Supporting Information
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Supporting Information

An Efficient Pyrrole Synthesis by Silaphenylmercuric Triflate-Catalyzed Cyclization of Homopropargyl Azides

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General.
FTIR spectra were measured on a JASCO FT/IR-410 infrared spectrophotometer, ν_{max} in cm\(^{-1}\). NMR spectra were recorded on a Varian Mercury prus-300-4N spectrometer, Varian 400-MR spectrometer and Varian 500-MR spectrometer. Chemical shifts are reported in parts per million (ppm). For \(^1\)H NMR spectra (CDCl\(_3\)), the residual solvent peak was used as the internal reference (7.26 ppm), whereas the central solvent peak as the reference (77.03 ppm) for \(^{13}\)C NMR spectra (CDCl\(_3\)). For \(^1\)H NMR spectra (CD\(_3\)OD), the residual solvent peak was used as the internal reference (3.30 ppm). Data are reported as follow: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). Mass spectra were recorded on a JEOL the Mstation JMS-700. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography was performed on Kanto Chemical 60 (63-210) mesh silica gel. All reaction were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted.
**Preparation of 0.1 M CH₃CN solution of Hg(OTf)₂**

To a suspension of HgO (541.4 mg, 2.5 mmol) in CH₃CN (5 mL) was dropwise added Tf₂O (705.3 mg, 2.5 mmol) at 0 °C, and the mixture was stirred at 0 °C until the yellow color disappear. The resulting colorless solution was transferred to 25 mL of volumetric flask and diluted with anhydrous CH₃CN to give 0.1 M solution.

**Preparation of silaphenylmercuric acetate (9)**

To a suspension of SiliaBond® Phenyl (CILICYCLE, 230-400 mesh, loading 1.62 mmol/g)(250 mg, 405 mmol) in AcOH (2.7 mL) was added Hg(OAc)₂ (155 mg, 486 µmol) at 25 °C. The mixture was irradiated by 200 Watts microwave oven (Discover System instrument supplied from CEM Corporation) using a sealed vessel for 1 h at 140 °C. Resulted solid of silaphenylmercuric acetate (9) was filtered and successively washed with 10% AcOH (50 mL), MeOH (30 mL), AcOEt (30 mL), and Et₂O (30 mL). The mercury loading was determined to be 0.20 mmol/g by measuring the mercury content of the filtrate by using atomic absorption spectrometry (Nippon Instruments, Mercury Analyzer RA-2).

**Optimization of mercuric salt-catalyzed of 1 to 2 (Table 1)**

![Reaction Scheme](attachment:image)

**Hg(OTf)₂-catalyzed cyclization of 1 (Entries 1-6):** A 0.1 M CH₃CN solution of Hg(OTf)₂ (0.05 mL, 5.0 µmol) was added to a dried reaction flask under argon atmosphere, and the CH₃CN was evacuated under vacuum. To this was added a solution of 1 (17.1 mg, 0.1 mmol) in CH₃NO₂ (1.0 mL) at room temperature. After stirring for 15 min at same temperature, the reaction was quenched by the addition of Et₃N (56 µL, 0.4 mmol). The reaction mixture was directly concentrated under reduced pressure. The yield of pyrrole 2 was determined by ¹H NMR of the crude product using CH₂Br₂ as an internal standard.

**PhHgOTf-catalyzed cyclization of 1 (Entry 15):** To a stirred solution of phenyl mercuric acetate (76 mg, 0.23 mmol) in CH₃NO₂ (40 mL) was added TfOH (0.1 M CH₃NO₂ solution, 2.3 mL, 0.23 mmol) at room temperature, and the mixture was stirred for 10 min. To this was added a solution of 1 (1 g, 5.8 mmol) in CH₃NO₂ (18 mL), and the mixture was allowed to stir for 5 min at room temperature. The reaction was quenched by addition of Et₃N (3.3 mL, 23.2 mmol) and directly subjected to column chromatography on silica gel using hexane and AcOEt (10:1) as an eluent to give pyrrole 2 (822 mg, 99%) as white solid.

**Typical experimental procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1**
To a suspension of dried silaphenylmercuric acetate (9) (0.2 mmol/g, 500 mg, 0.1 mmol) in CH$_3$NO$_2$ (5 mL) was added TfOH (17.4 µL, 0.2 mmol), and the mixture was stirred for 10 min at room temperature. Filtrated residue was washed with CH$_3$NO$_2$ (10 mL), and dried to give silaphenylmercuric triflate (10). (When using CD$_3$NO$_2$ as reaction and wash solution under the same condition, liberation of AcOH in the filtrate was confirmed by $^1$H-NMR spectroscopy.) Next, CH$_3$NO$_2$ (4 mL) and prepared 10 were added to a dried two-neck flask. To the stirred suspension of 10 was added a solution of 1 (86 mg, 0.5 mmol) in CH$_3$NO$_2$ (1 mL) at room temperature. The mixture was stirred at room temperature for 5 min, and the catalyst was then removed by filtration and washed with 10 mL of CH$_3$NO$_2$. Recovery of 10 (499.9 mg, 99.91%) was determined by measuring the mercury content of the combined filtrates by using atomic absorption spectrometry (Nippon Instruments, Mercury Analyzer RA-3). The filtrates were concentrated under reduced pressure. Purification by column chromatography on silica gel using hexane and AcOEt (10:1) to give pyrrole 2 (70 mg, 97%) as white powder. 2: FT IR (neat) $\nu_{\text{max}}$ 3436, 3389, 3102, 3080, 3063, 3038, 3019, 3006, 1669, 1648, 1604, 1578 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) $\delta$ 6.30 (1H, dd, $J = 4.0, 3.5$ Hz), 6.52 (1H, d, $J = 4.0$ Hz), 6.86 (1H, d, $J = 3.5$ Hz), 7.20 (1H, m), 7.33-7.38 (2H, m), 7.45-7.50 (2H, m), 8.43 (NH, br s); $^{13}$C NMR (100 MHz in CDCl$_3$) $\delta$ 105.93, 110.10, 118.65, 118.83, 123.86, 126.21, 128.88, 132.73; MS (CI) m/z 143 (M$^+$); HRMS (CI) m/z calcd for C$_{10}$H$_9$N (M$^+$) 143.0735, found 143.0729.

**Recover and reuse of the silaphenylmercuric triflate (10)**

The recovered catalyst 10 was reused for the second reaction after drying under vacuum at room temperature for 30 min. CH$_3$NO$_2$ (4 mL) and recovered catalyst 10 (499.9 mg) were added to a dried two-neck flask. To the stirred suspension of 10 was added a solution of 1 (86 mg, 0.5 mmol) in CH$_3$NO$_2$ (1 mL) at room temperature. The mixture was stirred at room temperature for 10 min, and the catalyst was then removed by filtration and washed with 10 mL of CH$_3$NO$_2$ using filter paper (ADVANTEC 2, Toyo Roshi Co. Ltd.). After drying under vacuum at room temperature for 30 min, the recovered catalyst (499.8 mg) was reused for the subsequent reactions.

**Preparation of homopropargyl azide derivatives**

(4-Azidobut-1-yn-1-yl)benzene (1)

![Compound 1](image)

Compound 1 was prepared according to the procedure described in the reference$^a)$. 1: colorless liquid; FT IR (neat) $\nu_{\text{max}}$ 3080, 3056, 3033, 3021, 2956, 2937, 2876, 2127 cm$^{-1}$; $^1$H NMR (500 MHz in CDCl$_3$) $\delta$ 2.72 (2H, t, $J = 7.0$ Hz), 3.48 (2H, t, $J = 7.0$ Hz), 7.28-7.31 (3H, m), 7.41-7.43 (2H, m);
$^{13}$C NMR (125 MHz in CDCl$_3$) δ 20.64, 49.96, 82.53, 85.77, 123.15, 128.07, 128.28, 131.61; MS (Cl) m/z 171 (M$^+$); HRMS (Cl) m/z calcd for C$_{16}$H$_{19}$N$_3$ (M$^+$) 171.0796, found 171.0785.

(4-Azidonon-1-yn-1-yl)benzene (11)

\[
\text{C}_2\text{H}_{11}\text{N}_3\quad \text{Ph}
\]

To a stirred solution of 1-phenylnon-1-yn-4-ol\(^b\) (2.41 g, 11.2 mmol) and Et$_3$N (6.2 mL, 44.8 mmol) in CH$_2$Cl$_2$ (37 mL) was added MsCl (1.3 mL, 16.8 mmol) at 0 °C. After stirring for 10 min at 0 °C, the reaction was quenched by addition of distilled water. The organic materials were extracted with CH$_2$Cl$_2$. After drying over Na$_2$SO$_4$, the filtrates were concentrated under reduced pressure. Next, the residue was added to DMF solution (37 mL) of NaN$_3$ (2.2 g, 33.6 mmol) at room temperature, and then stirred for 3 h at 70 °C. After cooling to ambient temperature, the reaction was quenched by addition of distilled water and the organic materials were extracted with Et$_2$O. The dried and concentrated extract was subjected to column chromatography on silica gel using hexane to give compound 11 (1.9 g, 70%) as a colorless syrup. **11**: FT IR (neat) $\nu$$_\text{max}$ 3080, 3056, 3033, 3021, 2956, 2931, 2871, 2859, 2731, 2109 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) δ 0.91 (3H, t, $J$ = 7.2 Hz), 1.28-1.38 (4H, m), 1.38-1.53 (2H, m), 2.67 (2H, br d, $J$ = 7.2 Hz), 3.53 (1H, m), 7.27-7.31 (3H, m), 7.40-7.43 (2H, m); $^{13}$C NMR (100 MHz in CDCl$_3$) δ 13.99, 22.52, 25.68, 25.89, 31.49, 33.62, 61.21, 82.98, 85.48, 123.30, 127.98, 128.25, 131.59; MS (Cl) m/z 241 (M$^+$); HRMS (Cl) m/z calcd for C$_{16}$H$_{19}$N$_3$ (M$^+$) 241.1579, found 241.1583.

(4-Azido-4-cyclohexylbut-1-yn-1-yl)benzene (13)

\[
\text{Cy}\quad \text{N}_3\quad \text{Ph}
\]

Compound 13 (298 mg, 67%) was prepared from 1-cyclohexyl-4-phenylbut-3-yn-1-ol\(^c\) (400 mg, 1.75 mmol) according to the procedure described for compound 11. **13**: colorless syrup; FT IR (neat) $\nu$$_\text{max}$ 3079, 3056, 3033, 3020, 2937, 2854, 2125 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) δ 0.91 (3H, t, $J$ = 7.2 Hz), 1.15-1.88 (6H, m), 2.67 (1H, dd, $J$ = 17.2, 7.2 Hz), 2.73 (1H, dd, $J$ = 17.2, 4.8 Hz), 3.37 (1H, m), 7.27-7.31 (3H, m), 7.40-7.44 (2H, m); $^{13}$C NMR (100 MHz in CDCl$_3$) δ 23.44, 25.22, 25.68, 25.89, 31.49, 33.62, 61.21, 82.98, 85.48, 123.30, 127.98, 128.25, 131.59; MS (Cl) m/z 254 (M$^+$+H); HRMS (Cl) m/z calcd for C$_{16}$H$_{20}$N$_3$ (M$^+$+H) 254.1657, found 254.1627.

(4-Azidobut-1-yn-1,4-diyl)dibenzene (15)

\[
\text{Ph}\quad \text{N}_3\quad \text{Ph}
\]

Compound 15 was prepared according to the procedure described in the reference\(^a\). **15**: colorless
 Compound 17 was prepared according to the procedure described in the reference. 17: colorless syrup; FT IR (neat) \( \nu_{\text{max}} \) 3081, 3057, 3033, 3021, 2939, 2903, 2859, 2106 cm\(^{-1}\); \(^1\)H NMR (400 MHz in CDCl\(_3\)) \( \delta \) 1.33-1.51 (2H, m), 1.59-1.80 (4H, m), 2.13 (2H, tt, \( J = 7.2, 2.4 \) Hz), 2.63 (2H, m), 4.61 (1H, t, \( J = 7.2 \) Hz), 7.31-7.41 (5H, m); \(^13\)C NMR (100 MHz in CDCl\(_3\)) \( \delta \) 14.00, 18.68, 22.21, 27.37, 28.42, 30.98, 65.08, 75.55, 83.50, 126.81, 128.43, 128.69, 138.75; MS (CI) \( m/z \) 242 (M\(^++\)H); HRMS (CI) \( m/z \) calcd for C\(_{15}\)H\(_{20}\)N\(_3\) (M\(^++\)H) 242.1658, found 242.1682.

 Compound 19 (211 mg, 70%) was prepared from 1-phenylnon-3-yn-1-ol\(^d\) (270 mg, 1.25 mmol) according to the procedure described for compound 11. 19: colorless syrup; FT IR (neat) \( \nu_{\text{max}} \) 3087, 3064, 3033, 2956, 2931, 2859, 2102 cm\(^{-1}\); \(^1\)H NMR (400 MHz in CDCl\(_3\)) \( \delta \) 0.88 (3H, t, \( J = 7.2 \) Hz), 1.26-1.32 (4H, m), 1.44 (2H, m), 2.13 (2H, tt, \( J = 7.2, 2.4 \) Hz), 2.63 (2H, m), 4.61 (1H, t, \( J = 7.2 \) Hz), 7.31-7.41 (5H, m); \(^13\)C NMR (100 MHz in CDCl\(_3\)) \( \delta \) 14.00, 18.68, 22.21, 27.37, 28.42, 30.98, 65.08, 75.55, 83.50, 126.81, 128.43, 128.69, 138.75; MS (CI) \( m/z \) 242 (M\(^++\)H); HRMS (CI) \( m/z \) calcd for C\(_{14}\)H\(_{20}\)N\(_3\) (M\(^++\)H) 242.1658, found 242.1682.

 Compound 20 (2.6 g, 71%) was prepared from 1,5-diphenylpent-3-yn-1-ol\(^e\) (3.3 g, 14.0 mmol) according to the procedure described for compound 11. 20: yellow syrup; FT IR (neat) \( \nu_{\text{max}} \) 3105, 3086, 3062, 3030, 3005, 2910, 2854, 2827, 2113 cm\(^{-1}\); \(^1\)H NMR (400 MHz in CDCl\(_3\)) \( \delta \) 3.56 (2H, t, \( J = 2.4 \) Hz), 4.66 (1H, t, \( J = 6.8 \) Hz), 7.21-7.30 (5H, m), 7.33-7.41 (5H, m); \(^13\)C
NMR (100 MHz in CDCl₃) δ 24.96, 27.13, 64.76, 77.93, 80.69, 126.40, 126.81, 127.75, 128.25, 128.34, 128.40, 128.66, 136.74, 138.46; MS (Cl) m/z 262 (M⁺+H); HRMS (Cl) m/z calcd for C₁₇H₁₆N₃ (M⁺+H) 262.1345, found 262.1357.

(1-Azido-5,5-dimethylhex-3-yn-1-yl)benzene (22)

Compound 22 (312 mg, 71%) was prepared from 1-cyclohexyl-4-phenylbut-3-yn-1-ol⁹ (400 mg, 1.90 mmol) according to the procedure described for compound 11. 22: colorless liquid; FT IR (neat) vmax 3087, 3065, 3032, 2969, 2928, 2903, 2867, 2102 cm⁻¹; ¹H NMR (400 MHz in CDCl₃) δ 1.16 (9H, s), 2.59 (1H, dd, J = 16.8, 6.4 Hz), 2.66 (1H, dd, J = 16.8, 7.6 Hz), 4.60 (1H, dd, J = 7.6, 6.4 Hz), 7.30-7.39 (5H, m); ¹³C NMR (100 MHz in CDCl₃) δ 27.31, 27.57, 30.91, 64.99, 74.05, 91.84, 126.72, 128.23, 128.50, 138.86; MS (Cl) m/z 228 (M⁺+H); HRMS (Cl) m/z calcd for C₁₄H₁₈N₃ (M⁺+H) 228.1501, found 228.1490.

Procedure for the preparation of 24 from 2-(4-(oxiran-2-yl)butoxy)tetrahydro-2H-pyran

1-Phenyl-8-((tetrahydro-2H-pyran-2-yl)oxy)oct-1-yn-4-ol

To a solution of ethynylbenzene (14 g, 138 mmol) in THF (250 mL) was added dropwise n-butyllithium (1.6 M solution in hexane, 86 mL, 138 mmol) at -78 °C. After stirring for 30 min at -78 °C, THF solution of 2-(4-(oxiran-2-yl)butoxy)tetrahydro-2H-pyran⁹ (18.4 g, 92 mmol) and BF₃•Et₂O (12.5 mL, 101.2 mmol) were successively added to the mixture at -78 °C. After stirring for 30 min at -78 °C, the reaction was quenched by addition of saturated aqueous NH₄Cl and the organic materials were extracted with AcOEt. Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and AcOEt (4:1) to give
1-phenyl-8-((tetrahydro-2H-pyran-2-yl)oxy)oct-1-yn-4-ol (22.2 g, 79%) as a colorless syrup; FT IR (neat) ν\textsubscript{max} 3438, 3078, 3055, 3032, 2943, 2736, 2658 cm\textsuperscript{-1}; ¹H NMR (400 MHz in CDCl\textsubscript{3}) δ 1.45-1.75 (11H, m), 1.83 (1H, m), 2.56 (1H, dd, J = 16.8, 6.8 Hz), 2.66 (1H, dd, J = 16.8, 4.8 Hz), 3.42 (1H, dt, J = 9.6, 6.0 Hz), 3.50 (1H, m), 3.77 (1H, m), 3.84-3.90 (2H, m), 4.58 (1H, dd, J = 4.0, 2.8 Hz), 7.28-7.31 (3H, m), 7.40-7.42 (2H, m); ¹³C NMR (100 MHz in CDCl\textsubscript{3}) δ 19.56, 22.30, 25.35, 28.28, 28.29, 29.64, 30.63, 36.00, 40.12, 62.23, 67.34, 67.37, 69.96, 82.80, 86.23, 88.80, 123.33, 127.77, 128.13, 131.51; MS (CI) m/z 303 (M\textsuperscript{+}+H); HRMS (CI) m/z calcd for C\textsubscript{19}H\textsubscript{27}O\textsubscript{3} (M\textsuperscript{+}+H) 303.1960, found 303.1950.

5-Azido-8-phenyloct-7-yn-1-ol (24)

\[
\text{HO} \quad \text{N}_3 \quad \text{===} \quad \text{Ph}
\]

To a solution of 1-phenyl-8-((tetrahydro-2H-pyran-2-yl)oxy)oct-1-yn-4-ol (22.2 g, 72.9 mmol) and Et\textsubscript{3}N (60.9 mL, 438 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (243 mL) was added MsCl (8.5 mL, 109 mmol) at 0 °C. After stirring for 10 min at 0 °C, the reaction was quenched by addition of distilled water. The organic materials were extracted with CH\textsubscript{2}Cl\textsubscript{2}. After drying over Na\textsubscript{2}SO\textsubscript{4}, the filtrates were concentrated under reduced pressure. The residue was added to DMF solution (243 mL) of NaN\textsubscript{3} (14.2 g, 218.7 mmol) at room temperature, and then stirred for 3 h at 70 °C. After cooling to ambient temperature. The reaction was quenched by addition of distilled water and the organic materials were extracted with CH\textsubscript{2}Cl\textsubscript{2}. After drying over Na\textsubscript{2}SO\textsubscript{4}, the filtrates were concentrated under reduced pressure. Next, the residue was dissolved in MeOH (200 mL), and then added 1 N HCl (50 mL) at 0 °C. After stirring for 2 h at 0 °C, the reaction was quenched by addition of Et\textsubscript{3}N (56 µL, 0.4 mmol). The reaction mixture was directly concentrated under reduced pressure. After removing MeOH, the concentrated mixture was extracted with Et\textsubscript{2}O, and washed with brine. After drying over MgSO\textsubscript{4}, the filtrates were concentrated under reduced pressure. Purification by column chromatography on silica gel using hexane and AcOEt (2:1) to give compound 24 (10.2 g, 58%) as a colorless syrup. 24: IR (neat) ν\textsubscript{max} 3355, 3080, 3056, 3036, 3018, 2940, 2865, 2121 cm\textsuperscript{-1}; ¹H NMR (400 MHz in CDCl\textsubscript{3}) δ 1.45-1.80 (6H, m), 2.69 (2H, d, J = 6.0 Hz), 3.56 (1H, m), 3.69 (2H, br t, J = 6.0 Hz), 7.28-7.32 (3H, m), 7.40-7.43 (2H, m); ¹³C NMR (100 MHz in CDCl\textsubscript{3}) δ 22.35, 25.90, 32.33, 33.45, 61.14, 62.64, 83.11, 85.28, 123.21, 128.05, 128.29, 131.60; MS (CI) m/z 244 (M\textsuperscript{+}+H); HRMS (CI) m/z calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{3}N\textsubscript{3} (M\textsuperscript{+}+H) 244.1450, found 244.1475.

((5-Azido-8-phenyloct-7-yn-1-yl)oxy)(tert-butyl)dimethylsilane (26)
To a solution of 24 (500 mg, 2.06 mmol) in CH$_2$Cl$_2$ (6 mL) was successively added Et$_3$N (0.43 mL, 4.12 mmol), DMAP (49 mg, 0.41 mmol) and TBSCl (466 mg, 3.09 mmol) at 0 °C, and the mixture was stirred for 1 h at 0 °C. To this was added distilled water and organic materials were extracted with CH$_2$Cl$_2$. Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and AcOEt (50:1) to give compound 26 (662 mg, 90%) as a colorless syrup. 26: FT IR (neat) $\nu_{\text{max}}$ 3081, 3056, 3033, 3022, 2936, 2900, 2886, 2858, 2118 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) $\delta$ 0.05 (6H, s), 0.89 (9H, s), 1.43-1.78 (6H, m), 2.68 (2H, d, $J = 6.0$ Hz), 3.56 (1H, m), 3.63 (2H, t, $J = 6.0$ Hz), 7.29-7.30 (3H, m), 7.41-7.43 (2H, m); $^{13}$C NMR (100 MHz in CDCl$_3$) $\delta$ -5.27, 18.36, 22.43, 25.90, 25.97, 32.46, 33.51, 61.20, 62.83, 83.03, 85.40, 123.28, 128.00, 128.26, 131.60; MS (CI) $m/z$ 358 (M$^+$+H); HRMS (CI) $m/z$ calcd for C$_{20}$H$_{32}$ON$_3$Si (M$^+$+H) 358.2314, found 358.2315.

((5-Azido-8-phenyloct-7-yn-1-yl)oxy)(tert-butyl)diphenylsilane (27)

To a solution of 27 (500 mg, 2.06 mmol) in CH$_2$Cl$_2$ (6 mL) was successively added Et$_3$N (0.43 mL, 4.12 mmol), DMAP (49 mg, 0.41 mmol) and TBDPSCl (0.8 mL, 3.09 mmol) at 0 °C, and the mixture was stirred for 2 h at 0 °C. To this was added distilled water and organic materials were extracted with CH$_2$Cl$_2$. Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and AcOEt (50:1) to give compound 27 (941 mg, 95%) as a colorless syrup. 27: FT IR (neat) $\nu_{\text{max}}$ 3070, 3051, 3028, 2998, 2931, 2896, 2858, 2103 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) $\delta$ 1.05 (9H, s), 1.43-1.73 (6H, m), 2.65 (2H, br d, $J = 6.0$ Hz), 3.50 (1H, m), 3.68 (2H, t, $J = 6.0$ Hz), 7.27-7.31 (3H, m), 7.36-7.44 (8H, m), 7.65-7.68 (4H, m); $^{13}$C NMR (100 MHz in CDCl$_3$) $\delta$ 19.23, 22.39, 25.91, 26.88, 32.17, 33.45, 61.17, 63.53, 83.01, 85.41, 123.27, 127.64, 128.00, 128.26, 129.59, 131.60, 133.96, 135.58; MS (CI) $m/z$ 482 (M$^+$+H); HRMS (CI) $m/z$ calcd for C$_{30}$H$_{36}$ON$_3$Si (M$^+$+H) 482.2627, found 482.2650.

5-Azido-8-phenyloct-7-yn-1-yl acetate (29)

To a solution of 29 (500 mg, 2.06 mmol) in CH$_2$Cl$_2$ (6 mL) was successively added Et$_3$N (0.43 mL, 4.12 mmol), DMAP (49 mg, 0.41 mmol) and Ac$_2$O (0.29 mL, 3.09 mmol) at 0 °C, and the mixture was stirred for 6 h at 0 °C. To this was added distilled water and organic materials were extracted with CH$_2$Cl$_2$. Dried and concentrated extract was subjected to column chromatography on silica gel using hexane and AcOEt (10:1) to give compound 29 (517 mg, 88%) as a colorless syrup. 29: FT IR (neat) $\nu_{\text{max}}$ 3077, 3055, 3032, 2945, 2867, 2108, 1739 cm$^{-1}$; $^1$H NMR (400 MHz in CDCl$_3$) $\delta$ 1.43-1.79
(6H, m), 2.05 (3H, s), 2.61 (2H, d, J = 6.4 Hz), 3.55 (1H, m), 4.09 (2H, t, J = 6.4 Hz), 7.28-7.31 (3H, m), 7.40-7.43 (2H, m); 13C NMR (100 MHz in CDCl3) δ 20.98, 22.56, 25.89, 28.30, 33.29, 61.00, 64.12, 83.13, 85.16, 123.15, 128.05, 128.26, 131.56, 171.18; MS (Cl) m/z 286 (M+'H); HRMS (Cl) m/z calcd for C16H20O2N3 (M+'H) 286.1566, found 286.1574.

(4-Azido-8-(benzyloxy)oct-1-yn-1-yl)benzene (31)

To a mixture of 24 (300 mg, 1.23 mmol) and benzyl 2,2,2-trichloroacetimidate (622 mg, 2.46 mmol) in CH2Cl2 (4 mL) and cyclohexane (8 mL) was added TfOH (0.02 mL, 20 mol %) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was quenched with saturated NaHCO3 at 0 °C and extracted with CH2Cl2. The organic materials were washed with brine and dried over MgSO4. The filtrates were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane and AcOEt (20:1) to give compound 31 (205 mg, 50%) as a colorless syrup. 31: FT IR (neat) νmax 3077, 3061, 3031, 2938, 2860, 2794, 2121, 1952, 1879, 1809, 1725 cm−1; 1H NMR (500 MHz in CDCl3) δ 1.46-1.76 (6H, m), 2.67 (2H, d, J = 5.5 Hz), 3.50 (2H, t, J = 6.5 Hz), 3.54 (1H, m), 4.51 (2H, s), 7.27-7.30 (4H, m), 7.33-7.35 (4H, m), 7.40-7.42 (2H, m); 13C NMR (125 MHz in CDCl3) δ 22.84, 25.89, 29.47, 33.50, 61.16, 69.99, 72.99, 83.06, 85.37, 123.25, 127.58, 127.66, 128.01, 128.26, 128.40, 131.60, 138.50; MS (Cl) m/z 334 (M+'H); HRMS (Cl) m/z calcd for C21H24ON3 (M+'H) 334.1920, found 334.1938.

Silaphenylmercuric triflate (10)-catalyzed cyclization of various homopropargyl azides (Table 3)

2-Pentyl-5-phenyl-1H-pyrrole (12)

The product 12 (10.6 mg, 99%, recovery of 10: 99.73%) was obtained from 11 (12.1 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). In the case of reaction with 19 (12.1 mg, 0.05 mmol), the product 12 (8.1 mg, 76%, recovery of 10: 99.29%) was also obtained. 12: white powder; FT IR (neat) νmax 3432, 3106, 3062, 3026, 2955, 2929, 2868, 2857 cm−1; 1H NMR (400 MHz in CDCl3) δ 0.91 (3H, t, J = 7.2 Hz), 1.33-1.39 (4H, m), 1.66 (2H, m), 2.63 (2H, t, J = 7.6 Hz), 5.97 (1H, t, J = 3.2 Hz), 6.41 (1H, t, J = 3.2 Hz), 7.15 (1H, m), 7.30-7.34 (2H, m), 7.41-7.44 (2H, m), 8.11 (NH, br s); 13C NMR (100 MHz in CDCl3) δ 14.04, 21.50, 27.89, 29.36, 31.56, 106.00, 106.92, 123.35, 125.61, 128.80, 130.47, 133.00, 134.37; MS (Cl) m/z 214 (M+'H); HRMS (Cl) m/z calcd for C15H20N (M+'H) 214.1596, found 214.1588.
2-Cyclohexyl-5-phenyl-1H-pyrrole (14)

\[
\begin{align*}
\text{Cy} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

The product **14** (11.0 mg, 97%, recovery of **10**: 99.60%) was obtained from **13** (12.7 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (**10**)-catalyzed cyclization of **1** using 20 mol % of **10** (50 mg, 0.01 mmol). **14**: white powder; FT IR (neat) \(v_{\text{max}}\) 3432, 3104, 3060, 3026, 2925, 2850 cm\(^{-1}\); \(^1\)H NMR (400 MHz in CDCl\(_3\)) \(\delta\) 1.25 (1H, m), 1.33-1.48 (4H, m), 1.73 (1H, m), 1.83 (2H, m), 2.05 (2H, m), 2.60 (1H, m), 5.97 (1H, br t, \(J = 3.2\) Hz), 6.41 (1H, br t, \(J = 3.2\) Hz), 7.15 (1H, tt, \(J = 7.6, 1.2\) Hz), 7.31-7.35 (2H, m), 7.41-7.44 (2H, m), 8.13 (NH, br s); \(^{13}\)C NMR (100 MHz in CDCl\(_3\)) \(\delta\) 26.10, 26.28, 33.24, 36.97, 105.01, 105.82, 123.41, 125.62, 128.79, 130.20, 133.05, 139.61; MS (CI) \(m/z\) 226 (M\(^+\)+H); HRMS (CI) \(m/z\) calcd for C\(_{16}\)H\(_{20}\)N (M\(^+\)) 226.1596, found 226.1591.

2,5-Diphenyl-1H-pyrrole (16)

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

The product **16** (10.0 mg, 91%, recovery of **10**: 99.62%) was obtained from **15** (12.4 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (**10**)-catalyzed cyclization of **1** using 20 mol % of **10** (50 mg, 0.01 mmol). **16**: white powder; FT IR (neat) \(v_{\text{max}}\) 3458, 3109, 3095, 3060, 3048, 3031, 3003, 2964, 2925, 2851, 1943, 1869, 1804 cm\(^{-1}\); \(^1\)H NMR (400 MHz in CDCl\(_3\)) \(\delta\) 6.58 (2H, d, \(J = 2.4\) Hz), 7.20-7.24 (2H, m), 7.36-7.41 (4H, m), 7.51-7.54 (4H, m), 8.58 (NH, br s); \(^{13}\)C NMR (100 MHz in CDCl\(_3\)) \(\delta\) 107.93, 123.79, 126.39, 128.96, 132.47, 133.12; MS (CI) \(m/z\) 219 (M\(^+\)); HRMS (CI) \(m/z\) calcd for C\(_{16}\)H\(_{13}\)N (M\(^+\)) 219.1049, found 219.1047.

2-Phenyl-4,5,6,7-tetrahydro-1H-indole (18)

\[
\begin{align*}
\text{Ph} & \quad \text{N} \\
& \quad \text{H}
\end{align*}
\]

The product **18** (8.8 mg, 89%, recovery of **10**: 99.63%) was obtained from **17** (11.3 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (**10**)-catalyzed cyclization of **1** using 30 mol % of **10** (75 mg, 0.015 mmol). **18**: white powder; FT IR (neat) \(v_{\text{max}}\) 3430, 3108, 3068, 2923, 2842, 1940, 1862, 1794, 1726 cm\(^{-1}\); \(^1\)H NMR (200 MHz in CDCl\(_3\)) \(\delta\) 1.72-1.91 (4H, m), 2.54 (2H, t, \(J = 6.0\) Hz), 2.64 (2H, t, \(J = 6.0\) Hz), 6.28 (1H, d, \(J = 2.6\) Hz), 7.14 (1H, m), 7.27-7.44 (4H, m), 7.94 (NH, br s); \(^{13}\)C NMR (50 MHz in CDCl\(_3\)) \(\delta\) 22.87, 22.89, 23.37, 23.77, 105.16, 118.97, 123.38, 125.55, 128.50, 128.78, 130.25, 133.17; MS (CI) \(m/z\) 197 (M\(^+\)); HRMS (CI) \(m/z\) calcd for C\(_{14}\)H\(_{15}\)N (M\(^+\)) 197.1204,
found 197.1201.

**2-Benzyl-5-phenyl-1H-pyrrole (21)**

![Chemical Structure](image)

The product 21 (10.1 mg, 87%, recovery of 10: 99.90%) was obtained from 20 (13.1 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). 21: white powder; FT IR (neat) ν<sub>max</sub> 3443, 3105, 3082, 3062, 3027, 2954, 2914, 2896, 2853, 1945, 1867, 1810, 1705 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>) δ 4.03 (2H, s), 6.05 (1H, br t, <i>J</i> = 3.2 Hz), 6.43 (1H, t, <i>J</i> = 3.2 Hz), 7.15 (1H, m), 7.22-7.40 (9H, m), 8.04 (NH, br s); <sup>13</sup>C NMR (100 MHz in CDCl<sub>3</sub>) δ 34.27, 106.10, 108.63, 123.46, 125.85, 126.57, 128.68, 128.71, 128.81, 131.52, 132.01, 132.81, 139.27; MS (CI) m/z 233 (M<sup>+</sup>); HRMS (CI) m/z calcd for C<sub>17</sub>H<sub>15</sub>N (M<sup>+</sup>) 233.1205, found 233.1195.

**2-(tert-Butyl)-5-phenyl-1H-pyrrole (23)**

![Chemical Structure](image)

The product 23 (9.1 mg, 91%, recovery of 10: 99.82%) was obtained from 22 (11.4 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). 23: white powder; FT IR (neat) ν<sub>max</sub> 3464, 3105, 3061, 3025, 2962, 2903, 2867 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz in CDCl<sub>3</sub>) δ 1.35 (9H, s), 6.00 (1H, t, <i>J</i> = 3.5 Hz), 6.40 (1H, t, <i>J</i> = 3.5 Hz), 7.16 (1H, m), 7.32-7.36 (2H, m), 7.43-7.45 (2H, m), 8.13 (NH, br s); <sup>13</sup>C NMR (125 MHz in CDCl<sub>3</sub>) δ 30.59, 31.51, 104.50, 105.71, 123.48, 125.71, 128.81, 130.38, 133.07, 143.26; MS (CI) m/z 199 (M<sup>+</sup>); HRMS (CI) m/z calcd for C<sub>14</sub>H<sub>17</sub>N (M<sup>+</sup>) 199.1361, found 199.1352.

**4-(5-Phenyl-1H-pyrrol-2-yl)butan-1-ol (25)**

![Chemical Structure](image)

The product 25 (8.0 mg, 74%, recovery of 10: 99.79%) was obtained from 24 (12.2 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). In the case of reaction with 26 (17.9 mg, 0.05 mmol), the product 25 (10.6 mg, 99%, recovery of 10: 99.88%) was also obtained. 25: white powder; FT IR (neat) ν<sub>max</sub> 3373, 3307, 3104, 3064, 3027, 2937, 2862, 2103 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz in CDCl<sub>3</sub>) δ 1.65 (2H, m), 1.75 (2H, m), 2.69 (2H, t, <i>J</i> = 7.2 Hz), 3.70 (2H, t, <i>J</i> = 6.4 Hz), 5.97 (1H, t, <i>J</i> = 3.2 Hz), 6.41 (1H, t, <i>J</i> = 3.2
Hz), 7.15 (1H, t, J = 7.2 Hz), 7.33 (2H, t, J = 7.2 Hz), 7.44 (2H, d, J = 7.2 Hz), 8.40 (NH, br s); 13C NMR (100 MHz in CDCl₃) δ 26.04, 27.47, 31.99, 62.69, 105.94, 107.09, 123.36, 125.63, 128.80, 130.66, 132.97, 133.78; MS (Cl) m/z 216 (M⁺+H); HRMS (Cl) m/z calcd for C₁₄H₁₈ON (M⁺+H) 216.1388, found 216.1380.

2-(4-((tert-Butyldiphenylsilyl)oxy)butyl)-5-phenyl-1H-pyrrole (28)

The product 28 (22.4 mg, 91%, recovery of 10: 99.85%) was obtained from 27 (24.1 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). 28: white powder; FT IR (neat) νmax 3437, 3069, 3049, 3027, 2998, 2931, 2896, 2857 cm⁻¹; ¹H NMR (500 MHz in CDCl₃) δ 1.05 (9H, s), 1.65 (2H, m), 1.76 (2H, m), 2.64 (2H, t, J = 7.5 Hz), 3.71 (2H, t, J = 6.0 Hz), 5.96 (1H, t, J = 3.5 Hz), 6.40 (1H, t, J = 3.5 Hz), 7.15 (1H, m), 7.31-7.43 (10H, m), 7.66-7.68 (4H, m), 8.08 (NH, br s); 13C NMR (125 MHz in CDCl₃) δ 19.25, 25.99, 26.91, 27.57, 32.05, 63.67, 106.02, 107.06, 123.37, 125.62, 127.63, 128.79, 129.57, 130.54, 132.97, 133.99, 135.59; MS (Cl) m/z 454 (M⁺+H); HRMS (Cl) m/z calcd for C₃₀H₃₆ONSi (M⁺+H) 454.2566, found 454.2556.

4-(5-Phenyl-1H-pyrrol-2-yl)butyl acetate (30)

The product 30 (12.7 mg, 99%, recovery of 10: 99.77%) was obtained from 29 (14.3 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). 30: white powder; FT IR (neat) νmax 3378, 3105, 3058, 3027, 2940, 2864, 1722 cm⁻¹; ¹H NMR (400 MHz in CDCl₃) δ 1.70-1.76 (4H, m), 2.05 (3H, s), 2.68 (2H, br t, J = 7.2 Hz), 4.11 (2H, br t, J = 6.4 Hz), 5.98 (1H, br t, J = 3.2 Hz), 6.41 (1H, br t, J = 3.2 Hz), 7.16 (1H, m), 7.31-7.36 (2H, m), 7.43-7.46 (2H, m), 8.27 (NH, br s); 13C NMR (100 MHz in CDCl₃) δ 21.04, 26.06, 27.32, 28.12, 64.17, 106.02, 107.19, 123.39, 125.70, 128.81, 130.76, 132.91, 133.39, 171.36; MS (Cl) m/z 258 (M⁺+H); HRMS (Cl) m/z calcd for C₁₆H₂₀O₂N (M⁺+H) 258.1494, found 258.1487.

2-(4-(Benzyloxy)butyl)-5-phenyl-1H-pyrrole (32)

The product 32 (14.0 mg, 92%, recovery of 10: 99.70%) was obtained from 31 (16.7 mg, 0.05 mmol) according to the procedure for silaphenylmercuric triflate (10)-catalyzed cyclization of 1 using 20 mol % of 10 (50 mg, 0.01 mmol). 32: white powder; FT IR (neat) νmax 3437, 3069, 3049, 3027, 2940, 2864, 1722 cm⁻¹; ¹H NMR (400 MHz in CDCl₃) δ 1.05 (9H, s), 1.65 (2H, m), 1.76 (2H, m), 2.64 (2H, t, J = 7.5 Hz), 3.71 (2H, t, J = 6.0 Hz), 5.96 (1H, t, J = 3.5 Hz), 6.40 (1H, t, J = 3.5 Hz), 7.15 (1H, m), 7.31-7.43 (10H, m), 7.66-7.68 (4H, m), 8.08 (NH, br s); 13C NMR (125 MHz in CDCl₃) δ 19.25, 25.99, 26.91, 27.57, 32.05, 63.67, 106.02, 107.06, 123.37, 125.62, 127.63, 128.79, 129.57, 130.54, 132.97, 133.99, 135.59; MS (Cl) m/z 454 (M⁺+H); HRMS (Cl) m/z calcd for C₃₀H₃₆ONSi (M⁺+H) 454.2566, found 454.2556.
mol % of 10 (50 mg, 0.01 mmol). 32: white powder; FT IR (neat) ν\textsubscript{max} 3373, 3100, 3086, 3061, 3029, 2936, 2860, 2794 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz in CDCl\textsubscript{3}) δ 1.67-1.80 (4H, m), 2.71 (2H, t, J = 7.2 Hz), 3.56 (2H, t, J = 6.0 Hz), 4.53 (2H, s), 5.96 (1H, t, J = 3.2 Hz), 6.40 (1H, t, J = 3.2 Hz), 7.13 (1H, m), 7.27-7.37 (9H, m), 8.42 (NH, br s); \textsuperscript{13}C NMR (100 MHz in CDCl\textsubscript{3}) δ 27.14, 27.31, 28.80, 70.58, 73.18, 105.85, 107.02, 123.30, 125.48, 127.71, 127.88, 128.46, 128.74, 130.54, 133.01, 133.88, 138.32; MS (Cl) \textit{m/z} 306 (M\textsuperscript{+}+H); HRMS (Cl) \textit{m/z} calcd for C\textsubscript{21}H\textsubscript{24}ON (M\textsuperscript{+}+H) 306.1858, found 306.1840.

**Mechanism study of Hg(OTf)\textsubscript{2} catalized cyclization of homopropargyl azide 1**

(2-Phenyl-1H-pyrrol-3-yl)mercury(II) chloride

A 0.1 M CH\textsubscript{3}CN solution of Hg(OTf)\textsubscript{2} (0.2 mL, 20.0 µmol) was added to a dried reaction flask under argon atmosphere, and the CH\textsubscript{3}CN was evacuated under vacuum. To this was added dropwise a solution of 1 (17.1 mg, 0.1 mmol) in CH\textsubscript{3}NO\textsubscript{2} (1.0 mL) at -20 °C. After stirring for 5 min at -20 °C, the reaction was quenched by the addition of Et\textsubscript{3}N (56 µL, 0.4 mmol) and NaCl salt. To the reaction mixture was added AcOEt, and the organic phase was washed with distilled water at room temperature. The organic phase was separated and dried over Na\textsubscript{2}SO\textsubscript{4}. The filtrates were concentrated under reduced pressure. The residue was analyzed by \textsuperscript{1}HNMR spectroscopy. As the result, the formation of (2-phenyl-1H-pyrrol-3-yl)mercury(II) chloride was confirmed. (2-phenyl-1H-pyrrol-3-yl)mercury(II) chloride: \textsuperscript{1}H NMR (500 MHz in CD\textsubscript{3}OD) δ 4.87 (H\textsubscript{2}O in CD\textsubscript{3}OD), 6.16 (1H, d, J = 3.0 Hz), 6.72 (1H, d, J = 3.0 Hz), 7.19 (1H, br t, J = 8.0 Hz), 7.35 (1H, br t, J = 8.0 Hz), 7.49 (1H, br d, J = 8.0 Hz).

**References and Notes**


C₈H₁₂

12
NMR spectra of compounds 2 and HgCl. (in CD$_3$OD)