Supporting Information

Stereoselective Synthesis of Axially Chiral A-B Ring System of Vancomycin Utilizing Planar Chiral Arene Chromium Complex

Ken Kamikawa,[†,‡] Atsushi Tachibana,[†] Suguru Sugimoto,[†] Motokazu Uemura*,[†,‡]

[†] *Department of Chemistry, Faculty of Integrated Arts and Sciences, Osaka Prefecture University, Sakai, Osaka, 599-8531, (Japan)*

[‡] *Research Institute for Advanced Sciences and Technology, Osaka Prefecture University, Sakai, Osaka 599-8570 (Japan)*

Fax; +81(722)54-9931; E-mail; uemura@ms.cias.osakafu-u.ac.jp

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using an inert gas/vacuum double manifold techniques. All melting points were determined on a Yanagimoto MPJ-2 micromelting point apparatus and were uncorrected. ^{1}H NMR spectra were measured on JEOL ECP-500, EX-270 instrument, and all NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as an internal reference. IR spectra were determined in $CHCl_3$ solution on a JASCO A-100 spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 240C and Perkin-Elmer Model 2400 automatic analyzers. Mass spectra were determined on a JEOL JMS-DX 303 with EI mode. Optical rotations were obtained on a JASCO DIP-370 automatic polarimeter at wavelength 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 3 mL. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use.

Preparation of Cyanohydrin Chromium Complex 10

To a solution of (+)-(2-bromo-3,5-dimethoxybenzaldehyde)chromium complex (**9**) (950 mg, 2.5

mmol) and ZnI_2 (80 mg, 0.13 mmol) in CH_2Cl_2 (50 mL) was added trimethylsilylcyanide (992 mg, 10.0 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 15 min and extracted with CH_2Cl_2. The extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (35% ether in hexane) to give the chromium complex **10** (1.14 g, 95%) as yellow crystals. mp 130 °C; $[\alpha]_D^{29}$ –105.9 (*c* 0.92, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.39 (9H, s), 3.76 (3H, s), 3.90 (3H, s), 5.16 (1H, d, *J* = 2.2 Hz), 5.23 (1H, d, *J* = 2.2 Hz) 5.61 (1H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) 0.32, 56.33, 57.15, 62.83, 65.97, 67.83, 78.20, 106.65, 117.72, 139.84, 140.91, 231.54; IR ($CHCl_3$) 2300, 1975, 1890, 1525, 1320, 1170 cm^{-1}. Anal. Calcd for $C_{16}H_{18}NO_6SiBrCr$: C, 40.01; H, 3.78; N, 2.92. Found: C, 40.26; H, 3.68; N, 2.93.

Preparation of Diol Complex 13

To a solution of the chromium complex **10** (883 mg, 1.83 mmol) in CH_2Cl_2 (30 mL) was added diisobutylaluminum hydride (4.8 mL, 0.95 M in hexane, 4.76 mmol) at -78 °C under argon. The reaction mixture was stirred for 30 min at -78 °C and quenched with saturated aqueous NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and the extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography to give aldehyde **11** (500 mg, 56%). The obtained aldehyde complex was used for next step without further purifucation. To a solution of the aldehyde **11** (500 mg, 1.03 mmol) in ether (30 mL) was added $Zn(BH_4)_2$ (0.6 mL, 1.0 M in THF, 0.6 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (25% ethyl acetate in hexane) to give the alcohol **12** as yellow foam (360 mg, 72%). To a solution of the alcohol **12** (360 mg, 0.74 mmol) in THF (7 mL) was added *n*-tetrabutylammonium fluoride (122 mg, 0.47 mmol) at 0 °C under argon. The reaction mixture was stirred at 25 °C for 20 min and extracted with ethyl acetate, washed with brine, dried over $MgSO_4$. The extract was evaporated under reduced pressure. The residue was purified by silica gel chromatography to give diol chromium complex **13** (166 mg, 62%) as yellow foam. $[\alpha]_D^{27}$ –254.8 (*c* 0.23, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.66 (2H, br), 3.60-3.74 (1H, m), 3.74 (3H, s), 3.89 (3H, s), 4.03-4.07 (1H, m), 5.14 (2H, brs), 5.23 (1H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) 14.27, 56.12, 56.81, 65.99, 68.97, 72.64, 78.74, 110.96, 140.47, 141.65, 232.40; IR ($CHCl_3$) 3000, 1960, 1880, 1530, 1400, 1200 cm^{-1}; MS (relative intensity) *m/z* 411 (M^+, 27), 356 (35), 334 (3), 310 (100); HRMS calcd for $C_{13}H_{13}O_7BrCr$: 411.9250. found: 411.9258.

Preparation of Complex 14

To a solution of the chromium complex **13** (120 mg, 0.29 mmol) in CH_2Cl_2 (8 mL) *tert*-butyldimethylsilyltriflate (77 mg, 0.29 mmol) and triethylamine (59 mg, 0.59 mmol) was added. The reaction mixture was stirred at 25 °C for 15 min, and quenched with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (35% of ethylactate in hexane) to give **14** as yellow foam (133 mg, 87%). $[\alpha]_D^{26}$ –77.3 (*c* 0.44, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.08 (3H, s), 0.11 (3H, s), 0.92 (9H, s), 3.11 (1H, d, *J* = 3.6 Hz), 3.67 (1H, dd, *J* = 10.3, 6.5 Hz), 3.75 (3H, s), 3.90 (3H, s), 4.09 (1H, dd, *J* = 10.3, 3.3 Hz), 5.04-5.06 (1H, m), 5.16 (1H, d, *J* = 2.3 Hz), 5.21 (1H, d, *J* = 2.3 Hz); IR ($CHCl_3$) 3300, 1960, 1880, 1500, 1520, 1200, 840 cm^{-1}; MS (relative intensity) *m/z* 526 (M^+, 4), 472 (70), 442 (38), 411 (8), 387 (39), 364 (35), 347 (20), 305 (62), 291(34), 275 (15), 255 (34), 237 (65), 218 (52), 207 (20), 179 (20), 164 (90), 127 (20), 89 (30), 75 (100); HRMS calcd for $C_{19}H_{27}O_7SiBrCr$: 526.0089. found: 526.0102.

Preparation of *o*-Methoxyphenylboronic acid 15

To a solution of 4-(3'-iodo-4'-methoxyphenyl)-2,2'-dimethyl-oxazolidine-3-carboxylic acid tert-butyl ester (690 mg, 1.6 mmol) in dry THF (15 mL) was added n-BuLi (2.5 mL, 1.6M in hexane, 4.0 mmol) at –78 °C under argon. The resulting mixture was stirred for 40 min and then trimethyl borate (665 mg, 6.4 mmol) was added at –78 °C. The reaxtion mixture was gradually warmed at 25 °C over 4 h and quenched with cold aqueous 1N-HCl solution. The mixture was extracted with ethyl acetate and the extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (25% ethyl acetate in hexane) to give **15** as colorless crystals (460 mg, 82%). mp 107 °C; $[\alpha]_D^{31}$ –28.2 (*c* 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) 1.23-1.90 (15H, m), 3.85 (1H, dd, *J* = 8.9, 6.5 Hz), 3.91 (3H, s), 4.26 (1H, dd, *J* = 8.9, 6.5 Hz), 4.73-4.93 (1H, m), 6.39 (2H, brs), 6.88 (1H, d, *J* = 8.6 Hz), 7.41 (1H, d, *J* = 8.6 Hz), 7.78 (1H, brs); IR ($CHCl_3$) 3000, 1685, 1500, 1380, 1210, 1100 cm^{-1}; Anal. Calcd for $C_{17}H_{26}BNO_6$: C, 58.14; H, 7.46; N, 3.99. Found: C, 58.27; H, 7.80; N, 3.83.

Palladium(0)-Catalyzed Cross-Coupling of 14 to Give *Syn*-Chromium Complex 16.

A mixture of the chromium complex **14** (240 mg, 0.45 mmol), phenylboronic acid **15** (238 mg, 0.09 mmol) and $Pd_2(dba)_3$ (24 mg, 0.02 mmol) in a mixture of aqueous 1.0 M Na_2CO_3 (0.7 mL),

MeOH (2.0 mL) and toluene (2.0 mL) was degassed by three freeze/vacuum/thaw cycles and heated at 80 °C for 10 min under argon. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography with ether/hexane to give *syn*-cross-coupling product **16** (282 mg, 85%) as yellow foam. $[\alpha]_D^{22}$ –124.5 (*c* 0.51, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ –0.16 (6H, s), 0.79 (9H, s), 1.22-1.76 (15H, m), 2.88 (1H, s), 3.25 (1H, d, *J* = 8.1 Hz), 3.41 (1H, d, *J* = 8.1 Hz), 3.61 (3H, s), 3.77 (3H, s), 3.92 (3H, s), 4.22-4.26 (1H, m), 4.47-4.52 (1H, brs), 4.73-4.90 (1H, m), 5.17 (2H, s), 6.94 (1H, d, *J* = 8.6 Hz), 7.04-7.34 (2H, m); IR ($CHCl_3$) 3000, 1950, 1870, 1680, 1540, 1200 cm^{-1}; MS (relative intensity) *m/z* 753 (M^+, 3), 736 (3), 669 (100), 568 (12); HRMS calcd for $C_{36}H_{51}NO_{11}SiCr$: 753.2637. found: 753.2646.

Preparation of Biaryl 17

A solution of the chromium complex **16** (170 mg, 0.23 mmol) in ether (20 mL) was exposed to sunlight until a yellow solution became colorless. The precipitate was filtered off, and the solution was evaporated under reduced pressure and purified by silica gel chromatography to give demetalated compound **17** (89 mg, 73%) as colorless oil. $[\alpha]_D^{20}$ –47.3 (*c* 0.30, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ –0.13 (3H, s), –0.09 (3H, s), 0.81 (9H, s), 1.28-1.75 (15H, m), 2.83 (1H, s), 3.39-3.48 (2H, m), 3.62 (3H, s), 3.73 (3H, s), 3.86 (3H, s), 3.90-3.95 (1H, m), 4.23-4.25 (1H, m), 4.42-4.48 (1H, m), 4.71-4.95 (1H, bs), 6.46 (1H, d, *J* = 2.3 Hz), 6.81 (1H, d, *J* = 2.3 Hz), 6.93-7.10 (2H, m), 7.34 (1H, brs); IR ($CHCl_3$) 3000, 1680, 1380, 1200 cm^{-1}; MS (relative intensity) *m/z* 617 (M^+, 10), 560 (10), 486 (72), 471 (18), 446 (15), 410 (8), 385 (23), 370 (33), 356 (26), 311 (26), 293 (40), 269 (100); HRMS calcd for $C_{33}H_{51}NO_8Si$: 617.3384. found: 617.3378.

Preparation of 18

To a solution of **17** (67 mg, 0.10 mmol) and PPh_3 (52 mg, 0.20 mmol) in dry THF (8 mL) were added diethyl azodicarboxylate (0.08 mL, 40% in toluene, 0.2 mmol) and diphenylphosphorylazide (83 mg, 0.3 mmol) at 0 °C under argon. The reaction mixture was stirred at 0 °C for 2 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give the azide **18** (59 mg, 92%) as colorless foam. $[\alpha]_D^{21}$ 9.1 (*c* 0.13, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ –0.09 (3H, s), –0.07 (3H, s), 0.82 (9H, s), 1.26-1.76 (15H, m), 3.63 (3H, s), 3.68-3.70 (2H, m), 3.71 (3H, s), 3.85 (3H, s), 3.91-3.95 (1H, m), 4.24-4.30 (1H, m), 4.36-4.38 (1H, m), 4.73-4.93 (1H, m), 6.46 (1H, d, *J* = 2.3 Hz),

6.58 (1H, d, J = 2.3 Hz), 6.89-6.93 (1H, m), 6.99-7.14 (1H, m), 7.35 (1H, dd, J = 8.6, 1.9 Hz); IR ($CHCl_3$) 2100, 1720(w), 1680, 1460, 1370, 1210, 1100 cm^{-1}; MS (relative intensity) m/z 642 (M^+, 10), 614 (35), 599 (20), 585 (34), 543 (10), 527 (20), 501 (11), 486 (63), 469 (40), 413 (20), 385 (40), 343 (50), 326 (60), 310 (22), 293 (33), 269 (100); HRMS calcd for $C_{33}H_{50}N_4O_7Si$: 642.3449. found: 642.3440.

Preparation of 19

To a solution of **18** (57 mg, 0.083 mmol) in THF (5 mL) was added *n*-tetrabutylammonium fluoride (0.12 mL, 0.13 mmol) at 25 °C under argon. The reaction mixture was stirred for 1 h and extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$. The extract was evaporated under reduced pressure. The residue was purified by silica gel chromatography (50% ethyl acetate in hexane) to give an alcohol **19** as a colorless foam (36 mg, 83%). $[\alpha]_D^{23}$ –32.7 (*c* 0.42, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.23-1.75 (15H, m), 2.55 (1H, brs), 3.60 (2H, m), 3.65 (3H, s), 3.71 (3H, s), 3.87 (3H, s), 3.92 (1H, dd, J = 9.0, 3.0 Hz), 4.24 (1H, dd, J = 9.0, 6.5 Hz), 4.42-4.46 (1H, m), 4.74-4.89 (1H, m), 6.51 (1H, d, J = 9.0, 6.5 Hz), 6.59 (1H, d, J = 2.4 Hz), 6.93 (1H, d, J = 8.6 Hz), 6.99-7.08 (1H, m), 7.35 (1H, d, J = 8.6 Hz); IR ($CHCl_3$) 3000, 2100, 1680, 1380, 1200 cm^{-1}; MS (relative intensity) m/z 528 (M^+, 12), 439 (35), 413 (12), 311 (12), 287 (18), 186 (32), 154 (100); HRMS calcd for $C_{27}H_{36}N_4O_7$: 528.2584. found: 528.2606.

Preparation of 20

To a solution of the alcohol **19** (36 mg, 0.07 mmol) in DMF (5.0 mL) was added NaH (5 mg, 60% oil, 0.14 mmol) at 25 °C. To the resulting suspension was stirred for 5 min at 25 °C and benzylbromide (17 mg, 0.14 mmol) was added and the reaction mixture was stirred for 10 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution, and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (25% ethyl acetate in hexane) to give benzyl ether **20** (43 mg, 93%) as colorless oil. $[\alpha]_D^{23}$ –6.8 (*c* 0.30, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.26-1.76 (15H, m), 3.44-3.47 (2H, m), 3.52 (3H, s), 3.52-3.56 (1H, m), 3.63 (3H, s), 3.84 (3H, s), 3.88-3.95 (1H, m), 4.26 (1H, dd, J = 8.9, 6.5 Hz), 4.40 (1H, brs), 4.47-4.53 (1H, m), 4.71-4.91 (1H, m), 6.47 (1H, d, J = 2.3 Hz), 6.58 (1H, d, J = 2.3 Hz), 6.82-6.85 (1H, m), 6.99-7.12 (1H, m) 7.24-7.37 (6H, m); MS (relative intensity) m/z 618 (M^+, 8), 590 (14), 535 (13), 519 (8), 481 (40), 469 (15), 462 (8), 418 (8), 311 (7), 270 (13), 154 (20), 136 (14), 91 (100); HRMS calcd for $C_{34}H_{42}N_4O_7$: 618.3053. found: 618.3060.

Preparation of 21

To a solution of the benzyl ether **20** (135 mg, 0.21 mmol) in MeOH (20 mL) was added *p*-TsOH (40 mg, 0.21 mmol) at 25 °C, and stirred for 3h at 25 °C. The solution was extracted with ethyl acetate, washed with brine. The extract was dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (25 % ethyl acetate in hexane) to give the alcohol **21** (83 mg, 85 %) as colorless foam. $[\alpha]_D^{22}$ -2.2 (*c* 0.44, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.29 (9H, s), 2.72 (1H, bs), 3.54 (3H, s), 3.55-3.58 (2H, m), 3.62 (3H, s), 3.84 (4H, s), 4.40 (1H, d, *J* = 12.2 Hz), 4.48-4.53 (2H, m), 4.77 (1H, bs), 5.19-5.21 (1H, m), 6.49 (1H, d, *J* = 2.4 Hz), 6.57 (1H, d, *J* = 2.4 Hz), 6.89 (1H, d, *J* = 8.6 Hz), 7.02 (1H, d, *J* = 2.4 Hz), 7.24-7.34 (6H, m); IR ($CHCl_3$) 2100, 1690, 1540, 1200, 1040 cm^{-1}; MS (relative intensity) *m/z* 578 (M^+, 2), 547 (63), 491 (5), 447 (100); HRMS calcd for $C_{31}H_{38}N_4O_7$ 578.2741, found 578.2741.

Preparation of 23

A solution of **21** (30 mg, 0.053 mmol) in acetone (0.2 mL) at 0 °C was added to an aqueous 5% $NaHCO_3$ solution (0.2 mL), and additional acetone (0.2 mL), was added until stirring became possible. This heterogeneous mixture was treated sequentially with KBr (1 mg, 0.0050 mmol) and TEMPO (18 mg, 0.064 mmol). Soduim hypochloride (NaOCl, 5% solution, 0.2 mL, 0.10 mmol) was added dropwise and mixture was stirred for 1h. After 1h, additional NaOCl (0.1 mL) was added. The reaction mixture was stirred for 1h and extracted with ethyl acetate, washed with brine. The extract was dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give crude **22.** The unpurified acid **22** was diluted with DME (10 mL) and treated with an excess of CH_2N_2. The excess of CH_2N_2 was removed by bubbling N_2 through the solution. The solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography (25 % ethyl acetate in hexane) to give **23** (16 mg, 53 %) as colorless foam. $[\alpha]_D^{19}$ -19.0 (*c* 0.29, $CHCl_3$); ^1H NMR (270 MHz, acetone-d^6) δ 1.39 (9H, s), 3.49-3.50 (1H, m), 3.56-3.60 (1H, m), 3.59 (3H, s), 3.65 (6H, s), 3.84 (3H, s), 4.35 (2H, s), 4.62 (1H, dd, *J* = 9.2, 3.0 Hz), 5.29 (1H, d, *J* = 8.0 Hz), 6.58 (1H, d, *J* = 2.5 Hz), 6.63 (1H, d, *J* = 2.5 Hz), 6.67 (1H, d, *J* = 6.0 Hz), 7.01 (1H, d, *J* = 8.5 Hz), 7.16 (1H, d, *J* = 2.0 Hz), 7.21-7.32 (5H, m), 7.43 (1H, dd, *J* = 8.5, 2.0 Hz); MS (relative intensity) *m/z* 606 (M^+, 8), 578 (22), 547 (28), 507 (5), 491 (10), 447 (100); HRMS calcd for $C_{32}H_{38}N_4O_8$: 606.2687. found: 606.2693.

Palladium(0)-Catalyzed Cross-Coupling of *Ent*-(–)-9 to Give *Anti*-Chromium Complex 24.

A mixture of (–)-*ent*-**9** (1.3 g, 2.95 mmol), phenylboronic acid **15** (1.3 g, 3.72 mmol), $Pd_2(dba)_3$ (153 mg, 0.15 mmol) and (*o*-tolyl)$_3$P (180 mg, 0.59 mmol) in aqueous 1.0 M Na_2CO_3 (1.0 mL), MeOH (3.0 mL) and toluene (3.0 mL) was degassed and refluxed for 30 min under argon. The solvent was evaporated *in vacuo*. The residue was extracted with ethyl acetate, and the extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (25% ethyl acetate in hexane) to give *anti*-cross-coupling product **24** (1.29 g, 72%) as red foam. $[\alpha]_D^{22}$ –223.1 (*c* 0.26, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.26-1.79 (15H, m), 3.70 (3H, s), 3.72 (3H, s), 3.77 (3H, s), 3.89-3.96 (1H, m), 4.30 (1H, dd, *J* = 8.9, 6.8 Hz), 4.82-4.93 (1H, m), 5.23 (1H, d, *J* = 1.9 Hz), 5.35 (1H, d, *J* = 1.9 Hz), 6.88 (1H, d, *J* = 8.1 Hz), 7.34 (1H, d, *J* = 8.1 Hz), 7.46 (1H, bs), 9.48 (1H, brs); IR ($CHCl_3$) 1970, 1900, 1690, 1380 cm^{-1}; MS (relative intensity) *m/z* 607 (M^+, 11), 523 (70), 501 (3), 452 (4), 422 (18), 407 (8), 392 (37), 356 (100); HRMS calcd for $C_{29}H_{33}NO_{10}Cr$: 607.1515. found: 607.1512.

Preparation of Epoxide Complex 25

To a solution of the complex **24** (500 mg, 0.80 mmol) and chloroiodomethane (155 mg, 0.90 mmol) in dry THF (5.0 mL) was slowly added MeLi (0.70 mL, 1.1M in ether, 0.80 mmol) at -78 °C under argon. The reaction mixture was warmed to 25 °C and stirred for 20 min. The solution was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The extract was washed with brine and dried over anhydrous $MgSO_4$ evaporated under reduced pressure. The residue was purified by silica gel chromatography (25% ethyl acetate in hexane) to give the complex epoxide complex **25** (363 mg, 73%). $[\alpha]_D^{31}$ 24.9 (*c* 0.53, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.17-1.81 (15H, m), 2.63-2.65 (1H, m), 2.84 (1H, brs), 3.44-3.48 (1H, m), 3.65-3.89 (10H, m), 4.29 (1H, dd, *J* = 8.9, 6.6 Hz), 4.76 (1H, s), 4.82-4.90 (1H, m), 5.13 (1H, s), 6.87 (1H, d, *J* = 8.4 Hz), 7.31-7.36 (1H, m), 7.45 (1H, s); IR ($CHCl_3$) 1960, 1870, 1680, 1540, 1380, 1200, 1040 cm^{-1}; MS (relative intensity) *m/z* 621 (M^+, 13), 605 (3), 537 (32), 521 (20), 481 (40), 469 (12), 450 (8), 437 (38), 422 (100); HRMS calcd for $C_{30}H_{35}NO_{10}Cr$: 621.1665. found: 621.1669.

Preparation of 26

To a solution of epoxide complex **25** (600 mg, 1.02 mmol) and trimethylsilyl azide (235 mg, 2.04 mmol) in THF (3.0 mL), was added $BF_3{\cdot}OEt_2$ (290 mg, 2.04 mmol) at –10 °C under argon. The reaction mixture was stirred for 1 h at -10 °C, and extracted with ethyl acetate, washed with brine. The extract was dried over anhydrous $MgSO_4$, and evaporated under reduced

pressure. The residue was purified by silica gel chromatography (25 % ethyl acetate in hexane) to give the azide complex **26** (541 mg, 80 %) as yellow foam. $[\alpha]_D^{17}$ 39.5 (*c* 0.40, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.20-1.78 (15H, m), 2.80 (1H, bs), 3.42 (2H, bs), 3.62 (4H, s), 3.74 (3H, s), 3.80 (3H, s), 3.88 (1H, dd, *J* = 9.2, 4.9 Hz), 4.26-4.32 (2H, m), 4.86-4.92 (1H, m), 5.14 (1H, dd, *J* = 1.9 Hz), 6.88 (1H, d, *J* = 8.6 Hz), 7.28-7.36 (2H, m); IR ($CHCl_3$) 2100, 1950, 1870, 1725, 1670, 1540, 1460, 1390, 1250 cm^{-1}. MS (relative intensity) *m/z* 664 (M^+, 7), 552 (57), 522 (17), 481 (5), 466 (32), 453 (23), 422 (100); HRMS calcd for $C_{30}H_{36}N_4O_{10}Cr$: 664.1831. found: 664.1844.

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