Electronic Supplementary Information

A synthetic approach to a molecular crank mechanism:
toward intramolecular motion transformation between rotation and translation

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1. General experimental method
All reactions were carried out in oven dried glasswares with commercial dehydrated solvents (Wako Pure Chemical Industries). 4-Iodobenzylalcohol and 3,4,5-trimethoxybenzaldehyde were purchased from Tokyo Chemical Industry. S1, S6, S8, [4-(aminomethyl)phenyl]methanol and 2-picoline-borane were prepared according to previously published procedure. Silica gel column chromatography was performed using Silica gel 60 (70 – 230 mesh ASTM, Merck). 1H, 13C, 1H-1H COSY and NOESY spectra were measured by a Bruker DRX 500 (500 MHz 1H, 125.65 MHz 13C) spectrometer. The spectra are referenced to Me4Si in chloroform- or signal of solvent (methanol-d4; 3.31 ppm). Chemical shifts (d) are reported in ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), dd (double doublet), m (multiplet), br (broad). Coupling constants, J, are reported in Hz. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT spectrometer KB 201. Gel permeation chromatography (GPC) was performed on a recycling preparative HPLC (Japan Analytical Industry; LC-9204) with an UV-vis absorbance detector (S-3740) with a JAIGEL-2H-40 (40 × 600 mm) column.
2. Synthesis of alkyne 3

Scheme 1 Synthesis of 3.

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\begin{align*}
\text{S1} & \xrightarrow{\text{BuLi (1.58 M solution in n-hexane, 15.4 mL, 24.3 mmol, 1.05 equiv) were added dropwise to a}}\nonumber \\
& \xrightarrow{\text{CO}_2} \text{S2} \quad \text{S2.} \quad \text{N}^\text{hydroxysuccinimide (348 mg, 3.03 mmol, 1.0 equiv) was added to a solution of tert-butyl(4-ethynylbenzyloxy)dimethylsilane (S1) to (5.71 g, 23.2 mmol, 1.0 equiv) in THF (23 mL) at -78 °C over 20 min. The mixture was stirred at -78 °C for 1 h, then CO}_2 \text{ gas was bubbled into the reaction mixture for 10 min. The resulting mixture was stirred at room temperature for 1 h. Water (5 mL) was added to the mixture, and then concentrated in vacuo. 1.0 N HCl (200 mL) was added to the residue, and then extracted with AcOEt. The organic layer was dried over MgSO}_4 \text{ and concentrated in vacuo to yield S2 (5.12 g, 17.6 mmol, 76%) as a yellow solid; \text{H NMR (500 MHz; CDCl}_3; 293 K \delta 0.11 (s, 6H, SiMe}_2), 0.95 (s, 9H, Si(Bu)), 4.77 (s, 2H, CH}_2\text{OTBDMS), 7.35 (d, J = 8.0 Hz, 2H, C}_6\text{H}_4), 7.59 (d, J = 8.0 Hz, 2H, C}_6\text{H}_4); \text{C NMR (125 MHz, CDCl}_3; 293 K \delta -5.3 (SiMe}_2), 18.4 (SiCMe}_3), 25.9 (SiCMe}_3), 64.4 (CH}_2\text{OTBDMS), 79.8 (C≡C}_6\text{H}_4), 89.2 (C≡C}_6\text{H}_4), 117.4 (ipso-C}_6\text{H}_4), 126.0 (CH of C}_6\text{H}_4), 133.3 (CH of C}_6\text{H}_4), 145.0 (ipso-C}_6\text{H}_4), 158.0 (C=O).}
\end{align*}
\]

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\begin{align*}
\text{S3.} & \quad \text{N}^\text{-hydroxysuccinimide (348 mg, 3.03 mmol, 1.0 equiv) was added to a solution of S2 (871 mg, 3.00 mmol, 1.0 equiv) in 1,4-dioxane (3 mL, 1.0 M), and then N,N'-dicyclohexylcarbodiimide (620 mg, 3.01 mmol, 1.0 equiv) at 0 °C was added. The mixture was stirred at room temperature for 30 min. The suspension was filtered and washed with AcOEt. The filtrate solution was added 2-aminoethanol (0.18 mL, 3.0 mmol, 1.0 equiv) and stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and then s\text{at NaHCO}_3 aq. (10 mL) was added. The mixture was extracted with AcOEt (15 mL × 3). The organic extracts were combined and dried over anhydrous MgSO}_4. The solvent was removed under reduced pressure. Crude S3 (1.24 g, 3.72 mmol, quant.) was obtained as a yellow solid; \text{H NMR (500 MHz; CDCl}_3; 293 K \delta 0.10 (s, 6H, SiMe}_2), 0.94 (s, 9H, Si(Bu)), 3.53 (dt, J = 4.8, 4.8 Hz, 2H, NHCH}_2), 3.80 (t, J = 4.8 Hz, 2H, CH}_2\text{OH), 4.75 (s, 2H, CH}_2\text{OTBDMS), 6.47 (br, 1H, C=ONH), 7.31 (d, J = 8.3 Hz, 2H, C}_6\text{H}_4), 7.50 (d, J = 8.3 Hz, 2H, C}_6\text{H}_4); \text{C NMR (125 MHz, CDCl}_3; 293 K \delta -5.31}
\end{align*}
\]

S2
(SiMe₂), 18.4 (SiCMe₃), 25.9 (SiCMe₃), 42.5 (NHCH₂), 61.7 (CH₂OH), 64.4 (CH₂OTBDMS), 82.5 (C₆H₄C≡C), 85.6 (C₆H₄C≡C), 118.4 (ipso-C₆H₄), 125.9 (CH of C₆H₄), 132.5 (CH of C₆H₄), 144.0 (ipso-C₆H₄), 154.3 (C=O).

S4. 4-Dimethylaminopyridine (170 mg, 1.37 mmol, 0.10 equiv), triethylamine (2.9 mL, 21 mmol, 1.5 equiv) and p-toluenesulfonyl chloride (2.63 g, 1.38 mmol, 1.0 equiv) were added to a solution of S3 (4.57 g, 13.7 mmol, 1.0 equiv) in CH₂Cl₂ (27 mL, 0.5 M). The mixture was stirred at room temperature for 9 h. The reaction was quenched with H₂O (30 mL), and extracted with CHCl₃ (30 mL × 3). The organic extracts were combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give crude tosyl compound as a brown oil. The intermediate was dissolved in MeOH (27 mL, 0.5 M), and then NaOH (2.75 g, 68.5 mmol, 5.0 equiv) was added at 0 °C. The mixture was stirred at room temperature for 9 h. The reaction was quenched with H₂O (30 mL), and concentrated under reduced pressure. The mixture was extracted with AcOEt (30 mL × 3). The organic extracts were combined and dried over anhydrous MgSO₄. The crude oil was purified by silica gel column chromatography (n-hexane/AcOEt = 5:1 – 2:1) to give desired S4 (1.77 g, 5.60 mmol, 41%) as a yellow solid and S5 (779 mg, 3.87 mmol, 28%) as a yellow solid; ¹H NMR (500 MHz; CDCl₃; 293 K) δ 0.10 (s, 6H, SiMe₂), 0.94 (s, 9H, Si₄Bu), 4.01 (t, J = 9.5 Hz, 2H, NCH₂C₄H₂O), 4.36 (t, J = 9.5 Hz, 2H, NCH₂CH₂O), 4.75 (s, 2H, CH₂OTBDMS), 7.32 (d, J = 8.0 Hz, 2H, C₆H₄), 7.53 (d, J = 8.0 Hz, 2H, C₆H₄); ¹³C NMR (125 MHz, CDCl₃; 293 K) δ -5.3 (SiMe₂), 18.4 (SiCMe₃), 25.9 (SiCMe₃), 55.1 (NCH₂CH₂O), 64.5 (CH₂OTBDMS), 67.5 (NCH₂CH₂O), 77.1 (C≡CC₆H₄), 89.9 (C≡CC₆H₄), 118.7 (ipso-C₆H₄), 125.9 (CH of C₆H₄), 132.4 (CH of C₆H₄), 143.9 (ipso-C₆H₄), 150.8 (C≡N); m/z (ESI-TOF) 338.1516 (M + Na⁺. C₁₈H₂₅NaNO₂Si requires 338.1552).

S5. Tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran, 6.0 mL, 6.0 mmol, 1.0 equiv), MeOH (1 drop) were added to a solution of S4 (1.90 g, 6.01 mmol, 1.0 equiv) in THF (6 mL, 1.0 M). The solution was stirred at room temperature for 30 min. Then the solvent was removed under reduced pressure. The crude oil was purified by silica gel column chromatography (n-hexane/AcOEt = 1:2) to give desired S5 (848 mg, 4.21 mmol, 70%) as a colorless solid; ¹H NMR (500 MHz; CDCl₃; 293 K) δ 2.19 (t, J = 6.0 Hz, 1H, OH), 4.01 (t, J = 9.5 Hz, 2H, NCH₂CH₂O), 4.37 (t, J = 9.5 Hz, 2H, NCH₂CH₂O), 4.73 (d, J = 6.0 Hz, 2H, CH₂OH), 7.36 (d, J = 8.0 Hz, 2H, C₆H₄), 7.52 (d, J = 8.0 Hz, 2H, C₆H₄); ¹³C NMR (125 MHz, CDCl₃; 293 K) δ 55.0 (NCH₂CH₂O), 64.6 (CH₂OH), 67.5 (NCH₂CH₂O), 89.7 (C≡CC₆H₄), 119.3 (ipso-C₆H₄), 126.7 (CH of C₆H₄), 132.7 (CH of C₆H₄), 143.2 (ipso-C₆H₄), 150.8 (C≡N); m/z (ESI-TOF) 224.0664 (M + Na⁺. C₁₈H₂₃NaNO₂Si requires 224.0678).
3. Acetic acid anhydrate (1.3 mL, 14 mmol, 1.5 equiv) was added to a solution of S5 (1.88 g, 9.34 mmol, 1.0 equiv) in pyridine (9.5 mL, 1.0 M). The solution was stirred at room temperature for 30 min. The reaction was quenched with H2O (1.0 mL), and then the solvent was removed under reduced pressure. The crude oil was purified by silica gel column chromatography (n-hexane/AcOEt = 1:1) to give desired 3 (1.49 g, 6.11 mmol, 65%) as a colorless solid; 1H NMR (500 MHz; CDCl3; 293 K) δ 2.12 (s, 3H, OAc), 4.02 (t, J = 9.5 Hz, 2H, NCH2CH2O), 4.37 (t, J = 9.5 Hz, 2H, NCH2CH2O), 5.11 (s, 2H, CH2OAc), 7.35 (d, J = 8.0 Hz, 2H, C6H4), 7.56 (d, J = 8.0 Hz, 2H, C6H4); 13C NMR (125 MHz, CDCl3; 293 K) δ 20.9 (C=O C6H3), 55.1 (NCH2CH2O), 65.5 (CH2OAc), 67.5 (NCH2CH2O), 77.7 (C≡CC6H4), 89.1 (C≡CC6H4), 120.1 (ipso-C6H4), 128.0 (CH of C6H4), 132.6 (CH of C6H4), 138.0 (ipso-C6H4), 150.6 (C=N), 170.7 (C=O); m/z (ESI-TOF) 244.0991 (M + H+. C14H14NO3 requires 244.0974).

3. Synthesis of alkyne 13

Scheme 2 Synthesis of axle 13.

S7. 4-Iodobenzylalcohol (117 mg, 0.500 mmol, 1.0 equiv), S62 (232 mg, 0.607 mmol, 1.2 equiv), PdCl2(PPh3)2 (7.3 mg, 0.010 mmol, 2.1 mol%), CuI (0.4 mg, 0.02 mmol, 0.4 mol%), diisopropylamine (175 μL, 1.25 mmol, 2.5 equiv) and THF (1.5 mL, 0.3 M) were placed in a pressure bottle. The mixture was degassed under N2 and stirred at room temperature for 4 h. The mixture was filtered and washed with AcOEt. The solvent was removed under reduced pressure. Purification of the residue oil by silica gel column chromatography (n-hexane/AcOEt = 100:1 – 5:1) afforded the crude S7 (251 mg, 0.514 mmol, quant.) as a yellow solid; 1H NMR (500 MHz; CDCl3; 293 K) δ 1.14 (s, 21H, iPr), 1.71 (t, J = 6.0 Hz, 1H, OH), 4.73 (d, J = 6.0 Hz, 2H, CH2OH), 7.37 (d, J = 8.0 Hz, 2H, C6H4CH2OH), 7.46 (s, 4H, C≡CC6H4-C≡C), 7.51 (s, 4H, C≡CC6H4-C≡C), 7.54 (d, J = 8.0 Hz, 2H, C6H4CH2OH); 13C NMR (125 MHz, CDCl3; 293 K) δ 11.4 (SiC6HMe2), 18.8 (SiCHMe2), 65.1 (CH2OH), 89.3 (C≡C), 91.0 (C≡C), 91.1 (C≡C), 91.3 (C≡C), 93.1 (C≡C), 106.7 (Si≡C), 122.4 (ipso-C≡C≡C), 122.7 (ipso-C≡C≡C), 123.4 (ipso-C≡C≡C), 123.7 (ipso-C≡C≡C), 127.0 (CH of C6H4), 131.5 (CH of C6H4), 131.7
13. S7 (244 mg, 0.499 mmol, 1.0 equiv) was dissolved in THF (5 mL). Tetrabutylammonium fluoride (1.0 M in THF, 0.50 mL, 0.50 mmol, 1.0 equiv) and MeOH (1 drop) were added to the solution, and stirred at room temperature for 1 h. The solvent was removed under reduced pressure. The residue solid was washed with AcOEt and dried in vacuo to give 13 (145 mg, 0.436 mmol, 87%) as a beige solid; \(^1\)H NMR (500 MHz; CDCl\(_3; 293 \text{ K}) \delta 3.19 (s, 1H, C≡CH), 4.74 (s, 2H, CH\(_2\)OH), 7.37 (d, \(J = 8.0 \text{ Hz}, 2H, \text{C}_6\text{H}_4\text{CH}_2\text{OH}\)), 7.48 (s, 4H, C≡C-C\_6H\_4-C≡C), 7.51 (s, 4H, C≡C-C\_6H\_4-C≡C), 7.54 (d, \(J = 8.0 \text{ Hz}, 2H, \text{C}_6\text{H}_4\text{CH}_2\text{OH}\)).

4. Synthesis of a stopper derivative 15

Scheme 3 Synthesis of a stopper derivative 15

15. Freshly distilled 3,5-dimethylbenzoic chloride (S8)\(^3\) (0.88 g, 4.8 mmol, 1.0 equiv) and trifluoromethanesulfonic acid (0.42 mL, 4.8 mmol, 1.0 equiv) was stirred at room temperature for 10 h. The mixture was pumped up to remove HCl gas. Then the mixture was distilled (0.3 mmHg, 65 - 68 °C) to obtain asymmetric anhydrate compound of trifluoromethanesulfonic acid and 3,5-dimethylbenzoic acid (yellow oil). The anhydrate compounds was stored at -78 °C under N\(_2\) atmosphere.

5. Synthesis of short axle 17

Scheme 4 Synthesis of short axle 17

To a solution of 3,4,5-trimethoxybenzaldehyde (107 mg, 0.545 mmol, 1.0 equiv) and [4-(aminomethyl)phenyl]methanol\(^4\) (81.6 mg, 0.595 mmol, 1.1 equiv) in MeOH (1.5 mL, 0.4 M), 2-picoline-borane\(^5\) (61.6 mg, 0.576 mmol, 1.1 equiv) and acetic acid (0.15 mL, 2.6 mmol, 4.8 equiv) were added. The mixture was stirred at room temperature for 5 h. The solvent was removed under reduced
pressure. 1.0 \text{N} \text{HCl} (2 \text{mL}) was added to the residue and stirred at room temperature for 10 min. Then the pH of the suspension was adjusted to 11 with 1.0 M NaOH aq. The mixture was extracted with chloroform (5 mL \times 3). The organic extracts were combined and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The crude oil was purified by GPC (CHCl₃) to give desired 17 (77.9 mg, 0.245 mmol, 46%) as a colorless solid; \(^1\text{H} \text{NMR} (500 \text{MHz; CDCl}_3; 293 \text{K}; \text{Me}_4\text{Si}) \delta 3.73 (s, 2\text{H}, \text{CH}_2\text{NH}), 3.76 (s, 2\text{H}, \text{CH}_2\text{NH}), 3.84 (s, 3\text{H}, \text{OMe}), 3.86 (s, 6\text{H}, \text{OMe}), 4.70 (s, 2\text{H}, \text{CH}_2\text{OH}), 6.58 (s, 2\text{H}, \text{C}_6\text{H}_2(\text{OMe})_3), 7.35 (s, 4\text{H}, \text{C}_6\text{H}_4); \(^1\text{C} \text{NMR} (125 \text{MHz, CDCl}_3; 293 \text{K}; \text{CDCl}_3) \delta 52.7 (\text{CH}_2\text{NH}), 53.5 (\text{CH}_2\text{NH}), 56.2 (\text{OMe}), 61.0 (\text{OMe}), 65.1 (\text{CH}_2\text{OH}), 105.0 (\text{CH of C}_6\text{H}_2(\text{OMe})_3), 127.3 (\text{CH of C}_6\text{H}_4), 128.5 (\text{CH of C}_6\text{H}_4), 136.0 (\text{ipso-C}_6\text{H}_2(\text{OMe})_3), 139.6 (\text{ipso-C}_6\text{H}_4), 139.9 (\text{ipso-C}_6\text{H}_2(\text{OMe})_3), 153.3 (\text{ipso-C}_6\text{H}_2(\text{OMe})_3); m/z (ESI-TOF) 340.1509 (M + H\textsuperscript{+}, \text{C}_{18}\text{H}_{24}\text{NO}_4 \text{requires 340.1525}).

6. References


