SUPPORTING INFORMATION

SYNTHESIS OF HEPTA-ARBUTIN-BRANCHED β-CYCLODEXTRINS AT THEIR PRIMARY SIDES *VIA* CLICK REACTION

Yoshiki Oda,[1]* Junki Nakagawa,[2] and Takashi Yamanoi[3]*

[1]Technology Joint Management Office, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan, [2]Department of Chemistry, School of Science, Tokai University, 4-1-1 Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan, [3]Faculty of Pharmacy and Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan

---

Experimental

1. General

β-CyD, 2-propynyl bromide and 4-hydroxyphenyl β-D-glucopyranoside (arbutin) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a JEOL ECA-600 spectrometer at 600 MHz (^{1}H), and 150 MHz (^{13}C). The MALDI-TOF-MS spectra were recorded on a Voyager DE STR spectrometer. Microwave-assisted synthesis was performed using a CEM Microwave Synthesizer Discover®. All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 precoated plates (0.25 mm). Colum chromatography was conducted using silica gel 60 N (40–50 μm, Kanto Chemical Co., INC.).

2. Preparation of **3**

After **1** (5.01 g, 18.4 mmol) in 0.5 M NaOH aq. solution (37 mL, 19 mmol) was stirred for 20 min at room temperature, the solvent was evaporated under reduced pressure. To the reaction residue was added DMF (70 ml) and 2-propynyl bromide (1.7 mL, 22.6 mmol). After the reaction mixture was stirred for 24 h, the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica-gel (chloroform/methanol = 10/1) to afford **3** (4.67 g, 82% yield) as amorphous crystal. ^{1}H NMR (CD_3OD): δ 2.90 (1H, t, *J* = 2.8 Hz, CH_2CCH), 3.38-3.47 (4H, m, H-2, 3, 4, 5), 3.69 (1H, dd, *J* = 5.5 Hz, *J* = 12.4 Hz, H_a -6), 3.88 (1H, dd, *J* = 2.1 Hz, *J* = 12.4 Hz, H_b-6), 4.66 (2H, d, *J* = 2.7 Hz, CH_2CCH), 4.78 (1H, d, *J* = 7.6 Hz, H-1), 6.90 (2H, d, *J* = 9.0 Hz, Ph), 7.05 (2H, d, *J* = 8.9 Hz, Ph); ^{13}C NMR (CD_3OD): δ 57.2 (CH_2CCH), 62.5 (C-6), 71.4 (C-5), 74.9 (C-4), 76.6 (CH_2CCH), 77.9 (C-2), 78.1 (C-3), 80.0 (CH_2CCH), 103.3 (C-1), 116.9, 119.1, 153.8, 154.5 (Ph).

3. Preparation of **4**

To a solution of **3** (2 g, 6.8 mmol) in pyridine (5.5 mL) was added acetic anhydride (11.0 mL). After the reaction mixture was stirred for 24 h at room temperature, the reaction was then quenched by adding citric acid aq. solution (5 mL). The mixture was extracted with EtOAc (three times) and the combined organic solvent was dried over anhydrous Na_2SO_4. The organic solvent was filtered and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica-gel (hexane/ethyl acetate = 3/1) to afford **4** (2.8g, 91% yield) as amorphous crystal. ^{1}H NMR ($CDCl_3$): δ 2.04 (3H, s, Ac), 2.05 (3H, s, Ac), 2.08 (3H, s, Ac), 2.08 (3H, s, Ac), 2.52 (1H, t, *J* = 2.1 Hz, CH_2CCH), 3.78-3.83 (1H, m, H-5), 4.16 (1H, dd, *J* = 2.8 Hz, *J* = 12.4 Hz, H_a-6), 4.29 (1H, dd, *J* = 5.5 Hz, *J* = 12.3 Hz, H_b-6), 4.65 (2H, d, *J* = 2.1 Hz, CH_2CCH), 4.97 (1H, d, *J* = 7.6 Hz, H-1), 5.16 (1H, t, *J* = 9.0 Hz, H-4), 5.22-5.30 (2H, m, H-2, 3), 6.19 (2H, d, *J* = 9.6 Hz, Ph), 6.96 (2H, d, *J* = 9.0 Hz, Ph); ^{13}C NMR ($CDCl_3$): δ 20.56, 20.59, 20.62, 20.67 (Ac), 56.3 (CH_2CCH), 61.9 (C-6), 68.3 (C-4), 71.2 (C-3), 71.9 (C-5), 72.7 (C-2), 75.5 (CH_2CCH), 78.5 (CH_2CCH), 100.0 (C-1), 115.9, 118.5, 151.5, 153.6 (Ph), 169.2, 169.4, 170.2, 170.6 (C=O).

4. Preparation of **7**

Sodium ascorbate (8.4 mg, 0.042 mmol) and copper(II) sulfate (14.1 mg, 0.056 mmol) were added to a solution of **4** (217.1 mg, 0.45 mmol) and **6** (102.4 mg, 0.054 mmol) in THF (3.5 mL)–H_2O (3.5 mL). After the reaction mixture was heated up to 70 °C by microwave irradiation at 18 W for 40 min, the reaction was quenched by adding sat. NaCl aq. solution (3 mL). The mixture was extracted with EtOAc (three times), and the combined organic solvent was dried over anhydrous Na_2SO_4. The organic solvent was filtered and evaporated under reduced pressure. The crude product was purified by preparative silica-gel TLC (CH_2Cl_2/MeOH = 15/1) to afford **7** (263.2 mg, 93% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.02-2.08 (126H, m, Ac), 3.55 (7H, t, *J* = 8.2 Hz, CD-4), 3.89-3.90 (7H, m, Arb-5), 4.16 (7H, dd, *J* = 2.1 Hz, *J* = 12.3 Hz, Arb-6_a), 4.29 (7H, dd, *J* = 4.8 Hz, *J* = 12.4 Hz, Arb-6_b), 4.40-4.81 (14H, m, CD-5, CD-6_a), 4.75 (7H, dd, *J* = 3.41 Hz, *J* = 10.4 Hz, CD-2), 4.76-4.84 (7H, m, CD-6_b), 4.95-4.99 (14H, m, CH_2CCH), 5.01 (7H, d, *J* = 8.2 Hz, Arb-1), 5.17 (7H, t, *J* = 9.6 Hz, Arb-4), 5.22 (7H, t, *J* = 7.5 Hz, Arb-3), 5.28-5.31 (7H, m, Arb-2), 5.47 (7H, d, *J* = 3.4 Hz, CD-1), 6.83 (14H, d, *J* = 8.9 Hz, Ph), 6.90 (14H, d, *J* = 8.9 Hz, Ph), 7.56 (7H, s, CH_2CCHN); ^{13}C NMR ($CDCl_3$): δ 20.58, 20.63, 20.64, 20.69, 20.72, 20.76 (Ac), 50.2 (CD-6), 61.8 (Arb-6), 62.0 (OCH_2-triazole), 68.3 (Arb-4), 69.8 (CD-5), 69.9 (CD-2), 70.4 (CD-3), 71.2 (Arb-3), 71.8 (Arb-5), 72.8 (Arb-2), 77.2 (CD-4), 96.1 (CD-1), 99.9 (Arb-1), 115.5, 118.5 (Ph), 125.9 (CH_2CCH), 143.6 (CH_2CCH), 151.3, 154.3 (Ph), 169.3, 169.3, 169.4, 170.2, 170.5, 170.6 (C=O); MALDI-TOF MS: *m/z* calcd for $C_{231}H_{273}N_{21}O_{119}$ •Na^+: 5267.58; found 5265.24.

5. Preparation of **8**

A 28% sodium methylate methanol solution (0.3 mL, 0.002 mmol) was added to a solution of **7** (266.2 mg, 0.05 mmol) in MeOH (5 mL). The resulting mixture was stirred for 16 h. The solvent was evaporated under reduced pressure. The crude product was purified by reprecipitation in MeOH to

afford **8** (157.2 mg, 88% yield) as amorphous crystal. (Data of ^{1}H NMR and ^{13}C NMR, see Reference 16)

6. Preparation of **10**

To a solution of **9** (692 mg, 2.98 mmol) in DMF (10 mL) was added triphenylphosphine (1.17 g, 4.47 mmol) and iodine (1.14 g, 4.49 mmol) at 40 ^{o}C under an argon atmosphere. After the reaction mixture was stirred for 24 h, the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica-gel (hexane/ethyl acetate = 8/1) to afford **10** (763.6 mg, 75% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.44 (1H, t, *J* = 1.4 Hz, CH_2CCH), 3.26 (2H, t, *J* = 6.9 Hz, ICH_2), 3.66-3.77 (14H, m, OCH_2CH_2), 4.21 (2H, d, *J* = 1.4 Hz, CH_2CCH); ^{13}C NMR ($CDCl_3$): δ 2.9 (ICH_2), 58.4 (CH_2CCH), 69.0, 70.1, 70.4, 70.5, 70.5, 70.6 (OCH_2CH_2), 71.9 (CH_2CH_2I), 74.5 (CH_2CCH), 79.6 (CH_2CCH).

7. Preparation of **12**

The above similar procedure (preparation of **10**) using **11** (341 mg, 0.83 mmol), triphenylphosphine (654 mg, 2.49 mmol) and iodine (631.1 mg, 2.49 mmol) in DMF (3.5 mL) afforded **12** (368 mg, 85% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.37 (1H, t, *J* = 2.1 Hz, CH_2CCH), 3.19 (2H, t, *J* = 6.8 Hz, ICH_2), 3.58-3.63 (28H, m, OCH_2CH_2), 3.69 (2H, t, *J* = 6.8 Hz, ICH_2CH_2), 4.13 (2H, d, *J* = 2.8 Hz, CH_2CCH); ^{13}C NMR ($CDCl_3$): δ 2.9 (ICH_2), 58.3 (CH_2CCH), 69.1-70.6 (OCH_2CH_2), 71.9 (CH_2CH_2I), 74.5 (CH_2CCH), 79.6 (CH_2CCH).

8. Preparation of **13**

The above similar procedure (preparation of **3**) using sodium salt of **1** (100.6 mg, 0.37 mmol) and **10** (126.4 mg, 0.37 mmol) in DMF (2 ml) afforded **13** (135.8 mg, 76% yield) as a colorless oil. ^{1}H NMR (CD_3OD): δ 2.75 (1H, d, *J* = 1.4 Hz, CH_2CCH), 3.24-3.29 (2H, m, H-3, 5), 3.30-3.34 (2H, m, H-2, 4), 3.52- 3.58 (12H, m, OCH_2CH_2), 3.60 (1H, m, H_a-6), 3.70 (2H, d, *J* = 2.0 Hz, OCH_2CH_2), 3.78 (1H, d, *J* = 12.3 Hz, H_b-6), 3.96 (2H, d, *J* = 2.7 Hz, OCH_2CH_2), 4.07 (2H, s, CH_2CCH), 4.67 (1H, d, *J* = 7.6 Hz, H-1), 6.76 (2H, d, *J* = 6.9 Hz, Ph), 6.95 (2H, d, *J* = 7.6 Hz, Ph); ^{13}C NMR (CD_3OD): δ 59.0 (CH_2CCH), 62.4 (C-6), 69.0, 70.0, 70.8, 71.21 (OCH_2CH_2), 71.25 (C-5), 71.38, 71.42, 71.42, 71.6 (OCH_2CH_2), 74.8 (C-4), 75.9 (CH_2CCH), 77.8 (C-2), 77.9 (C-3), 80.5 (CH_2CCH), 103.1 (C-1), 116.2, 118.9, 153.0, 155.3 (Ph).

9. Preparation of **15**

The above similar procedure (preparation of **3**) using sodium salt of **1** (20.8 mg, 0.076 mmol)) and **12** (37.5 mg, 0.072 mmol) in DMF (1 ml) afforded **15** (29.1 mg, 61% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.47 (1H, t, *J* = 2.0 Hz, CH_2CCH), 3.00 (1H, bs, H-5), 3.30 (1H, d, *J* = 6.9 Hz, H_a-6), 3.36-3.79 (31H, m, OCH_2CH_2, H_b-6), 3.98- 4.04 (2H, m, OCH_2CH_2), 4.18 (2H, d, *J* = 2.0 Hz, CH_2CCH), 4.76 (1H, bs, H-1), 4.89 (1H, bs, H-4), 5.03 (1H, bs, H-2), 5.40 (1H, bs, H-3), 6.75 (2H, d, *J* = 8.9 Hz,

Ph), 6.93 (2H, d, J = 8.9 Hz, Ph); ^{13}C NMR ($CDCl_3$): δ 58.3 (CH$_2$CCH), 61.3 (C-6), 69.0 (OCH$_2$CH$_2$), 69.4 (C-4), 69.7, 70.3, 70.4, 70.4, 70.4, 70.4, 70.6 (OCH$_2$CH$_2$), 73.2 (C-5), 74.7 (CH$_2$CCH), 75.6 (C-2), 76.2 (C-3), 79.6 (CH$_2$$C$CH), 102.0 (C-1), 115.3, 118.3, 151.0, 154.0 (Ph).

10. Preparation of **14**

The above similar procedure (preparation of **4**) using **13** (297.4 mg, 0.61 mmol) and acetic anhydride (10 mL) in pyridine (5 mL) afforded **14** (378.1 mg, 95% yield) as amorphous crystal. ^{1}H NMR ($CDCl_3$): δ 2.03 (3H, s, Ac), 2.04 (3H, s, Ac), 2.08 (3H, s, Ac), 2.09 (3H, s, Ac), 2.43 (1H, t, J = 2.8 Hz, CH$_2$CCH), 3.56-3.73 (12H, m, OCH$_2$CH$_2$), 3.79-3.82 (1H, m, H-5), 3.83-3.84 (2H, m, OCH$_2$CH$_2$), 4.08-4.09 (2H, m, OCH$_2$CH$_2$), 4.16 (1H, dd, J = 2.8 Hz, J = 12.4 Hz, H$_a$-6), 4.20 (2H, d, J = 2.8 Hz, CH_2CCH), 4.29 (1H, dd, J = 5.5 Hz, J = 12.4 Hz, H$_b$-6), 4.95 (1H, d, J = 7.6 Hz, H-1), 5.16 (1H, t, J = 9.6 Hz, H-4), 5.22-5.30 (2H, m, H-2, 3), 6.83 (2H, d, J = 9.0 Hz, Ph), 6.93 (2H, d, J = 8.9 Hz, Ph); ^{13}C NMR ($CDCl_3$): δ 20.61, 20.62, 20.67, 20.7 (Ac), 58.4 (CH$_2$CCH), 61.9 (C-6), 68.0 (OCH$_2$CH$_2$), 68.3 (C-4), 69.1 (OCH$_2$CH$_2$), 69.8 (C-5), 70.4, 70.61, 70.62, 70.64, 70.8 (OCH$_2$CH$_2$), 71.2 (C-2), 72.0 (OCH$_2$CH$_2$), 72.8 (C-3), 74.5 (CH$_2$CCH), 79.7 (CH$_2$$C$CH), 100.3 (C-1), 115.4, 118.6, 151.0, 155.0 (Ph), 169.3, 169.4, 170.3, 170.6 (C=O).

11. Preparation of **16**

The above similar procedure (preparation of **4**) using **15** (29.1 mg, 0.056 mmol) and acetic anhydride (2 mL) in pyridine (1 mL) afforded **16** (32.9 mg, 90% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.03 (3H, s, Ac), 2.04 (3H, s, Ac), 2.08 (3H, s, Ac), 2.09 (3H, s, Ac), 2.45 (1H, t, J = 2.5 Hz, CH$_2$CCH), 3.64-3.73 (28H, m, OCH$_2$CH$_2$), 3.80-3.82 (1H, m, H-5), 3.82-3.85 (2H, m, OCH$_2$CH$_2$), 4.07-4.09 (2H, m, OCH$_2$CH$_2$), 4.16 (1H, dd, J = 2.5 Hz, J = 12.2 Hz, H$_a$-6), 4.20 (2H, d, J = 2.4 Hz, CH_2CCH), 4.29 (1H, dd, J = 5.1 Hz, J = 12.2 Hz, H$_b$-6), 4.95 (1H, d, J = 7.5 Hz, H-1), 5.16 (1H, t, J = 9.2 Hz, H-4), 5.21-5.28 (2H, m, H-2, 3), 6.82 (2H, d, J = 9.0 Hz, Ph), 6.92 (2H, d, J = 9.1 Hz, Ph); ^{13}C NMR ($CDCl_3$): δ 20.6, 20.63, 20.67, 20.73 (Ac), 58.3 (CH$_2$CCH), 61.9 (C-6), 67.9 (OCH$_2$CH$_2$), 68.2 (C-4), 69.0 (OCH$_2$CH$_2$), 69.7 (C-5), 70.3-70.7 (OCH$_2$CH$_2$), 71.1 (C-2), 71.9 (OCH$_2$CH$_2$), 72.7 (C-3), 74.5 (CH$_2$CCH), 79.6 (CH$_2$$C$CH), 100.1 (C-1), 115.3, 118.5, 150.9, 154.8 (Ph), 169.1, 169.2, 170.3, 170.4 (C=O).

12. Preparation of **17**

The above similar procedure (preparation of **7**) using sodium ascorbate (5.7 mg, 0.029 mmol), copper(II) sulfate (9.5 mg, 0.035 mmol), **14** (200.6 mg, 0.306 mmol) and **6** (69.1 mg, 0.036 mmol) in THF (2.4 mL)-H$_2$O (2.4 mL) afforded **17** (221 mg, 94% yield) as amorphous crystal. ^{1}H NMR ($CDCl_3$): δ 1.94-2.08 (126H, m, Ac), 3.51 (1H, t, J = 8.3 Hz, CD-4), 3.62-3.71 (84H, m, OCH$_2$CH$_2$), 3.81-3.82 (21H, m, Arb-5, OCH$_2$CH$_2$), 4.06 (14H, t, J = 4.8 Hz, OCH$_2$-triazole), 4.15 (7H, d, J = 11.6 Hz, Arb-6$_a$), 4.29 (7H, dd, J = 5.5 Hz, J = 12.4 Hz, Arb-6$_b$), 4.47-4.49 (7H, m, CD-5), 4.52-4.57 (14H, m, OCH$_2$CH$_2$), 4.72-4.74 (14H, m, CD-2, CD-6$_a$), 4.85 (7H, d, J = 13.2 Hz, CD-6$_b$), 4.95 (7H, d, J =

7.5 Hz, Arb-1), 5.16 (7H, t, J = 10.3 Hz, Arb-4), 5.21-5.29 (14H, m, Arb-2, 3), 5.37 (7H, t, J = 8.9 Hz, CD-3), 5.50 (7H, d, J = 3.1 Hz, CD-1), 6.82 (14H, d, J = 8.9 Hz, Ph), 6.92 (14H, d, J = 9.0 Hz, Ph), 7.76 (7H, s, $CH_2CC\mathit{H}N$); ^{13}C NMR ($CDCl_3$): δ 20.53, 20.54, 20.56, 20.61, 20.66, 20.70 (Ac), 50.0 (CD-6), 61.9 (Arb-6), 64.4 (OCH_2-triazole), 67.9 (OCH_2CH_2), 68.3 (Arb-4), 69.7 (OCH_2CH_2), 69.9 (CD-5), 69.9 (Arb-5), 70.4 (CD-2), 70.4-70.5 (OCH_2CH_2), 70.7 (CD-3), 70.7 (OCH_2CH_2), 71.2 (Arb-2), 71.9 (OCH_2CH_2), 72.7 (Arb-3), 76.6 (CD-4), 96.3 (CD-1), 100.2 (Arb-1), 115.3, 118.6 (Ph), 125.6 ($CH_2C\mathit{C}H$), 144.8 ($CH_2\mathit{C}CH$), 150.9, 154.9 (Ph), 169.2, 169.3, 169.3, 170.2, 170.3, 170.5 (C=O); MALDI-TOF MS: *m/z* calcd for $C_{287}H_{385}N_{21}O_{147}\bullet Na^+$: 6477.33; found 6479.71.

13. Preparation of **19**

The above similar procedure (preparation of **7**) using sodium ascorbate (0.9 mg, 0.005 mmol), copper(II) sulfate (1.6 mg, 0.006 mmol), **16** (32.9 mg, 0.040 mmol) and **6** (11.3 mg, 0.006 mmol) in THF (0.4 mL)-H_2O (0.4 mL) afforded **19** (40.2 mg, 87% yield) as amorphous crystal. ^1H NMR ($CDCl_3$): δ 2.02 (21H, s, Ac), 2.03 (21H, s, Ac), 2.04 (21H, s, Ac), 2.06 (21H, s, Ac), 2.07 (21H, s, Ac), 2.08 (21H, s, Ac), 3.53 (7H, t, J = 8.2 Hz, CD-4), 3.61-3.72 (196H, m, OCH_2CH_2), 3.80-3.82 (7H, m, Arb-5), 3.82-3.84 (14H, m, OCH_2CH_2), 4.08 (14H, t, J = 4.8 Hz, OCH_2-triazole), 4.16 (7H, dd, J = 2.1 Hz, J = 12.4 Hz, Arb-6_a), 4.29 (7H, dd, J = 5.5 Hz, J = 12.4 Hz, Arb-6_b), 4.43-4.44 (7H, m, CD-5), 4.48-4.52 (14H, m, OCH_2CH_2), 4.69-4.70 (14H, m, CD-2, CD-6_a), 4.81 (7H, d, J = 13.1 Hz, CD-6_b), 4.96 (7H, d, J = 8.3 Hz, Arb-1), 5.16 (7H, t, J = 9.6 Hz, Arb-4), 5.22-5.31 (14H, m, Arb-2, 3), 5.36 (7H, t, J = 9.0 Hz, CD-3), 5.51 (7H, d, J = 2.0 Hz, CD-1), 6.83 (14H, d, J = 9.0 Hz, Ph), 6.93 (14H, d, J = 9.0 Hz, Ph), 7.76 (7H, s, $CH_2CC\mathit{H}N$); ^{13}C NMR ($CDCl_3$): δ 20.5, 20.60, 20.60, 20.65, 20.65, 20.7 (Ac), 49.9 (CD-6), 61.8 (Arb-6), 64.4 (OCH_2-triazole), 67.8 (OCH_2CH_2), 68.2 (Arb-4), 69.7 (CD-5), 69.7 (OCH_2CH_2), 69.9 (Arb-5), 70.2 (CD-2), 70.3-70.5 (OCH_2CH_2), 70.7 (CD-3), 70.7 (OCH_2CH_2O), 71.2 (Arb-2), 71.9 (OCH_2CH_2), 72.7 (Arb-3), 76.4 (CD-4), 96.2 (CD-1), 100.2 (Arb-1), 115.3, 118.6 (Ph), 125.6 ($CH_2C\mathit{C}H$), 144.8 ($CH_2\mathit{C}CH$), 151.0, 154.9 (Ph), 169.2, 169.3, 170.2, 170.2, 170.3, 170.5 (C=O); MALDI-TOF MS: *m/z* calcd for $C_{343}H_{497}N_{21}O_{175}\bullet Na^+$: 7733.05; found 7732.90.

14. Preparation of **18**

The above similar procedure (preparation of **8**) using **17** (124.3 mg, 0.019 mmol) in the presence of NaOMe (0.3 mL of a 28% sodium methylate methanol solution, 0.002 mmol) in MeOH (1 mL)-THF (0.5 mL) afforded **18** (87.8 mg, 97% yield) as amorphous crystal. (Data of ^1H NMR and ^{13}C NMR, see Reference 18)

15. Preparation of **20**

The above similar procedure (preparation of **8**) using **19** (34.7 mg, 0.0045 mmol) in the presence of NaOMe (0.3 mL of a 28% sodium methylate methanol solution, 0.002 mmol) in MeOH (2.5 mL)-THF (2.5 mL) afforded **19** (24.5 mg, 91% yield) as amorphous crystal. (Data of ^1H NMR and ^{13}C NMR, see Reference 19)