Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

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

Erika Okuno,[a] Shuichi Hiraoka*[a,b] and Mitsuhiko Shionoya*[a]

[a] *Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan. E-mail: shionoya@chem.s.u-tokyo.ac.jp; Fax: +81 3 5841 8061; Tel: +81 3 5841 8061*

[b] *Precursory Research for Embryonic Science and Technology (PRESTO) Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan. Fax: +81 3 5841 1530*

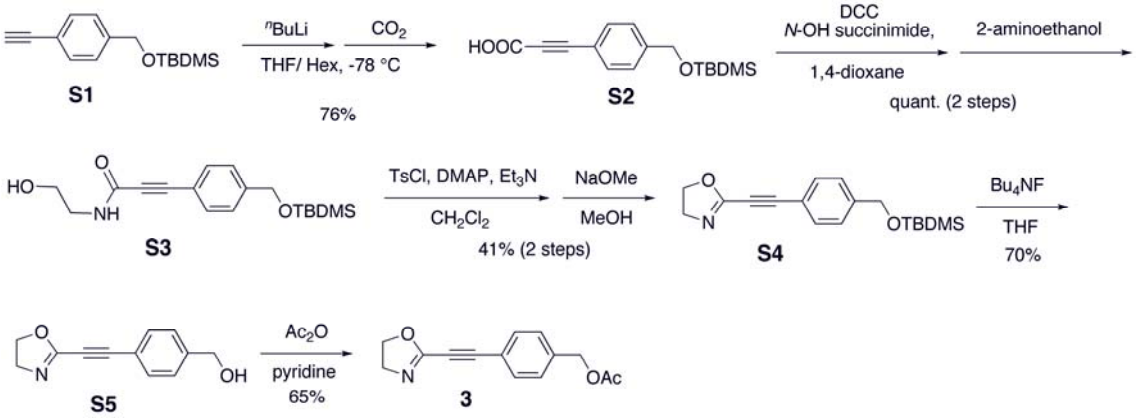
Contents

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**[1], **S6**[2], **S8**[3], [4-(aminomethyl)phenyl]methanol[4] and 2-picoline-borane[5] were prepared according to previously published procedure. Silica gel column chromatography was performed using Silica gel 60 (70 – 230 mesh ASTM, Merck). ^{1}H, ^{13}C, ^{1}H-^{1}H COSY and NOESY spectra were measured by a Bruker DRX 500 (500 MHz ^{1}H, 125.65 MHz ^{13}C) spectrometer. The spectra are referenced to Me_4Si in chloroform-*d* or signal of solvent (methanol-d_4; 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**.



S2. ^{n}BuLi (1.58 M solution in *n*-hexane, 15.4 mL, 24.3 mmol, 1.05 equiv) was added dropwise to a solution of *tert*-butyl(4-ethynylbenzyloxy)dimethylsilane (**S1**)[1] (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 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 $MgSO_4$ and concentrated in vacuo to yield **S2** (5.12 g, 17.6 mmol, 76%) as a yellow solid; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 0.11 (s, 6H, $SiMe_2$), 0.95 (s, 9H, Si^{t}Bu), 4.77 (s, 2H, CH_2OTBDMS), 7.35 (d, J = 8.0 Hz, 2H, C_6H_4), 7.59 (d, J = 8.0Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ -5.3 ($SiMe_2$), 18.4 (Si*C*Me_3), 25.9 (Si*C*Me_3), 64.4 (*C*H_2OTBDMS), 79.8 (C≡*C*C_6H_4), 89.2 (*C*≡CC_6H_4), 117.4 (*ipso*-C_6H_4), 126.0 (*C*H of C_6H_4), 133.3 (*C*H of C_6H_4), 145.0 (*ipso*-C_6H_4), 158.0 (C=O).

S3. *N*-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 sat $NaHCO_3$ 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; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 0.10 (s, 6H, $SiMe_2$), 0.94 (s, 9H, Si^{t}Bu), 3.53 (dt, J = 4.8, 4.8 Hz, 2H, NHCH_2), 3.80 (t, J = 4.8 Hz, 2H, CH_2OH), 4.75 (s, 2H, CH_2OTBDMS), 6.47 (br, 1H, C=ONH), 7.31 (d, J = 8.3 Hz, 2H, C_6H_4), 7.50 (d, J = 8.3 Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ -5.31

($SiMe_2$), 18.4 (Si*C*Me_3), 25.9 (Si*C*Me_3), 42.5 ($NHCH_2$), 61.7 (CH_2OH), 64.4 (*C*H_2OTBDMS), 82.5 (C_6H_4*C*≡C), 85.6 (C_6H_4C≡*C*), 118.4 (ipso-C_6H_4), 125.9 (CH of C_6H_4), 132.5 (CH of C_6H_4), 144.0 (ipso-C_6H_4), 154.3 (C=O).

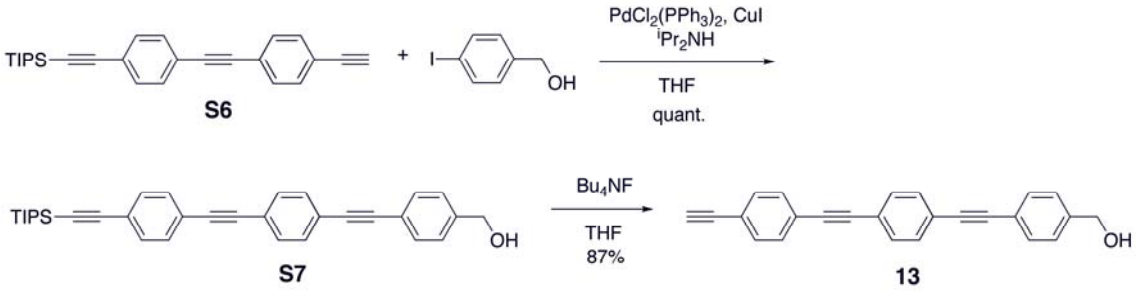
S4. 4-Dimethylaminopyridine (170 mg, 1.37 mmol, 0.10 equiv), triethylamine (2.9 mL, 21 mmol, 1.5 equiv) and *p*-toluenesulfonyl chloride (2.63 g, 1.38 mmol, 1.0 equiv) were added to a solution of **S3** (4.57 g, 13.7 mmol, 1.0 equiv) in CH_2Cl_2 (27 mL, 0.5 M). The mixture was stirred at room temperature for 9 h. The reaction was quenched with H_2O (30 mL), and extracted with $CHCl_3$ (30 mL × 3). The organic extracts were combined and dried over anhydrous $MgSO_4$. 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 H_2O (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 $MgSO_4$. The solvent was removed under reduced pressure. 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; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 0.10 (s, 6H, $SiMe_2$), 0.94 (s, 9H, Si^{t}Bu), 4.01 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 4.36 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 4.75 (s, 2H, C*H*$_2$OTBDMS), 7.32 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.53 (d, *J* = 8.0 Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ -5.3 ($SiMe_2$), 18.4 (Si*C*Me_3), 25.9 (Si*C*Me_3), 55.1 (NCH_2CH_2O), 64.5 (*C*H_2OTBDMS), 67.5 (NCH_2CH_2O), 77.1 (C≡*C*C_6H_4), 89.9 (*C*≡CC_6H_4), 118.7 (*ipso*-C_6H_4), 125.9 (CH of C_6H_4), 132.4 (CH of C_6H_4), 143.9 (*ipso*-C_6H_4), 150.8 (C=N); *m*/*z* (ESI-TOF) 338.1516 (M + Na^+. $C_{18}H_{25}NaNO_2Si$ 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; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 2.19 (t, *J* = 6.0 Hz, 1H, OH), 4.01 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 4.37 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 4.73 (d, *J* = 6.0 Hz, 2H, C*H*$_2$OH), 7.36 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.52 (d, *J* = 8.0 Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ 55.0 (NCH_2CH_2O), 64.6 (*C*H_2OH), 67.5 (NCH_2CH_2O), 89.7 (*C*≡CC_6H_4), 119.3 (*ipso*-C_6H_4), 126.7 (CH of C_6H_4), 132.7 (CH of C_6H_4), 143.2 (*ipso*-C_6H_4), 150.8 (C=N); *m*/*z* (ESI-TOF) 224.0664 (M + Na^+. $C_{11}H_{11}NaNO_2$ 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 H_2O (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; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 2.12 (s, 3H, OAc), 4.02 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 4.37 (t, *J* = 9.5 Hz, 2H, NCH_2CH_2O), 5.11 (s, 2H, CH_2OAc), 7.35 (d, *J* = 8.0 Hz, 2H, C_6H_4), 7.56 (d, *J* = 8.0 Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ 20.9 ($C=OCH_3$), 55.1 (NCH_2CH_2O), 65.5 (CH_2OAc), 67.5 (NCH_2CH_2O), 77.7 ($C\equiv CC_6H_4$), 89.1 ($C\equiv CC_6H_4$), 120.1 (*ipso*-C_6H_4), 128.0 (CH of C_6H_4), 132.6 (CH of C_6H_4), 138.0 (*ipso*-C_6H_4), 150.6 (C=N), 170.7 (C=O); *m*/*z* (ESI-TOF) 244.0991 ($M + H^+$. $C_{14}H_{14}NO_3$ requires 244.0974).

3. Synthesis of alkyne 13

Scheme 2 Synthesis of axle **13**.



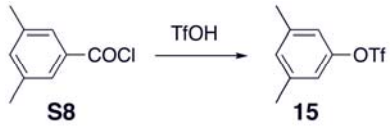
S7. 4-Iodobenzylalcohol (117 mg, 0.500 mmol, 1.0 equiv), **S6**[2] (232 mg, 0.607 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (7.3 mg, 0.010 mmol, 2.1 mol%), CuI (0.4 mg, 0.02 mmol, 0.4 mol%), diisopropylamine (175 μL, 1.25 mmol, 2.5 equiv) and THF (1.5 mL, 0.3 M) were placed in a pressure bottle. The mixture was degassed under N_2 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; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 1.14 (s, 21H, ^{i}Pr), 1.71 (t, *J* = 6.0 Hz, 1H, OH), 4.73 (d, *J* = 6.0 Hz, 2H, CH_2OH), 7.37 (d, *J* = 8.0 Hz, 2H, $C_6H_4CH_2OH$), 7.46 (s, 4H, $C\equiv C\text{-}C_6H_4\text{-}C\equiv C$), 7.51 (s, 4H, $C\equiv C\text{-}C_6H_4\text{-}C\equiv C$), 7.54 (d, *J* = 8.0 Hz, 2H, $C_6H_4CH_2OH$); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ 11.4 ($SiCHMe_2$), 18.8 ($SiCHMe_2$), 65.1 (CH_2OH), 89.3 (C≡C), 91.0 (C≡C), 91.1 (C≡C), 91.3 (C≡C), 93.1 (C≡C), 106.7 (Si-*C*≡C), 122.4 (*ipso*-*C*-C≡C), 122.7 (*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 C_6H_4), 131.5 (CH of C_6H_4), 131.7

(CH of C_6H_4), 131.7 (CH of C_6H_4), 132.0 (CH of C_6H_4), 132.1 (CH of C_6H_4), 141.4 (CH of C_6H_4); *m*/*z* (ESI-TOF) 511.2467 ($M + Na^+$. $C_{34}H_{36}NaOSi$ requires 511.2433).

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 K) δ 3.19 (s, 1H, C≡CH), 4.74 (s, 2H, C*H*$_2$OH), 7.37 (d, *J* = 8.0 Hz, 2H, $C_6H_4CH_2OH$), 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 Hz, 2H, $C_6H_4CH_2OH$).

4. Synthesis of a stopper derivative 15

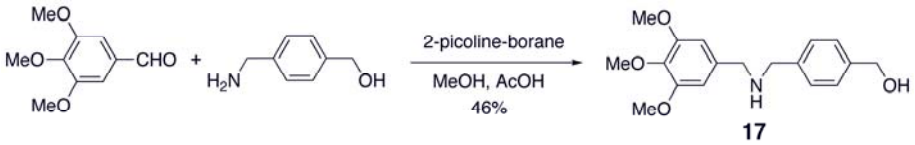
Scheme 3 Synthesis of a stopper derivative **15**



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 *N* HCl (2 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 × 3). The organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude oil was purified by GPC ($CHCl_3$) to give desired **17** (77.9 mg, 0.245 mmol, 46%) as a colorless solid; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K; Me_4Si) δ 3.73 (s, 2H, C*H*$_2$NH), 3.76 (s, *2*H, C*H*$_2$NH), 3.84 (s, 3H, OMe), 3.86 (s, 6H, OMe), 4.70 (s, 2H, CH_2OH), 6.58 (s, 2H, $C_6H_2(OMe)_3$), 7.35 (s, 4H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K; $CDCl_3$) δ 52.7 (CH_2NH), 53.5 (CH_2NH), 56.2 (OMe), 61.0 (OMe), 65.1 (CH_2OH), 105.0 (CH of $C_6H_2(OMe)_3$), 127.3 (CH of C_6H_4), 128.5 (CH of C_6H_4), 136.0 (*ipso*-$C_6H_2(OMe)_3$), 139.6 (*ipso*-C_6H_4), 139.9 (*ipso*-$C_6H_2(OMe)_3$), 153.3 (*ipso*-$C_6H_2(OMe)_3$); *m*/*z* (ESI-TOF) 340.1509 ($M + H^+$. $C_{18}H_{24}NO_4$ requires 340.1525).

6. References

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