Supporting Information

Metal-free Alkynylation of α-C-H Bonds of Ethers with Ethynylbenziodoxolones

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General information.

$^1$H-NMR, $^{13}$C-NMR spectra were measured on a Bruker AM400 NMR spectrometer ($^1$H 400 MHz, $^{13}$C 100 MHz) with CDCl$_3$ as solvent and recorded in ppm relative to internal tetramethylsilane (TMS) standard. APCI-MS spectral data were recorded on Waters APCI-Quattro Ptemier XE. All reagents were purchased from commercial suppliers and used without further purification. Ethynylbenziodoxolones were prepared according to the literature procedure.

General procedure for the aromatic ethynylbenziodoxolones

Following a reported procedure, trimethylsilyl triflate (7.50 mL, 41.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (10.0 g, 37.7 mmol, 1 equiv) in DCM (100 mL) at rt. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of the appropriate alkynyltrimethylsilane (slightly exothermic). The resulting suspension was stirred for 6 h at rt, during this time a white solid was formed. A saturated solution of NaHCO$_3$ (100 mL) was then added and the mixture was stirred vigorously. The resulting suspension was filtered on porosity 4 glass filter. The two layers of the mother liquors were separated and the organic layer was washed with sat. NaHCO$_3$, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by filtration and boiled in CH$_3$CN (300 mL). The mixture was cooled down, the formed solid was collected and dried under high vacuum to afford the product.

1-(Phenylethynyl)-1,2-benziodoxol-3(1H)-one (Ph-EBX). White solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41-8.40 (m, 1H), 8.26-8.24 (m, 1H), 7.79-7.72 (m, 2H), 7.60-7.58 (m, 2H), 7.50-7.40 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.77, 135.02, 132.97, 132.57, 131.69, 131.49, 130.88, 128.88, 126.44, 120.67, 116.32, 106.68, 50.28. MS (APCI) calcd for C$_{15}$H$_{10}$IO$_2$ $^+ [M + H]^+$: 348.97, found: 348.97.
1-(1-methyl-2-phenylethynyl)-1,2-benziodoxol-3(1H)-one (o-MePh-EBX). White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44-8.41 (m, 1H), 8.30-8.27 (m, 1H), 7.80-7.74 (m, 2H), 7.58-7.56 (m, 1H), 7.40-7.36 (m, 1H), 7.32-7.30 (m, 1H), 7.27-7.23 (m, 1H), 2.54 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.79, 142.01, 134.97, 133.52, 132.57, 131.67, 131.54, 130.85, 130.05, 126.36, 126.11, 120.55, 116.47, 105.85, 53.25, 20.94. MS (APCI) calcd for C$_{16}$H$_{12}$IO$_2^+$ [M + H]$^+$: 362.99, found: 362.99.

1-(1-methyl-3-phenylethynyl)-1,2-benziodoxol-3(1H)-one (m-MePh-EBX). White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.42-8.40 (m, 1H), 8.25-8.23 (m, 1H), 7.80-7.73 (m, 2H), 7.41-7.39 (m, 2H), 7.34-7.28 (m, 2H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.74, 138.79, 135.01, 133.44, 132.58, 131.84, 131.70, 131.50, 130.11, 128.78, 126.40, 120.44, 116.32, 107.08, 49.69, 21.36. MS (APCI) calcd for C$_{16}$H$_{12}$IO$_2^+$ [M + H]$^+$: 362.99, found: 362.99.

1-(1-methyl-4-phenylethynyl)-1,2-benziodoxol-3(1H)-one (p-MePh-EBX). White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43-8.41 (m, 1H), 8.26-8.24 (m, 1H), 7.80-7.74 (m, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.75, 141.67, 135.00, 132.97, 132.59, 131.70, 131.51, 129.66, 126.39, 117.54, 116.36, 107.33, 49.29, 21.88. MS (APCI) calcd for C$_{16}$H$_{12}$IO$_2^+$ [M + H]$^+$: 362.99, found: 362.99.
1-(1-Chloro-4-phenylethynyl)-1,2-benziodoxol-3(1H)-one (p-CIPh-EBX). White solid, \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.41-8.39 (m, 1H), 8.23-8.21 (m, 1H), 7.80-7.73 (m, 2H), 7.54-7.51 (m, 2H), 7.42-7.38 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.85, 137.19, 135.07, 134.16, 132.61, 131.73, 131.47, 129.29, 126.48, 119.16, 116.32, 105.21, 51.80. MS (APCI) calcd for C\(_{15}\)H\(_9\)ClIO\(_2\)\([M + H]^+\): 382.93, found : 382.93.

General procedure for silyl ethynylbenziodoxolones:

2-iodosylbenzoic acid (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirred. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 4 °C. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(trisopropylsilyl)acetylene (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in CH\(_2\)Cl\(_2\) (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (2 x 200 mL) and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (200 mL). The organic layers were combined, washed with a saturated solution of NaHCO\(_3\) (2 x 200 mL), dried over MgSO\(_4\), filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (120 mL) afforded the product.

1-[Triisopropylsilyl]ethynyl]-1,2-benziodoxol-3(1H)-one (TIPS-EBX), colorless crystals \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.42-8.40 (m, 1H), 8.30-8.28 (m, 1H), 7.77-7.74 (m, 2H), 1.15-1.14 (m, 21H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.51, 134.85, 132.64, 131.71, 131.56, 126.18, 115.75, 114.43, 64.87, 18.64, 11.33. MS (APCI) calcd for C\(_{18}\)H\(_{26}\)IO\(_2\)Si\([M + H]^+\): 429.07, found : 429.07.

General procedure for alkynylation of \(\alpha\)-C-H bonds

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with ethynylbenziodoxolones (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), solvent (1 mL), and the reaction mixture was heated under argon atmosphere for 16 h.
The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na₂SO₄. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by ¹H-NMR, ¹³C-NMR and GC-MS.

**General procedure for the kinetic isotope experiment**

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with Ph-EBX (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), mixture of THF (0.5 mL) and its deuterated derivative THF-d₈ (0.5 mL), and the reaction mixture was heated at 60°C under argon atmosphere for 16 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na₂SO₄. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by ¹H-NMR and GC-MS.

**General procedure for the radical inhibition experiments**

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with Ph-EBX (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), THF (1 mL), the radical scavenger (1.0 equiv), and the reaction mixture was heated at 60°C under argon atmosphere for 16 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na₂SO₄. After concentrated in vacuo, the crude product was purified by column chromatography.

**Reference**


**Spectroscopic data of products**

![3](image)

**2-(phenylethynyl)tetrahydrofuran** Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.42 (m, 2H), 7.30-7.28 (m, 3H), 4.83-4.80 (m, 1H), 4.04-3.99 (m, 1H), 3.89-3.83 (m, 1H), 2.20-2.19 (m, 1H), 2.12-2.05 (m, 1H), 1.97-1.92 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 131.86, 128.38, 128.35, 122.98, 89.22, 84.62, 68.76, 68.08, 33.57, 25.64. MS (APCI) caled for C₁₂H₁₃O⁺ [M + H]⁺ : 173.10, found : 173.10.
2-methyl-2-(phenylethynyl)tetrahydrofuran, 2-methyl-5-(phenylethynyl)tetrahydrofuran

Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43-7.41 (m, 2H), 7.30-7.28 (m, 3H), 4.94-4.91 (m, 0.12H), 4.31-4.26 (m, 0.12H), 4.50-3.96 (m, 1.77H), 2.33-2.27 (m, 1H), 2.19-2.13 (m, 1H), 2.02-1.98 (m, 1H), 1.90-1.85 (m, 1H), 1.64 (s, 2.48H), 1.36 (d, $J$ = 6.4 Hz, 0.36H). The ratio of 4a and 4b was 7.4 : 1, which was judged by $\delta$ 4.50 : ($\delta$ 4.94 + $\delta$ 4.31).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 131.81, 128.30, 128.20, 123.10, 92.45, 82.84, 76.53, 67.79, 40.29, 27.84, 25.84. MS (APCI) calcd for C$_{13}$H$_{15}$O $^+ [M + H]^+$ : 187.11, found : 187.11.

2-(phenylethynyl)-1,4-dioxane

Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47-7.44 (m, 2H), 7.33-7.30 (m, 3H), 4.59-4.56 (dd, $J$ = 8.4, 2.8 Hz, 1H), 3.96-3.92 (m, 2H), 3.78-3.67 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.01, 128.85, 128.41, 122.16, 86.69, 84.39, 70.54, 66.59, 66.53, 65.97. MS (APCI) calcd for C$_{12}$H$_{13}$O$_2$ $^+ [M + H]^+$ : 189.09, found : 189.09.

2-(phenylethynyl)tetrahydro-2$H$-pyran

Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.44 (m, 2H), 7.31-7.29 (m, 3H), 4.52-4.50 (dd, $J$ = 7.6, 2.8 Hz, 1H), 4.08-4.03 (m, 1H), 3.62-3.56 (m, 2H), 1.96-1.88 (m, 2H), 1.83-1.78 (m, 1H), 1.65-1.61 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 131.91, 128.42, 128.35, 122.91, 88.27, 85.35, 67.60, 66.78, 32.33, 25.83, 21.97. MS (APCI) calcd for C$_{13}$H$_{15}$O $^+ [M + H]^+$ : 187.11, found : 187.11.

2-(Phenylethynyl)-1,3-dioxolane, 4-(Phenylethynyl)-1,3-dioxolane

Colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.48-7.46 (m, 2H), 7.34-7.31 (m, 3H), 5.89 (s, 0.79H), 5.09 (s, 0.15H), 5.07 (s, 0.15H), 4.93 (t, $J$ = 6.4 Hz, 0.15H), 4.21-4.10 (m, 2H), 4.03-3.91 (m, 2H). The ratio of 7a and 7b was 5.3 : 1, which was judged by δ 5.89 : δ 5.09.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.06, 131.94, 129.10, 128.90, 128.44, 128.42,
121.71, 95.34, 93.57, 85.75, 85.34, 84.53, 70.72, 65.92. MS (APCI) calcd for 
C_{11}H_{11}O_2^+ [M + H]^+ : 175.08, found : 175.07.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{O}};
\node at (1,0) {\text{Ph}};
\node at (1.5,0) {\text{O}};
\node at (2,0) {\text{Ph}};
\end{tikzpicture}
\end{center}

\textbf{8a, 8b}

4-methyl-4-(phenylethynyl)-1,3-dioxane, 4-methyl-6-(phenylethynyl)-1,3-dioxane

Colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.48-7.45 (m, 2H), 7.35-7.31 (m, 3H), 5.34 (d, \( J = 6.4 \) Hz, 0.3H), 5.26 (d, \( J = 6.8 \) Hz, 0.74H), 5.06 (d, \( J = 4.4 \) Hz, 0.28H), 4.94 (d, \( J = 6.8 \) Hz, 0.83H), 4.16-4.00 (m, 1.85H), 2.12-1.99 (m, 1H), 1.74-1.71 (m, 1H), 1.62 (s, 2.22H), 1.26 (d, \( J = 6.4 \) Hz, 1.16H). The ratio of \textbf{8a} and \textbf{8b} was 1.9 : 1, which was judged by \( \delta 1.62 : \delta 1.26 \). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 131.87, 128.78, 128.71, 128.51, 128.49, 122.51, 90.05, 88.88, 88.66, 87.07, 70.176, 64.34, 64.24, 38.30, 38.21, 29.91, 21.53. MS (APCI) calcd for C\textsubscript{13}H\textsubscript{14}NaO\textsubscript{2}^+ [M + Na]^+ : 225.09, found : 225.09.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{O}};
\node at (1,0) {\text{N}};
\node at (1.5,0) {\text{Ph}};
\node at (2,0) {\text{O}};
\node at (2.5,0) {\text{Ph}};
\end{tikzpicture}
\end{center}

\textbf{9a, 9b}

1-methyl-5-(phenylethynyl)pyrrolidin-2-one, 1-(3-phenylprop-2-yn-1-yl)pyrrolidin-2-one

Colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.43-7.41 (m, 2H), 7.35-7.30 (m, 3H), 4.50-4.46 (m, 0.87H), 4.33 (s, 0.28H), 3.56 (t, \( J = 6.8 \) Hz, 0.31H), 2.94 (s, 2.67H), 2.59-2.53 (m, 1H), 2.47-2.36 (m, 2.22H), 2.23-2.17 (m, 1H), 2.08 (t, \( J = 7.6 \) Hz, 0.31H). The ratio of \textbf{9a} and \textbf{9b} was 6.2 : 1, which was judged by \( \delta 4.50 : 1/2 \delta 4.33 \). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 174.46, 131.89, 128.83, 128.52, 122.30, 86.57, 85.47, 51.99, 29.98, 28.19, 26.37. MS (APCI) calcd for C\textsubscript{13}H\textsubscript{14}NO^+ [M + H]^+ : 200.11, found : 200.11.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{O}};
\node at (1,0) {\text{N}};
\node at (1.5,0) {\text{Ph}};
\end{tikzpicture}
\end{center}

\textbf{10}

\textbf{N-methyl-N-(3-phenylprop-2-yn-1-yl)acetamide}

Yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.43-7.41 (m, 2H), 7.34-7.28 (m, 3H), 4.46 (s, 1.26H), 4.26 (s, 1.75H), 3.14 (s, 1.86H), 3.05 (s, 1.14H), 2.22 (s, 1.10H), 2.13 (s, 1.91H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 170.47, 131.93, 131.84, 128.79, 128.52, 128.48, 128.41, 122.89, 84.30, 83.77, 83.22, 77.36, 41.28, 36.85, 35.30, 33.47, 21.85, 21.65. MS (APCI) calcd for C\textsubscript{12}H\textsubscript{14}NO^+ [M + H]^+ : 188.11, found : 188.11.
(3-isopropoxy-3-methylbut-1-yn-1-yl)benzene Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.40 (m, 2H), 7.31-7.29 (m, 3H), 4.15-4.09 (m, 1H), 1.53 (s, 6H), 1.23 (d, $J = 6.4$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 128.39, 128.19, 126.80, 125.53, 123.29, 92.82, 83.12, 67.24, 30.02, 24.65. MS (APCI) calcd for C$_{14}$H$_{19}$O$^+$ [M + H]$^+$: 203.14, found : 203.14.

(3-ethoxybut-1-yn-1-yl)benzene Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.43 (m, 2H), 7.31-7.29 (m, 3H), 4.42-4.37 (q, $J = 6.8$ Hz, 1H), 3.90-3.82 (m, 1H), 3.55-3.48 (m, 1H), 1.54-1.52 (d, $J = 6.4$ Hz, 3H), 1.28-1.25 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.87, 128.38, 123.01, 89.59, 84.81, 65.67, 64.36, 22.43, 15.39. MS (APCI) calcd for C$_{12}$H$_{15}$O$^+$ [M + H]$^+$ : 175.11, found : 175.09.

2-(o-tolylethynyl)tetrahydrofuran Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.38 (m, 1H), 7.20-7.17 (m, 2H), 7.13-7.09 (m, 1H), 4.88-4.85 (m, 1H), 4.05-4.00 (m, 1H), 3.90-3.85 (m, 1H), 2.42 (s, 3H), 2.25-2.21 (m, 1H), 2.13-2.07 (m, 1H), 2.00-1.93 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.34, 132.14, 129.47, 125.58, 122.70, 93.21, 83.48, 68.85, 67.95, 33.73, 25.54, 20.77. MS (APCI) calcd for C$_{13}$H$_{15}$O$^+$ [M + H]$^+$ : 187.11, found : 187.10.

2-(m-tolylethynyl)tetrahydrofuran Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26-7.22 (m, 2H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.12-7.10 (m, 1H), 4.82-4.79 (m, 1H), 4.03-3.98 (m, 1H), 3.88-3.83 (m, 1H), 2.31 (s, 3H), 2.25-2.18 (m, 1H), 2.12-2.05 (m, 2H), 1.96-1.92 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.00, 132.45, 129.27, 128.90, 128.24, 122.75, 88.84, 84.77, 68.76, 68.04, 33.58, 25.62, 21.31. MS (APCI) calcd for C$_{13}$H$_{15}$O$^+$ [M + H]$^+$ : 187.11, found : 187.11.
2-(p-tolylethynyl)tetrahydrofuran Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 4.82-4.79 (m, 1H), 4.04-3.98 (m, 1H), 3.88-3.83 (m, 1H), 2.33 (s, 3H), 2.25-2.18 (m, 1H), 2.12-2.03 (m, 2H), 1.96-1.91 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.47, 131.75, 129.10, 119.88, 88.46, 84.74, 68.81, 68.04, 33.58, 25.64, 21.59. MS (APCI) calcd for C$_{13}$H$_{15}$O$^+ [M + H]^+$ : 187.11, found : 187.11.

2-((4-chlorophenyl)ethynyl)tetrahydrofuran Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.34 (m, 2H), 7.28-7.25 (m, 2H), 4.81-4.78 (m, 1H), 4.03-3.98 (m, 1H), 3.89-3.83 (m, 1H), 2.26-2.19 (m, 1H), 2.11-2.04 (m, 2H), 1.97-1.92 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.45, 133.09, 128.71, 131.47, 90.23, 83.52, 68.67, 68.16, 33.50, 25.66. MS (APCI) calcd for C$_{12}$H$_{12}$ClO$^+ [M + H]^+$ : 207.06, found : 207.06.

triisopropyl(tetrahydrofuran-2-yl)ethynyl)silane Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.64-4.61 (m, 1H), 3.98-3.93 (m, 1H), 3.85-3.80 (m, 1H), 2.16-2.10 (m, 1H), 2.08-1.95 (m, 2H), 1.92-1.86 (m, 1H), 1.07-1.06 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 107.93, 85.20, 68.73, 67.72, 33.84, 25.27, 18.73, 11.29. MS (APCI) calcd for C$_{15}$H$_{29}$OSi$^+ [M + H]^+$ : 253.20, found : 253.09.

2-methyl-2-(o-tolylethynyl)tetrahydrofuran, 2-methyl-5-(o-tolylethynyl)tetrahydrofuran Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.37 (m, 1H), 7.20-7.17 (m, 2H), 7.14-7.09 (m, 1H), 4.98-4.95 (m, 0.11H), 4.33-4.28 (m, 0.12H), 4.06-3.95 (m, 1.80H), 2.41 (s, 1H), 2.33-2.27 (m, 1H), 2.21-2.12 (m, 1H),
The ratio of 18a and 18b was 7.4 : 1, which was judged by δ 4.06 : (δ 4.98 + δ 4.33).

13C NMR (100 MHz, CDCl3) δ 140.24, 132.00, 129.45, 128.25, 125.58, 122.90, 96.56, 81.82, 76.70, 67.71, 40.45, 27.83, 25.83, 20.77. MS (APCI) calcd for C14H17O+ [M + H]+ : 201.13, found : 201.13.

2-(m-tolylethynyl)-2-methyltetrahydrofuran, 2-methyl-5-(m-tolylethynyl)tetrahydrofuran

Colorless oil.

1H NMR (400 MHz, CDCl3) δ 7.26-7.21 (m, 2H), 7.19-7.15 (m, 1H), 7.11-7.09 (m, 1H), 4.93-4.90 (m, 0.12H), 4.31-4.26 (m, 0.13H), 4.04-3.95 (m, 1.86H), 2.31 (s, 3H), 2.29-2.26 (m, 1H), 2.29-2.11 (m, 1H), 2.02-1.98 (m, 1H), 1.89-1.82 (m, 1H), 1.63 (s, 2.57H), 1.35 (d, J = 6.0 Hz, 0.32H).

The ratio of 19a and 19b was 7.4 : 1, which was judged by δ 4.04 : (δ 4.93 + δ 4.31).

13C NMR (100 MHz, CDCl3) δ 137.97, 132.44, 129.09, 128.87, 128.22, 122.95, 92.12, 83.02, 76.56, 67.77, 40.34, 27.86, 25.85, 21.32. MS (APCI) calcd for C14H17O+ [M + H]+ : 201.13, found : 201.12.

2-((4-chlorophenyl)ethynyl)-2-methyltetrahydrofuran, 2-((4-
chlorophenyl)ethynyl)-5-methyltetrahydrofuran Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.32 (m, 2H), 7.27-7.25 (m, 2H), 4.92-4.89 (m, 0.17H), 4.30-4.25 (m, 0.19H), 4.02-3.95 (m, 1.59H), 2.32-2.26 (m, 1H), 2.18-2.09 (m, 1.22H), 2.03-1.98 (m, 1H), 1.90-1.83 (m, 0.81H), 1.62 (s, 2.40H), 1.35 (d, $J$ = 6.0 Hz, 0.47H). The ratio of 21a and 21b was 4.4 : 1, which was judged by δ 4.04 : (δ 4.92 + δ 4.30).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.23, 133.06, 128.65, 121.66, 93.54, 81.78, 76.50, 67.87, 40.26, 27.82, 25.87. MS (APCI) calcd for C$_{13}$H$_{14}$ClO$^+$ [M + H]$^+$ : 221.07, found : 221.07.

triisopropyl((2-methyltetrahydrofuran-2-yl)ethynyl)silane, triisopropyl((5-methyltetrahydrofuran-2-yl)ethynyl)silane Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.73-4.70 (m, 0.26H), 4.57-4.54 (m, 0.13H), 4.26-4.21 (m, 0.25H), 4.06-3.92 (m, 1.27H), 2.21-1.93 (m, 3H), 1.78-1.71 (m, 0.66H), 1.55 (s, 1.48H), 1.47-1.40 (m, 0.53H), 1.25-1.23 (d, $J$ = 6.0 Hz, 1.48H), 1.06-1.05 (m, 21H). The ratio of 22a and 22b was 1 : 1, which was judged by 1/2 δ 4.73 : δ 4.57. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 111.19, 108.52, 84.93, 82.85, 76.44, 74.84, 68.57, 67.45, 40.52, 34.52, 34.19, 33.12, 32.78, 27.48, 25.59, 21.95, 21.02, 18.74, 11.29. MS (APCI) calcd for C$_{16}$H$_{31}$OSi$^+$ [M + H]$^+$ : 267.21, found : 267.11.

$^2$-(o-tolylethynyl)-1,4-dioxane Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43-7.41 (m, 1H), 7.25-7.18 (m, 2H), 7.14-7.10 (m, 1H), 4.62-4.60 (dd, $J$ = 8.4, 3.2 Hz, 1H), 3.98-3.93 (m, 2H), 3.79-3.68 (m, 4H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.56, 132.38, 129.55, 128.85, 125.65, 122.02, 88.38, 85.60, 70.71, 66.73, 66.58,
65.87, 20.79. MS (APCI) calcd for C_{13}H_{15}O_{2}^+ [M + H]^+ : 203.11, found : 203.10.

2-(m-tolylethynyl)-1,4-dioxane Pale yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.28-7.25 (m, 2H), 7.19 (t, \(J = 7.4\) Hz, 1H), 7.14-7.13 (m, 1H), 4.57-4.55 (dd, \(J = 8.4, 2.8\) Hz, 1H), 3.96-3.91 (m, 2H), 3.78-3.66 (m, 4H), 2.32 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 138.11, 132.62, 129.73, 129.08, 128.31, 122.02, 86.91, 84.09, 70.61, 66.64, 66.56, 65.94, 21.31. MS (APCI) calcd for C_{13}H_{15}O_{2}^+ [M + H]^+ : 203.11, found : 203.11.

2-(p-tolylethynyl)-1,4-dioxane Pale yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.34 (d, \(J = 8.0\) Hz, 2H), 7.11 (d, \(J = 8.0\) Hz, 2H), 4.57-4.54 (dd, \(J = 8.4, 2.8\) Hz, 1H), 3.95-3.91 (m, 2H), 3.78-3.66 (m, 4H), 2.34 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 139.02, 131.93, 129.18, 119.14, 86.89, 83.73, 70.63, 66.70, 66.55, 65.99, 21.62. MS (APCI) calcd for C_{13}H_{15}O_{2}^+ [M + H]^+ : 203.11, found : 203.10.

2-((4-chlorophenyl)ethynyl)-1,4-dioxane Yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.39-7.36 (m, 2H), 7.29-7.26 (m, 2H), 4.57-4.54 (dd, \(J = 8.4, 2.8\) Hz, 1H), 3.96-3.90 (m, 2H), 3.78-3.66 (m, 4H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 134.98, 133.25, 128.81, 120.72, 85.60, 85.50, 70.46, 66.56, 66.52, 65.92. MS (APCI) calcd for C_{12}H_{12}ClO_{2}^+ [M + H]^+ : 223.05, found : 223.06.

(benzo[d][1,3]dioxol-2-ylethynyl)triisopropylsilane Colorless oil. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\)
MHz, CDCl₃) δ 6.85 (s, 6.85H), 6.58 (s, 1H), 1.08 (s, 21H). ¹³C NMR (100 MHz, CDCl₃) δ 146.85, 122.01, 109.007, 99.81, 98.26, 91.03, 18.61, 11.10. MS (APCI) calcd for C₁₈H₂₇O₂Si⁺ [M + H]⁺ : 303.18, found : 303.14.

(isochroman-1-yethyl)triisopropylsilane, (isochroman-3-yethyl)triisopropylsilane Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.27 (m, 0.55H), 7.20-7.17 (m, 2H), 7.16-7.12 (m, 1H), 4.54-4.46 (m, 0.93H), 4.32 (s, 0.25H), 3.56 (t, J = 6.8 Hz, 0.28H), 2.94 (s, 0.28H), 2.58-2.52 (m, 1H), 2.47-2.38 (m, 2.28H), 2.33 (s,
2.81H), 2.32 (s, 0.46H), 2.23-2.16 (m, 1H), 2.10-2.06 (m, 0.32H). The ratio of 31a and 31b was 7.4 : 1, which was judged by δ 4.49 : 1/2 δ 4.32. 13C NMR (100 MHz, CDCl3) δ 174.46, 138.26, 132.44, 129.71, 128.91, 128.42, 122.08, 86.18, 85.63, 52.00, 29.97, 28.18, 26.39, 21.32. MS (APCI) calcd for C14H16NO+ [M + H]+ : 214.12, found: 214.12.

1H NMR and 13C NMR spectra of the products

1H NMR of 1a
$^{13}$C NMR of 1a

$^1$H NMR of 1b
$^{13}$C NMR of 1b

$^1$H NMR of 1c
$^{13}$C NMR of $1c$

$^1$H NMR of $1d$
$^1$C NMR of 1d

$^1$H NMR of 1e
$^{13}$C NMR of 1e

$^1$H NMR of 3
$^{13}$C NMR of 3

$^1$H NMR of 4a and 4b
$^{13}$C NMR of 4a and 4b

$^1$H NMR of 5
$^{13}$C NMR of 5

$^1$H NMR of 6
$^{13}$C NMR of 6

$^1$H NMR of 7a and 7b
$^{13}$C NMR of 7a and 7b

$^1$H NMR of 8a and 8b
$^{13}$C NMR of 8a and 8b

$^1$H NMR of 9
$^{13}$C NMR of 9

$^1$H NMR of 10
$^1$H NMR of 11
$^{13}$C NMR of 11

$^1$H NMR of 12
$^{13}$C NMR of 12

$^1$H NMR of 13

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$^{13}$C NMR of 13

$^1$H NMR of 14
$^{13}$C NMR of 14

$^1$H NMR of 15
$^{13}$C NMR of 15

$^1$H NMR of 16
$^{13}\text{C NMR of 16}$

$^1\text{H NMR of 17}$
$^{13}$C NMR of 17

$^1$H NMR of 18a and 18b
$^{13}$C NMR of 18a and 18b

$^1$H NMR of 19a and 19b
$^{13}$C NMR of 19a and 19b

$^1$H NMR of 20a and 20b
$^{13}$C NMR of 20a and 20b

$^1$H NMR of 21a and 21b
$^{13}\text{C NMR of 21a and 21b}$

$^1\text{H NMR of 22a and 22b}$
$^{13}$C NMR of 22a and 22b

$^1$H NMR of 23
$^{13}$C NMR of 23

$^1$H NMR of 24
$^{13}$C NMR of 24

$^1$H NMR of 25
$^{13}$C NMR of 25

$^1$H NMR of 26
$^{13}$C NMR of 26

$^1$H NMR of 27
13C NMR of 27

1H NMR of 28
$^{13}$C NMR of 28

$^1$H NMR of 29a and 29b
$^{13}$C NMR of 29a and 29b

$^1$H NMR of 30a and 30b
$^{13}$C NMR of 30a and 30b

$^1$H NMR of 31a and 31b
$^{13}$C NMR of 31a and 31b

$^{1}$H NMR of 32a and 32b
$^{13}$C NMR of 32a and 32b

$^1$H NMR of 33a and 33b
$^{13}$C NMR of 33a and 33b

Spectroscopic data of the kinetic isotope experiment