0 \text{ Hz}, 1H\)), 6.77 (dd, \(J = 15.6 \text{ Hz}, 0.8 \text{ Hz}, 1H\)), 7.26-7.36 (m, 3H), 7.39-7.42 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -5.0, 16.7, 26.0, 63.2, 71.4, 75.7, 87.3, 87.7, 126.8, 126.8, 128.3, 128.6, 132.7, 135.8. IR (neat) 3337,
2954, 2929, 2857, 2220, 2105, 1470, 1251, 1006, 963, 839, 825, 777 cm$^{-1}$. HRMS (EI) for C$_{19}$H$_{24}$OSi [M]$^+$: calcd 296.1596, found 296.1598.

5-(tert-Butyldimethylsilyl)-1-(naphthalen-1-yl)penta-2,4-diyn-1-ol (7g). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow solid in 67% yield. mp 108-109 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.14 (s, 6H), 0.96 (s, 9H), 2.47 (d, $J$ = 6.0 Hz, 1H), 6.17 (d, $J$ = 5.6 Hz, 1H), 7.26-7.61 (m, 3H), 7.80-7.90 (m, 3H), 8.24 (d, $J$ = 8.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -4.9, 16.7, 26.0, 63.2, 72.2, 76.1, 87.5, 87.8, 123.7, 124.8, 125.2, 126.0, 126.6, 128.8, 129.6, 130.3, 133.9, 134.6. IR (neat) 3389, 2953, 2929, 2857, 2248, 2105, 1705, 1511, 1470, 1362, 1252, 829, 777 cm$^{-1}$. HRMS (EI) for C$_{21}$H$_{24}$OSi [M]$^+$: calcd 320.1596, found 320.1601. Anal. Calc. for C$_{21}$H$_{24}$OSi: C, 78.70; H, 7.55. found: C, 78.64, H, 7.54.

1-Phenyl-5-(trimethylsilyl)penta-2,4-diyn-1-ol (7p). This compound was prepared in ethyl ether instead of THF$^2$. The crude product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) to afford the title compound as a pale yellow oil in 74% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.21 (s, 9H), 2.27 (d, $J$ = 6.0 Hz, 1H), 5.51 (d, $J$ = 6.4 Hz, 1H), 7.34-7.45 (m, 3H), 7.50-7.52 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -0.6, 64.8, 71.4, 76.9, 87.1, 88.5, 126.6, 128.6, 128.7, 139.4. IR (neat) 3360, 2960, 2900, 2221, 2107, 1454, 1409, 1252, 1003, 869, 760, 697 cm$^{-1}$. HRMS (EI) for C$_{14}$H$_{16}$OSi [M]$^+$: calcd 228.0970, found 228.0973.
5-(tert-Butyldiphenylsilyl)-1-phenylpenta-2,4-diyn-1-ol (7q). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) afforded the title compound as a colorless oil in 76% yield. 1H NMR (CDCl₃, Me₄Si, 400 MHz) δ 1.10 (s, 9H), 2.93 (d, J = 6.0 Hz, 1H), 5.46 (d, J = 6.0 Hz, 1H), 7.27-7.48 (m, 11H), 7.75-7.77 (m, 4H); 13C NMR (CDCl₃, Me₄Si, 100 MHz) δ 18.7, 26.9, 64.8, 71.5, 77.4, 83.9, 90.8, 126.6, 127.8, 128.6, 128.7, 129.7, 132.1, 135.5, 139.2. IR (neat) 3378, 3070, 2958, 2930, 2858, 2220, 1428, 1110, 999, 698, 508 cm⁻¹. HRMS (EI) for C₂₇H₂₆OSi [M]+: calcd 394.1753, found 394.1746.

Typical procedure for the preparation of penta-2,4-diynyl-1-ol 7i-7n.³ To a stirred solution of 1-phenylprop-2-yn-1-ol (5 mmol, 661 mg) in dry toluene (20 mL) were added CuCl (15 mol%, 75 mg), NH₂OH·HCl (30 mol%, 105 mg), BuNH₂ (7.5 mmol, 0.76 mL) and 1-bromohex-1-yne (5.5 mmol, 0.7 mL) at 0 °C, then the solution was warmed to room temperature and stirred for 3 h. The reaction mixture was quenched with 3 N HCl and extracted with EtOAc. Combined organic extracts were washed with brine, dried over MgSO₄, and concentrated. Column chromatography on silica gel afforded the product 7i in 81% yield.

1-Phenylconza-2,4-diyn-1-ol (7i). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a pale yellow oil in 81% yield. 1H NMR (CDCl₃, Me₄Si, 400 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 1.36-1.55 (m, 4H), 2.28 (td, J = 7.2 Hz, 0.8 Hz, 2H), 2.61 (d, J = 6.0 Hz, 1H), 5.46 (d, J = 6.0 Hz, 1H), 7.24-7.38 (m, 3H), 7.47-7.50 (m, 2H); 13C NMR (CDCl₃, Me₄Si, 100 MHz) δ 13.4, 18.9, 21.8, 30.1, 64.3, 64.9, 71.6, 74.7, 82.6, 126.6, 128.4, 128.6, 139.9. IR (neat) 3382, 2958, 2932, 2872, 2253, 1493, 1454, 1188, 1016, 699
cm\(^{-1}\). HRMS (EI) for C\(_{13}\)H\(_{16}\)O [M]: calc 212.1201, found 212.1203.

**1,5-Diphenylpenta-2,4-diyn-1-ol (7j).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title compound as a pale green solid in 82% yield. \(\text{^1H NMR (CDCl}_3, \text{Me}_4\text{Si, 400 MHz)}\) \(\delta\) 2.33(d, \(J = 6.0\) Hz, 1H), 5.60 (d, \(J = 6.4\) Hz, 1H), 7.30-7.43 (m, 6H), 7.48-7.57 (m, 4H); \(\text{^13C NMR (CDCl}_3, \text{Me}_4\text{Si, 100 MHz)}\) \(\delta\) 65.2, 71.3, 73.1, 79.4, 81.6, 121.3, 126.7, 128.4, 128.7, 128.8, 129.4, 132.6, 139.7.

**1-(4-Chlorophenyl)-5-phenylpenta-2,4-diyn-1-ol (7k).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title compound as a pale green solid in 67% yield. mp 97-98 °C. \(\text{^1H NMR (CDCl}_3, \text{Me}_4\text{Si, 400 MHz)}\) \(\delta\) 2.45 (d, \(J = 5.6\) Hz, 1H), 5.57 (d, \(J = 6.0\) Hz, 1H), 7.30-7.38 (m, 5H), 7.47-7.51 (m, 4H); \(\text{^13C NMR (CDCl}_3, \text{Me}_4\text{Si, 100 MHz)}\) \(\delta\) 64.3, 71.6, 72.9, 79.7, 81.0, 121.1, 128.0, 128.4, 128.8, 129.5, 132.6, 134.5, 138.0. IR (neat) 3328, 2242, 1595, 1489, 1442, 1407, 1091, 1014, 754, 688, 526 cm\(^{-1}\). HRMS (EI) for C\(_{17}\)H\(_{11}\)OCl [M]: calc 266.0498, found 266.0497.

**1-(4-Methoxyphenyl)-5-phenylpenta-2,4-diyn-1-ol (7l).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1)
afforded the title compound as a pale green solid in 84% yield. mp 80-82 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 2.25 (d, $J = 6.4$ Hz, 1H), 3.82 (s, 3H), 5.54 (d, $J = 6.4$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 2H), 7.31-7.38 (m, 3H), 7.47-7.51 (m, 4H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ 55.3, 64.8, 71.1, 73.2, 79.3, 81.9, 114.1, 121.4, 128.1, 128.4, 129.3, 132.0, 132.6, 159.9.

(E)-1,7-Diphenylepta-1-en-4,6-diyne-3-ol (7m). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title compound as a pale green solid in 74% yield. mp 108-110 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) δ 2.67 (d, $J = 5.4$ Hz, 1H), 5.18 (bs, 1H), 6.30 (dd, $J = 16.2$, 6.0 Hz, 1H), 6.76 (d, $J = 17.1$ Hz, 1H), 7.29-7.49 (m, 10H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ 63.4, 71.0, 73.1, 79.3, 80.9, 121.2, 126.8, 128.2, 128.4, 128.6, 129.3, 132.5, 132.6, 135.7. IR (neat) 3361, 2241, 1743, 1489, 1065, 1024, 987, 966, 751, 688, 526 cm$^{-1}$. HRMS (EI) for C$_{19}$H$_{14}$O [M$^+$]: calcd 258.1045, found 258.1042.

5-Phenyl-1-(thien-2-yl)penta-2,4-diyne-1-ol (7n). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the title compound as a pale yellow solid in 96% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) δ 2.64 (bs, 1H), 5.79(s, 1H), 6.99 (dd, $J = 4.8$, 3.6 Hz, 1H), 7.21 (d, $J = 3.6$ Hz, 1H), 7.29-7.38 (m, 4H), 7.48-7.52 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ 60.8, 70.8, 73.0, 79.7, 80.6, 121.2, 125.9, 126.4, 126.8, 128.4, 129.5, 132.6, 143.3. IR (neat) 3058, 2208, 1712, 1597, 1490, 1442, 1229, 1012, 850, 756, 701, 689 cm$^{-1}$. HRMS (EI) for C$_{15}$H$_{10}$OS [M$^+$]: calcd 238.0452, found 238.0456.
1-(Furan-2-yl)-5-phenylpenta-2,4-diyn-1-ol (7o). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the title compound as a pale yellow solid in 70% yield. mp 42-44 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 2.60 (d, $J = 7.2$ Hz, 1H), 5.59 (d, $J = 6.8$ Hz, 1H), 6.37 (ddd, $J = 3.4$, 1.0, 0.4 Hz, 1H), 6.50 (dt, $J = 3.2$, 0.8 Hz, 1H), 7.30-7.40 (m, 3H), 7.44 (dd, $J = 2.0$, 1.2 Hz, 1H), 7.48-7.51 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ 58.6, 70.5, 73.0, 79.0, 79.4, 108.2, 110.5, 121.1, 128.4, 129.5, 132.6, 143.3, 151.8. IR (neat) 3386, 2243, 2203, 1703, 1628, 1490, 1442, 1103, 1010, 755, 689, 527 cm$^{-1}$. HRMS (EI) for C$_{15}$H$_{10}$O$_2$ [M]$^+$: calcd 222.0681, found 222.0682.

Typical procedure for the selective formation of cis-enynones from 1,5-disubstituted-2,4-pentadiynyl silyl ethers catalyzed by KO'Bu (Method A). To a stirred solution of tert-Butyl(5-(tert-butyldimethylsilyl)-1-phenylpenta-2,4-diynyloxy)-dimethylsilane 1a (0.3 mmol, 115 mg) in THF (3 mL) was added KO'Bu powder (30 mol%, 0.09 mmol, 10 mg) at -78 °C under argon. After stirring for 25 min at the same temperature, the mixture was quenched at -78 °C with 3 N HCl (ca. 0.5 mL). At this stage the color of the solution changed from dark blue to pale yellow, then the suspension was warmed up to room temperature and stirred for several minutes (during this process, more dilute HCl was added to the solution). The mixture was extracted with EtOAc, and the combined organic extracts were washed with brine, dried over MgSO$_4$. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:1) to afford cis-enynones 2a and trans isomer 3a in 70% and 17% yields, respectively.

Typical procedure for the selective formation of cis-enynones from 1,5-disubstituted-2,4-pentadiynyl silyl ethers catalyzed by DBU (Method B). To a solution of 1a (0.4 mmol, 154 mg) in THF (4 mL) at 0 °C was added DBU (15 mol%, 0.06
mmol, 9.0 μL, in some cases, DBU was used as a 0.15 M solution in THF). After stirring for 4 h at 0 °C, the reaction mixture was quenched with 3 N HCl at 0 °C and extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:1) to afford cis-enynes 2a and trans isomer 3a in 70% and 19% yields, respectively.

(Z)-5-(tert-Butyldimethylsilyl)-1-phenylpent-2-en-4-yn-1-one (2a). Pale yellow solid. mp 43-44 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz) δ 0.05 (s, 6H), 0.88 (s, 9H), 6.21 (d, J = 11.6 Hz, 1H), 6.93 (d, J = 12.0 Hz, 1H), 7.43-7.48 (m, 2H), 7.53-7.58 (m, 1H), 7.93-7.96 (m, 2H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz) δ -5.0, 16.5, 26.0, 102.0, 105.8, 120.2, 128.5, 128.8, 133.0, 134.9, 137.4, 190.6. IR (neat) 3062, 3029, 2954, 2929, 2857, 2147, 1666, 1598, 1581, 1250, 1231, 839, 824, 776, 749, 691 cm⁻¹. HRMS (EI) for C₁₇H₂₂OSi [M]+: calcd 270.1440, found 270.1436.

(Z)-5-(tert-Butyldimethylsilyl)-1-(4-chlorophenyl)pent-2-en-4-yn-1-one (2b). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 6:1–4:1) afforded the title compound as a pale yellow oil in 66% yield (the trans isomer 3b was obtained in 18% yield) by method A. The title compound was obtained as a pale yellow oil in 70% yield (the trans isomer 3b was obtained in 17% yield) by method B. ¹H NMR (CDCl₃, Me₄Si, 300 MHz) δ 0.04 (s, 6H), 0.86 (s, 9H), 6.22 (d, J = 12.0 Hz, 1H), 6.85 (d, J = 11.7 Hz, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz) δ -5.0, 16.5, 25.9, 101.8, 106.6, 120.7, 128.8,
130.3, 134.4, 135.7, 139.4, 189.7. IR (neat) 2954, 2928, 2857, 2148, 1667, 1591, 1470, 1250, 1221, 1091, 984, 824, 778 cm\(^{-1}\). HRMS (EI) for C\(_{17}\)H\(_{21}\)OClSi [M]+: calcd 304.1050, found 304.1053.

\[(Z)-5-(tert-Butyldimethylsilyl)-1-(4-methoxyphenyl)pent-2-en-4-yn-1-one \quad (2c)\]

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60:1−40:1) afforded the title compound as a pale yellow oil in 56% yield (the trans isomer 3c was obtained in 18% yield) by method A. The title compound was obtained as a pale yellow oil in 43% yield (the trans isomer 3c was obtained in 39% yield) by method B. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 300 MHz) \(\delta\) 0.04 (s, 6H), 0.85 (s, 9H), 3.84 (s, 3H), 6.15 (d, \(J = 12.0\) Hz, 1H), 6.85-6.93 (m, 3H), 7.92 (d, \(J = 9.0\) Hz, 2H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 75 MHz) \(\delta\) -5.0, 16.5, 25.9, 55.4, 102.1, 105.0, 113.7, 119.2, 130.3, 131.2, 135.4, 163.5, 189.5. IR (neat) 3011, 2954, 2930, 2135, 1659, 1601, 1576, 1245, 1170, 982, 839 cm\(^{-1}\). HRMS (EI) for C\(_{18}\)H\(_{24}\)O\(_2\)Si [M]+: calcd 300.1546, found 300.1543.

\[(Z)-5-(tert-Butyldimethylsilyl)-1-(thien-2-yl)pent-2-en-4-yn-1-one \quad (2d)\]

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) afforded the title compound as a pale yellow oil in 63% yield (the trans isomer 3d was obtained in 17% yield) by method A. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.12 (s, 6H), 0.93 (s, 9H), 6.17 (d, \(J = 11.6\) Hz, 1H), 6.92 (d, \(J = 11.6\) Hz, 1H), 7.11 (dd, \(J = 4.8, 4.0\) Hz, 1H), 7.64 (dd, \(J = 5.2\) Hz, 1.2 Hz, 1H), 7.72 (dd, \(J = 3.6\) Hz, 0.8 Hz, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -4.9, 16.6, 26.0, 102.2, 106.5, 120.6, 128.1, 132.4, 133.6, 134.2, 144.8, 181.4. IR (neat) 3089, 2953, 2929, 2857, 2149, 1647, 1580, 1420,
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1245, 1218, 1027, 929, 838, 824, 809, 777, 722 cm\(^{-1}\). HRMS (EI) for C\(_{15}\)H\(_{20}\)O\(_2\)Si [M]\(^+\): calcd 276.1004, found 276.1005.

(Z)-5-(tert-Butyldimethylsilyl)-1-(furan-2-yl)pent-2-en-4-yn-1-one (2e). Purification of the crude product by flash chromatography on silica gel (elucent: petroleum ether/ethyl acetate = 30:1) afforded the title compound as a pale yellow oil in 70% yield (the trans isomer 3e was obtained in 17% yield) by method A. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.14 (s, 6H), 0.95 (s, 9H), 6.17 (d, \(J = 11.6\) Hz, 1H), 6.51-6.52 (m, 1H), 6.98 (d, \(J = 12.0\) Hz, 1H), 7.20-7.21 (m, 1H), 7.56-7.57 (m, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -4.9, 16.6, 26.0, 102.6, 107.1, 112.4, 117.7, 121.4, 132.4, 146.5, 153.1, 176.3. IR (neat) 3141, 2954, 2929, 2857, 2126, 1661, 1582, 1466, 1258, 1019, 992, 824, 776 cm\(^{-1}\). HRMS (EI) for C\(_{15}\)H\(_{20}\)O\(_2\)Si [M]\(^+\): calcd 260.1233, found 260.1228.

(1E,4Z)-7-(tert-Butyldimethylsilyl)-1-phenylhepta-1,4-dien-6-yn-3-one (2f). Purification of the crude product by flash chromatography on silica gel (elucent: petroleum ether/ethyl acetate = 40:1) afforded the title compound as a pale yellow oil in 46% yield (the trans isomer 3f was obtained in 23% yield) by method A. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 0.12 (s, 6H), 0.92 (s, 9H), 6.22 (d, \(J = 12.0\) Hz, 1H), 6.50 (d, \(J = 12.0\) Hz, 1H), 7.37-7.41 (m, 4H), 7.56-7.59 (m, 2H), 7.67 (d, \(J = 15.6\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) -4.9, 16.6, 26.0, 102.1, 107.0, 119.5, 125.2, 128.5, 128.8, 130.5, 134.8, 137.9, 143.8, 189.3. IR (neat) 3061, 2953, 2928, 2857, 2149, 1655, 1610, 1578, 1450, 1251, 777 cm\(^{-1}\). HRMS (EI) for C\(_{19}\)H\(_{24}\)O\(_2\)Si [M]\(^+\): calcd 296.1596, found 296.1604.
**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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(Z)-5-(tert-Butyldiphenylsilyl)-1-phenylpent-2-en-4-yn-1-one (2g). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 60:1~40:1) afforded the major product 2g as a pale yellow oil in 61% yield by method A. 

$^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) $\delta$ 1.09 (s, 9H), 6.31 (d, $J = 12.0$ Hz, 1H), 7.37 (d, $J = 11.4$ Hz, 1H), 7.31-7.53 (m, 9H), 7.73-7.76 (m, 4H), 7.99 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 75 MHz) $\delta$ 18.6, 26.9, 101.9, 105.0, 119.7, 127.7, 128.6, 128.8, 129.5, 132.7, 133.2, 135.6, 135.6, 137.1, 190.2. IR (neat) 3070, 3050, 2957, 2929, 2857, 2148, 1665, 1598, 1581, 1428, 1232, 110, 982, 700, 504 cm$^{-1}$. HRMS (EI) for C$_{27}$H$_{26}$OSi [M]$^+$: calcd 394.1753, found 394.1751.

The isomer of (E)-5-(tert-Butyldiphenylsilyl)-1-phenylpent-2-en-4-yn-1-one (3g) was obtained as a pale yellow oil in 20% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) $\delta$ 1.16 (s, 9H), 7.07 (d, $J = 15.3$ Hz, 1H), 7.40-7.65 (m, 10H), 7.82-8.01 (m, 4H), 8.02 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 75 MHz) $\delta$ 18.8, 27.0, 101.1, 106.2, 124.6, 127.9, 128.6, 128.8, 129.8, 132.5, 133.4, 134.8, 135.5, 135.9, 188.8. IR (neat) 3070, 3052, 2957, 2929, 2857, 2133, 1662, 1587, 1428, 1282, 1110, 1005, 698 cm$^{-1}$. HRMS (EI) for C$_{27}$H$_{26}$OSi [M]$^+$: calcd 394.1753, found 394.1760.

(Z)-1-Phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-one (2h). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:1~2:1) afforded the major product 2h as a pale yellow oil in 67% yield by method A. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) $\delta$ 1.13 (s, 9H), 6.20 (d, $J = 11.7$ Hz, 1H), 6.96 (d, $J = 11.7$ Hz, 1H), 7.41-7.46 (m, 2H), 7.52-7.57 (m, 1H), 7.90-7.93 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 75 MHz) $\delta$ -0.5, 101.5, 107.4, 126.0, 128.4, 128.7, 132.9, 134.6, 137.4, 190.3. IR
(neat) 3067, 2960, 2899, 2126, 1666, 1597, 1581, 1449, 1250, 1232, 983, 844, 751 cm⁻¹. HRMS (EI) for C₁₄H₁₆OSi [M]⁺: calcld 228.0970, found 228.0972.

The isomer (E)-1-Phenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-one (3h)² was obtained as a pale yellow oil in 15% yield. ¹H NMR (CDCl₃, Me₄Si, 300 MHz) δ 0.25 (s, 9H), 6.88 (d, J = 15.2 Hz, 1H), 7.38 (d, J = 15.6 Hz, 1H), 7.46-7.50 (m, 2H), 7.56-7.60 (m, 1H), 7.95-7.97 (m, 2H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz) δ 0.4, 102.6, 105.9, 124.8, 128.5, 128.7, 133.2, 134.1, 137.0, 188.8. IR (neat) 3064, 2959, 2899, 1663, 1587, 1581, 1448, 1283, 1251, 1209, 1005, 845 cm⁻¹. HRMS (EI) for C₁₄H₁₆O [M]⁺: calcld 228.0970, found 228.0972.

$\text{Bu}_2\text{O} \text{O} \text{Z}-1\text{-Phenylnon-2-en-4-yn-1-one (2i).}$ Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1~60:1) afforded the desired product 2i as a pale yellow oil in 63% yield (the trans isomer 3i was obtained in 27% yield) by method A. ¹H NMR (CDCl₃, Me₄Si, 300 MHz) δ 0.84 (t, J = 7.2 Hz, 3H), 1.31-1.53 (m, 4H), 2.37 (td, J = 7.2 Hz, 2.4 Hz, 2H), 6.23 (dt, J = 11.7 Hz, 2.4 Hz, 1H), 6.98 (d, J = 11.4 Hz, 1H), 7.43-7.57 (m, 3H), 7.93-7.96 (m, 2H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz) δ 13.5, 19.6, 21.8, 30.2, 78.7, 103.6, 122.4, 128.4, 128.5, 132.0, 132.8, 137.6, 189.8. IR (neat) 3062, 3029, 2958, 2932, 2263, 2203, 1665, 1597, 1581, 1448, 1226, 1004, 750 cm⁻¹. HRMS (EI) for C₁₅H₁₆O [M]⁺: calcld 212.1201, found 212.1204.

$\text{Ph} \text{O} \text{Z}-1,5\text{-Diphenylpent-2-en-4-yn-1-one (2j).}^5$ Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1~30:1) afforded cis-enynones 2j as a pale yellow solid in 44% yield (the trans isomer 3j was obtained in
34% yield) by method B. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) 6.44 (d, $J = 11.6$ Hz, 1H), 7.07 (d, $J = 11.2$ Hz, 1H), 7.27-7.32 (m, 3H), 7.40-7.43 (m, 2H), 7.45-7.49 (m, 2H), 7.54-7.58 (m, 1H), 7.97-7.99 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ 87.6, 100.7, 121.4, 122.5, 128.2, 128.5, 128.6, 129.1, 132.1, 132.7, 132.9, 137.7, 189.9. IR (neat) 3060, 2926, 2192, 1661, 1599, 1580, 1448, 1229, 1012, 971, 753, 690 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{12}$O $[M]^{+}$: calcd 232.0888, found 232.0890.

Typical procedure for the selective formation of trans-enynones from penta-2,4-diyn-1-ol catalyzed by KOH. To a stirred solution of KOH (15 mol%, 0.06 mmol, 3.4 mg) in DCE (4 mL) at 30 °C was added 5-(tert-Butyldimethylsilyl)-1-phenylpenta-2,4-diyn-1-ol 7a (0.4 mmol, 108 mg) under argon (KOH was weighted in Glove box due to its hydroscopic property). After stirring for 1 h at the same temperature, the reaction mixture was quenched with 3 N HCl and extracted with EtOAc (for the cases of 3j-3o, the reactions were quenched by saturated NH$_4$Cl solution). The combined organic extracts were washed with brine, and then dried over MgSO$_4$. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:1) to afford trans-enynones 3a in 87% yield.

$$\text{3a}$$

(E)-5-(tert-Butyldimethylsilyl)-1-phenylpent-2-en-4-yn-1-one (3a). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:1) afforded the title compound as a pale yellow oil in 87% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.18 (s, 6H), 0.98 (s, 9H), 6.88 (d, $J = 15.6$ Hz, 1H), 7.36 (d, $J = 16.0$ Hz, 1H), 7.44-7.48 (m, 2H), 7.54-7.58 (m, 1H), 7.93-7.96 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -4.9, 16.6, 26.0, 103.2, 104.5, 124.8, 128.5, 128.7, 133.2, 134.1, 137.0, 188.8. IR (neat) 3063, 2954, 2930, 2857, 2119, 1663, 1599, 1586, 1282, 1209, 1005, 846, 824, 776 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{22}$OSi $[M]^{+}$: calcd 270.1440,
found 270.1442.

(E)-5-(tert-Butyldimethylsilyl)-1-(4-chlorophenyl)pent-2-en-4-yn-1-one (3b).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 6:1~4:1) afforded the title compound as a pale yellow oil in 79% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.17 (s, 6H), 0.97 (s, 9H), 6.88 (d, $J = 15.2$ Hz, 1H), 7.30 (d, $J = 15.2$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -4.9, 16.6, 26.0, 103.1, 105.1, 125.4, 129.0, 129.9, 133.5, 135.3, 139.7, 187.4. IR (neat) 2953, 2929, 2858, 2121, 1663, 1591, 1470, 1290, 1208, 1086, 1006, 825, 777 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{21}$OClSi $[M]^+$: calcd 304.1050, found 304.1048.

(E)-5-(tert-Butyldimethylsilyl)-1-(4-methoxyphenyl)pent-2-en-4-yn-1-one (3c).

Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1~60:1) afforded the title compound as a pale yellow oil in 57% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) δ 0.17 (s, 6H), 0.97 (s, 9H), 3.86 (s, 3H), 6.86 (d, $J = 15.6$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 15.6$ Hz, 1H), 7.96 (d, $J = 9.2$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) δ -4.9, 16.6, 26.0, 55.4, 103.4, 103.7, 113.9, 123.9, 129.9, 130.9, 134.0, 163.7, 186.9. IR (neat) 3075, 2952, 2934, 2856, 2132, 1649, 1589, 1571, 1250, 1030, 827, 777 cm$^{-1}$. HRMS (EI) for C$_{18}$H$_{24}$O$_2$Si $[M]^+$: calcd 300.1546, found 300.1547.
(E)-5-(tert-Butyldimethylsilyl)-1-(thien-2-yl)pent-2-en-4-yn-1-one (3d). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) afforded the title compound as a pale yellow oil in 84% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 0.17 (s, 6H), 0.97 (s, 9H), 6.89 (d, $J$ = 15.6 Hz, 1H), 7.15 (dd, $J$ = 4.0 Hz, 3.6 Hz, 1H), 7.22 (d, $J$ = 15.6 Hz, 1H), 7.66 (dd, $J$ = 4.8 Hz, 1.2 Hz, 1H), 7.77 (dd, $J$ = 4.0 Hz, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -4.9, 16.6, 26.0, 103.0, 104.7, 124.1, 128.3, 132.4, 133.8, 134.6, 144.5, 180.6. IR (neat) 3092, 2953, 2929, 2857, 2113, 1588, 1515, 1414, 1283, 1059, 825, 813, 778 cm$^{-1}$. HRMS (EI) for C$_{15}$H$_{20}$OSi $[M]^+$: calcld 276.1004, found 276.1001.

(E)-5-(tert-Butyldimethylsilyl)-1-(furan-2-yl)pent-2-en-4-yn-1-one (3e). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1~20:1) afforded the title compound as a pale yellow oil in 57% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 0.13 (s, 6H), 0.93 (s, 9H), 6.54 (dd, $J$ = 3.6 Hz, 3.6 Hz, 1H), 6.88 (d, $J$ = 15.2 Hz, 1H), 7.12 (d, $J$ = 15.9 Hz, 1H), 7.25 (d, $J$ = 3.6 Hz, 1H), 7.60-7.61 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -5.0, 16.6, 26.0, 103.1, 104.7, 112.6, 118.2, 124.0, 133.5, 147.0, 152.7, 176.4. IR (neat) 3132, 2954, 2930, 2858, 2142, 1658, 1592, 1466, 1306,1024, 826, 777 cm$^{-1}$. HRMS (EI) for C$_{15}$H$_{20}$O$_2$Si $[M]^+$: calcld 260.1233, found 260.1228.
(1E,4E)-7-(tert-Butyldimethylsilyl)-1-phenylhepta-1,4-dien-6-yn-3-one (3f). Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) afforded the title compound as a pale yellow oil in 40% yield (the 1E, 4Z-isomer 2f was isolated in 18% yield). $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 0.18 (s, 6H), 0.98 (s, 9H), 6.81 (d, $J$ = 16.0 Hz, 1H), 6.90 (d, $J$ = 15.2 Hz, 1H), 6.94 (d, $J$ = 15.2 Hz, 1H), 7.40-7.41 (m, 3H), 7.56-7.58 (m, 2H), 7.67 (d, $J$ = 16.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -4.9, 16.6, 26.0, 103.1, 104.5, 123.5, 125.1, 128.4, 129.0, 130.7, 134.4, 136.9, 144.1, 187.6. IR (neat) 3061, 3028, 2953, 2929, 2857, 2163, 1650, 1611, 1586, 1333, 1252, 1046, 825 cm$^{-1}$. HRMS (EI) for C$_{19}$H$_{24}$OSi [M]$^+$: calcd 296.1596, found 296.1601.

![3i](image)

(E)-1-Phenylnon-2-en-4-yn-1-one (3i). $^6$ Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) afforded the title compound as a pale yellow oil in 63% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz) $\delta$ 0.94 (t, $J$ = 7.2 Hz, 3H), 1.40-1.49 (m, 2H), 1.53-1.60 (m, 2H), 2.42 (td, $J$ = 7.2 Hz, 2.0 Hz, 2H), 6.89 (dt, $J$ = 15.2 Hz, 2.4 Hz, 1H), 7.26 (d, $J$ = 15.6 Hz, 1H), 7.44-7.48 (m, 2H), 7.53-7.58 (m, 1H), 7.93-7.96 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ 13.5, 19.6, 21.9, 30.4, 79.2, 102.0, 126.3, 128.4, 128.6, 132.5, 133.0, 137.3, 189.1. IR (neat) 3061, 3028, 2953, 2929, 2857, 2163, 1650, 1611, 1586, 1333, 1252, 1046, 825 cm$^{-1}$. HRMS (EI) for C$_{15}$H$_{16}$O [M]$^+$: calcd 212.1201, found 212.1204.

![3j](image)

(E)-1,5-Diphenylpent-2-en-4-yn-1-one (3j). $^6$ The reaction was quenched by saturated NH$_4$Cl solution. Purification of the crude product by flash chromatography on silica gel
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(ELuent: Petroleum ether/ethyl acetate = 100:1) afforded the title compound as a pale yellow solid in 77% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 7.13 (d, $J = 15.6$ Hz, 1H), 7.33-7.37 (m, 3H), 7.43 (d, $J = 15.2$ Hz, 1H), 7.47-7.53 (m, 4H), 7.55-7.57 (m, 1H), 7.96-7.99 (m 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ 87.7, 99.3, 122.2, 125.1, 128.5, 128.7, 129.4, 130.0, 133.0, 137.2, 133.2, 188.8.

![3k](image)

(E)-1-(4-Chlorophenyl)-5-phenylpent-2-en-4-yn-1-one (3k). The reaction was quenched by saturated NH$_4$Cl solution. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the title compound as a pale yellow solid in 77% yield. mp 94-95 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 7.12 (d, $J = 15.2$ Hz, 1H), 7.34-7.38 (m, 4H), 7.42-7.44 (m, 2H), 7.49-7.52 (m, 2H), 7.89-7.91 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ 87.7, 99.7, 122.1, 125.5, 128.4, 128.9, 129.4, 129.8, 131.9, 132.3, 135.4, 139.5, 187.3. IR (neat) 3067, 3082, 2200, 1651, 1584, 1399, 962, 821, 753, 743, 730 cm$^{-1}$. HRMS (EI) for C$_{17}$H$_{11}$OCl $[M]^{+}$: calc 266.0498, found 266.0502. Anal. Calc. for C$_{17}$H$_{11}$ClO: C, 76.55; H, 4.16. found: C, 76.08; H, 3.90.

![3l](image)

(E)-1-(4-Methoxyphenyl)-5-phenylpent-2-en-4-yn-1-one (3l). The reaction was quenched by saturated NH$_4$Cl solution. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a brown solid in 66% yield. mp 84-85 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz) $\delta$ 3.84 (s, 3H), 6.93-6.96 (m, 2H), 7.10 (d, $J = 15.2$ Hz, 1H); 7.34-7.36 (m, 3H), 7.43 (d, $J = 15.2$ Hz, 1H), 7.50-7.52 (m, 2H), 7.97-7.99 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ 55.37, 87.83, 98.59, 113.86, 122.25, 124.02, 128.39, 129.19, 130.02, 130.79,
131.89, 132.94, 163.64, 186.85. IR (neat) 3063, 2839, 2195, 1652, 1602, 1584, 1333, 1255, 1213, 1170, 1024, 831, 757 cm\(^{-1}\). HRMS (EI) for \(\text{C}_{17}\text{H}_{11}\text{O}_{2}\) [M]\(^{+}\): calcd 262.0994, found 262.0996. Anal. Calc. for \(\text{C}_{18}\text{H}_{14}\text{O}_{2}\): C, 82.42; H, 5.38. found: C, 82.44; H, 5.37.

\[
\text{Ph} \quad \text{O} \quad \text{Ph}
\]

\(3m\)

\((1E,4E)-1,7\)-Diphenylhepta-1,4-dien-6-yn-3-one \((3m)\). The reaction was quenched by saturated NH\(_4\)Cl solution. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a white solid in 47% yield (isomeric purity: 97%). mp 65-67 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 6.94 (d, \(J = 16.0\) Hz, 1H), 6.99 (d, \(J = 15.6\) Hz, 1H), 7.06 (d, \(J = 15.6\) Hz, 1H), 7.35-7.42 (m, 6H), 7.51-7.54 (m, 2H), 7.58-7.60 (m, 2H), 7.71 (d, \(J = 16.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) 87.6, 99.3, 122.2, 123.7, 125.3, 128.4, 128.4, 128.9, 129.3, 130.7, 132.0, 134.5, 135.8, 144.0, 187.6. IR (neat) 3059, 2194, 1650, 1610, 1579, 1337, 1184, 1102, 976, 755, 690 cm\(^{-1}\). HRMS (EI) for \(\text{C}_{19}\text{H}_{14}\text{O}\) [M]\(^{+}\): calcd 258.1045, found 258.1040.

The 1\(E\), 4\(Z\)-isomer of \((1E,4Z)-1,7\)-diphenylhepta-1,4-dien-6-yn-3-one \((2m)\) was also obtained in 11% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz) \(\delta\) 6.43 (d, \(J = 12.0\) Hz, 1H); 6.60 (d, \(J = 11.6\) Hz, 1H), 7.25-7.39 (m, 6H), 7.42 (d, \(J = 16.0\) Hz, 1H), 7.47-7.49 (m, 2H), 7.58-7.60 (m, 2H), 7.71 (d, \(J = 16.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz) \(\delta\) 87.4, 101.5, 120.3, 122.3, 125.6, 128.38, 128.42, 128.9, 129.4, 130.5, 132.0, 134.8, 136.5, 143.5, 188.9. IR (neat) 3059, 3027, 2925, 2188, 1955, 1650, 1607, 1576, 1489, 1449, 1333, 1193, 1095, 750, 690 cm\(^{-1}\). HRMS (EI) for \(\text{C}_{19}\text{H}_{14}\text{O}\) [M]\(^{+}\): calcd 258.1045, found 258.1041.

\[
\text{Ph} \quad \text{O} \quad \text{S} \quad \text{Ph}
\]

\(3n\)

\((E)-5\)-Phenyl-1-(thien-2-yl)pent-2-en-4-yn-1-one \((3n)\). The reaction was quenched by
saturated NH₄Cl solution. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) afforded the title compound as a white solid in 68% yield. mp 72-73 °C. ¹H NMR (CDCl₃, Me₄Si, 300 MHz) δ 7.11-7.17 (m, 2H), 7.27-7.37 (m, 4H), 7.50-7.53 (m, 2H), 7.68 (d, J = 5.1 Hz, 1H), 7.79 (d, J = 3.3 Hz, 1H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz) δ 87.6, 99.5, 122.1, 124.3, 128.3, 128.4, 129.4, 132.0, 132.3, 132.7, 144.6, 180.6. IR (neat) 3079, 2194, 1642, 1584, 1414, 1354, 1256, 1234, 971, 809, 756 cm⁻¹. HRMS (EI) for C₁₅H₁₀O₂ [M]⁺: calcd 238.0452, found 238.0449. Anal. Calc. for C₁₅H₁₀O₂: C, 75.60; H, 4.23. found: C, 75.75; H, 4.12.

![Diagram](3o)

**(E)-1-(Furan-2-yl)-5-phenylpent-2-en-4-yn-1-one (3o).** The reaction was quenched by saturated NH₄Cl solution. Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound as a white solid in 66% yield. mp 58-59 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz) δ 6.58-6.59 (m, 1H), 7.15 (d, J = 15.6 Hz, 1H), 7.28-7.38 (m, 5H), 7.50-7.53 (m, 2H), 7.64-7.65 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz) δ 87.6, 99.5, 112.6, 118.2, 122.2, 124.3, 128.4, 129.4, 132.0, 132.5, 147.0, 152.9, 176.5. IR (neat) 3130, 3061, 2185, 1738, 1657, 1599, 1464, 1012, 757, 689, 530 cm⁻¹. HRMS (EI) for C₁₅H₁₀O₂ [M]⁺: calcd 222.0681, found 222.0677.

![Diagram](3p)

**(E)-5-(tert-Butyldimethylsilyl)-1-(naphthalen-1-yl)pent-2-en-4-yn-1-one (3p).** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 120:1~80:1) afforded the title compound as a pale yellow oil in 76% yield. ¹H NMR (CDCl₃, Me₄Si, 400 MHz) δ 0.18 (s, 6H), 0.98 (s, 9H), 6.76 (d, J = 16.0 Hz, 1H), 7.16 (d, J = 15.6 Hz, 1H), 7.48-7.61 (m, 3H), 7.75 (d, J = 7.2 Hz, 1H), 7.75 (dd, J = 1.2 Hz, 1H), 7.75 (dd, J = 1.2 Hz, 1H),
7.88-7.90 (m, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 8.37-8.39 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz) $\delta$ -4.9, 16.6, 26.0, 102.8, 105.7, 124.3, 125.5, 125.7, 126.5, 127.7, 127.7, 128.4, 130.4, 132.3, 133.8, 135.5, 138.7, 193.6. IR (neat) 3049, 2953, 2929, 2857, 2135, 1659, 1584, 1509, 1282, 1252, 1061, 962, 825, 777 cm$^{-1}$. HRMS (EI) for C$_{21}$H$_{24}$OSi [M]$^+$: calcd 320.1596, found 320.1599.

References:
