Enantioselective cis-β-Lactam Synthesis by Intramolecular C-H Functionalization from Enoldiazoacetamides and Derivative Donor-Acceptor Cyclopropenes

Xinfang Xu,*^a Yongming Deng,^b David N. Yim,^b Peter Y. Zavalij,^b and Michael P. Doyle*^b

^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

^b Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742 U.S.A.

Supporting Information

- S2-6 General Procedures for the Preparation of Enoldiazoacetates 1
- S6-15 General Procedure for Enantioselective C-H Functionalization of 1
- S16 Procedure for Reactions of Donor-Acceptor Cyclopropene 6 with Copper(I) and Silver(I) Catalysts
- S17 Procedure for Acidic Hydrolysis of β-Lactams 3c
- S18 Procedure for Enantioselective C-H Functionalization of 4a
- S18 References
- S19 Proton NMR Spectral Observation of Cyclopropene 6c
- S20 Chemoselectivity Determination by ¹H NMR Spectrum of the Reaction Mixture
- S21-50 NMR Spectra of 1, 2c, 3 and 5
- S51-62 HPLC Analyses of 3 and 5
- S63 Data Collection and Structure Refinement for (3*S*,4*R*)-3i

General Information

All reactions were performed in oven-dried (140 °C) glassware under an atmosphere of dry N₂. DCM (dichloromethane), DCE (1,2-dichloroethane) and toluene were distilled prior to use kept over activated 3 Å molecular sieves. TBME (*tert*-butyl methyl ether), DMB (2,2-dimethylbutane) and DCCl₃ were purchased from Sigma Aldrich and used without further treatment. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed with a UV lamp (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Enantioselectivity was determined on an Agilent 1200 Series HPLC using Daicel Chiralcel IB-3, AD-H and OD-H columns. Optical rotation was recorded on JASCO DIP-1000 digital polarimeter. High-resolution mass spectra (HRMS) were performed on a TOF-CS mass spectrometer using CsI as the standard.

Materials

 $Rh_2(S-DOSP)_4$ was purchased from Strem Chemicals. $Rh_2(esp)_2$ was purchased from Sigma Aldrich, and all other dirhodium carboxylates catalysts were prepared according to literature procedures.¹ The diazoacetamides **1** were prepared according to the literature procedures.²

General Procedure for the Preparation of Enoldiazoacetamides 1.²



Synthesis of S-1: To a 100-mL oven-dried flask containing a magnetic stirring bar, aldehyde (10 mmol) and amine (10 mmol) in EtOH (20 mL), was added anhydrous

Na₂SO₄ (10 g). After the reaction mixture was stirred at room temperature overnight, Na₂SO₄ was filtered, and the solid was washed with MeOH (10 mL). The combined organic phase was cooled to 0 °C in an ice bath, and NaBH₄ (10 mmol, 378 mg) was added in portions over 30 min. The mixture was then stirred for another 2 hours at room temperature [monitored by thin layer chromatography (TLC) until all the material was consumed]. The reaction was quenched by addition of saturated aqueous NaHCO₃ (20 mL) with stirring for 10 min, then extracted with EtOAc (60 mL). The organic phase was washed twice with saturated aqueous NaCl (40 mL X 2) and then dried over anhydrous Na₂SO₄. After evaporating the solvents, 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (TMD, 11 mmol, 1.56 g) and toluene (40 mL) were added, and the reaction mixture was refluxed at 110-120 °C for 2 hours [monitored by thin layer chromatography (TLC) until all the material was consumed]. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography to obtain **S-1** in 50-80 % yield.

<u>Synthesis of S-2</u>: To a 100-mL oven-dried flask containing a magnetic stirring bar, S-1 and *p*-ABSA (1.1 eq) in CH₃CN (50 mL/10 mmol) was added Et₃N (1.5 eq) slowly at 0 °C, and the resulting reaction mixture was stirred at room temperature overnight. Ether (30 mL) was then added, and the sulfonamide solid formed during the reaction was filtered through Celite. The solid was washed with ether (30 mL), and the ether washing was combined with the filtrate. The combined organic solution was washed with saturated aqueous NH₄Cl (50 mL), followed by saturated aqueous NaCl (50 mL), saturated aqueous NaHCO₃ (50 mL) and saturated aqueous NaCl (50 mL), then dried over anhydrous Na₂SO₄. After evaporating the solvents, the residue was purified by column chromatography and further purified by recrystallization from ether and hexanes to give pure S-2 in 40-60% yield. (For the NMR data of compounds S-2b^{2b}, S-2c^{2a}, S-2f and S-2g^{2c}, see reported references)

<u>Synthesis of 1</u>: To a 100-mL oven-dried flask containing a magnetic stirring bar, diazo compound **S-2** (2 mmol) and Et₃N (1.5 eq, 0.45 mL) in DCM (10 mL) was added TBSOTf (1.1 eq, 0.5 mL) slowly at 0 °C, then the reaction mixture was stirred for 0.5-1 h. Hexanes (30 mL) were added followed by saturated aqueous NaHCO₃ (40 mL), and the

organic phase was separated and washed two more times with saturated aqueous NaHCO₃ (40 mL X 2), then dried over anhydrous Na₂SO₄. After evaporating the solvents, the residue was used directly to assess its catalytic intramolecular reactions without further purification (>95% pure). Further purification by recrystallization using hexane gave the results presented below with >71% yield.

N-(tert-Butyl)-3-[(tert-butyldimethylsilyl)oxy]-2-diazo-N-(4-methoxybenzyl)but-3-

enamide (1a): 74% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.52 (s, 2H), 4.41 (d, J = 2.1 Hz, 1H), 4.16 (d, J = 2.1 Hz, 1H), 3.78 (s, 3H), 1.36 (s, 9H), 0.89 (s, 9H), 0.18 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 166.9, 158.7, 144.0, 131.2, 127.9, 113.8, 88.7, 58.0, 55.1, 50.4, 28.7, 25.5, 18.0, -4.9; HRMS (ESI) calculated for C₂₂H₃₆N₃O₃Si [M+H]⁺: 418.2520; found: 418.2523.

N-Benzyl-*N*-(*tert*-Butyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-diazobut-3-enamide (1b): 72% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.38-6.91 (comp, 5H), 4.60 (s, 2H), 4.42 (d, *J* = 2.1 Hz, 1H), 4.17 (d, *J* = 2.1 Hz, 1H), 1.39 (s, 9H), 0.90 (s, 9H), 0.19 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.9, 144.0, 139.4, 128.5, 127.2, 126.7, 88.7, 58.2, 51.0, 28.8, 25.5, 18.0, -4.8; HRMS (ESI) calculated for C₂₁H₃₄N₃O₂Si [M+H]⁺: 388.2415; found: 388.2451.

N-(tert-Butyl)-3-[(tert-butyldimethylsilyl)oxy]-2-diazo-N-(4-chlorobenzyl)but-3-

enamide (1c): 88% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.50 (s, 2H), 4.37 (d, *J* = 2.1 Hz, 1H), 4.12 (d, *J* = 2.1 Hz, 1H), 1.32 (s, 9H), 0.84 (s, 9H), 0.13 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.1, 143.8, 138.0, 133.0, 128.7, 128.1, 89.1, 58.3, 50.3, 28.8, 25.5, 18.0, -4.8; HRMS (ESI) calculated for C₂₁H₃₃ClN₃O₂Si [M+H]⁺: 422.2025; found: 422.2062.

*N-(tert-*Butyl)-3-[(triisopropylsilyloxy)vinyl]-2-diazo-*N-*(4-chlorobenzyl)but-3-

enamide (1c'): 92% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 4.55 (s, 2H), 4.40 (d, J = 2.2 Hz, 1H), 4.17 (d, J = 2.2 Hz, 1H), 1.39 (s, 9H), 1.25-1.18 (m, 3H), 1.07 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz): δ 167.5, 144.2,

138.2, 133.2, 129.0, 128.3, 88.5, 58.5, 50.5, 29.0, 18.1, 12.8; HRMS (ESI) calculated for C₂₄H₃₉ClN₃O₂Si [M+H]⁺: 464.2495; found: 464.2477.

*N-(tert-*Butyl)-3-[(*tert-*butyldimethylsilyl)oxy]-2-diazo-*N-*(4-methylbenzyl)but-3-

enamide (1d): 79% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.11 (s, 4H), 4.55 (s, 2H), 4.42 (d, J = 2.0 Hz, 1H), 4.16 (d, J = 2.0 Hz, 1H), 2.31 (s, 3H), 1.38 (s, 9H), 0.89 (s, 9H), 0.18 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.9, 144.1, 136.9, 136.3, 129.2, 126.7, 88.7, 58.2, 50.8, 28.8, 25.5, 21.0, 18.0, -4.8; HRMS (ESI) calculated for C₂₂H₃₆N₃O₂Si [M+H]⁺: 402.2571; found: 402.2578.

N-(tert-Butyl)-3-[(tert-butyldimethylsilyl)oxy]-2-diazo-N-(4-fluorobenzyl)but-3-

enamide (1e): 87% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.32 (comp, 4H), 4.85 (s, 2H), 4.45 (d, J = 1.9 Hz, 1H), 4.18 (d, J = 1.9 Hz, 1H), 1.42 (s, 9H), 0.84 (s, 9H), 0.13 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.1, 162.0 (d, J = 244.0 Hz), 143.9, 135.1 (d, J = 3.1 Hz), 128.3 (d, J = 8.1 Hz), 115.5 (d, J = 22.0 Hz), 89.0, 58.2, 50.2, 28.8, 25.5, 18.0, -4.8; HRMS (ESI) calculated for C₂₁H₃₃FN₃O₂Si [M+H] ⁺: 406.2321; found: 406.2333.

N-(4-Bromobenzyl)-*N*-(*tert*-butyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-diazobut-3-

enamide (1f): 88% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.50 (s, 2H), 4.38 (d, *J* = 2.1 Hz, 1H), 4.14 (d, *J* = 2.1 Hz, 1H), 1.35 (s, 9H), 0.86 (s, 9H), 0.16 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 143.8, 138.5, 131.6, 128.4, 121.0, 89.0, 58.3, 50.3, 28.8, 25.5, 18.0, -4.8; HRMS (ESI) calculated for C₂₁H₃₃BrN₃O₂Si [M+H] ⁺: 466.1520; found: 466.1513.

N-(tert-Butyl)-3-[(tert-butyldimethylsilyl)oxy]-2-diazo-N-(4-nitrobenzyl)but-3-

enamide (1g): 90% yield; ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 4.63 (s, 2H), 4.36 (d, J = 2.1 Hz, 1H), 4.11 (d, J = 2.1 Hz, 1H), 1.35 (s, 9H), 0.80 (s, 9H), 0.10 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.1, 147.2, 147.1, 143.5, 127.3, 123.8, 89.5, 58.5, 50.1, 28.8, 25.4, 18.0, -4.9; HRMS (ESI) calculated for C₂₁H₃₃N₄O₄Si [M+H] ⁺: 433.2266; found: 433.2255.

N-[(1,1'-Biphenyl)-4-ylmethyl]-*N*-(*tert*-butyl)-3-[(tert-butyldimethylsilyl)oxy]-2-

diazobut-3-enamide (**1h**): 80% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.26 (comp, 9H), 4.63 (s, 2H), 4.47 (d, *J* = 2.1 Hz, 1H), 4.21 (d, *J* = 2.1 Hz, 1H), 1.47 (s, 9H), 0.95 (s, 9H), 0.12 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 144.0, 140.5, 140.1, 138.5, 128.7, 127.3, 127.2, 127.2, 126.9, 88.8, 58.3, 50.7, 28.8, 25.5, 18.0, -4.8; HRMS (ESI) calculated for C₂₇H₃₈N₃O₂Si [M+H] ⁺: 464.2728; found: 464.2700.

N-(*tert*-Butyl)-3-[(*tert*-butyldimethylsilyl)oxy]-2-diazo-*N*-[4-(dimethylamino)benzyl]but-3-enamide (1i): 71% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.51 (s, 2H), 4.43 (d, *J* = 2.0 Hz, 1H), 4.16 (d, *J* = 2.0 Hz, 1H), 2.92 (s, 6H), 1.37 (s, 9H), 0.90 (s, 9H), 0.20 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.8, 149.8, 144.2, 127.8, 126.7, 112.5, 88.5, 58.0, 50.7, 40.5, 28.8, 25.6, 18.0, -4.8; HRMS (ESI) calculated for C₂₃H₃₉N₄O₂Si [M+H] ⁺: 431.2837; found: 431.2825.

General Procedure for Enantioselective C-H Functionalization of 1.

To an 10-mL oven-dried vial containing a magnetic stirring bar, $Rh_2(S-PTTL)_4$ (2.0 mol%, 5.0 mg) in DMB (0.5 mL), was added enoldiazoacetamide **1** (0.20 mmol) in DMB (0.5 mL) over 10 min via a syringe pump at 0 °C. The reaction mixture was stirred for the indicated time under this condition. After the reaction was complete, the reaction mixture was directly purified by column chromatography on silica gel without any additional treatment (eluent: hexanes:EtOAc = 100:0 to 90:10) to give pure β -lactams **3** in >80% yield with high to excellent enantioselectivity.



MeO 2-*tert*-Butyl-8a-[1-(*tert*-butyldimethylsilyloxy)vinyl]-6-methoxyl-2,3-dihydrocyclohepta[c]pyrrol-1(8aH)-one (2a). ¹H NMR (CDCl₃, 400 MHz) δ 6.13 (dd, J = 10.7, 2.0 Hz, 1H), 6.11-6.04 (m, 1H), 5.69 (d, J = 10.7 Hz, 1H), 5.64-5.56 (m, 1H), 4.26 (dd, *J* = 14.2, 1.4 Hz, 1H), 4.21 (d, *J* = 1.9 Hz, 1H), 4.11 (dd, *J* = 14.2, 1.4 Hz, 1H), 4.08 (d, *J* = 1.9 Hz, 1H), 3.57 (s, 3H), 1.42 (s, 9H), 0.87 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H).



Cl **2-tert-Butyl-8a-[1-(tert-butyldimethylsilyloxy)vinyl]-6-chloro-2,3dihydrocyclohepta[c]pyrrol-1(8aH)-one (2c).** White solid, mp = 79.8 °C - 84.1 °C. ¹H NMR (CDCl₃, 400 MHz) δ 6.57 (d, *J* = 6.8 Hz, 1H), 6.29 (dd, *J* = 10.4 Hz, *J* = 1.2 Hz, 1H), 6.12 (dt, *J* = 6.8 Hz, 2.0 Hz, 1H), 5.59 (d, *J* = 10.4 Hz, 1H), 4.29 (d, *J* = 15.2 Hz, 1H), 4.24 (d, *J* = 2.0 Hz, 1H), 4.17 (d, *J* = 15.2 Hz, 1H), 4.13 (d, *J* = 2.0 Hz, 1H), 1.44 (s, 9H), 0.87 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 173.3, 152.7, 134.4, 134.1, 128.8, 127.6, 126.2, 117.6, 91.2, 60.3, 54.5, 49.8, 27.6, 25.7, 18.1, -4.4, -5.3; HRMS (ESI) calculated for C₂₁H₃₃ClNO₂Si [M+H]⁺: 394.1964; found: 394.1966.



MeO **8a-[1-(***tert***-butyldimethylsilyloxy)vinyl]-2-(4-fluorophenyl)-6methoxy-2,3-dihydrocyclohepta[c]pyrrol-1(8a***H***)-one (2o). ¹H NMR (CDCl₃, 400 MHz) δ 7.70-7.59 (m, 2H), 7.08 (dd, J = 9.2, 8.4 Hz, 2H), 6.39 (d, J = 8.4 Hz, 2H), 6.23 (d, J = 8.4 Hz, 2H), 4.07 (s, 2H), 3.44 (s, 3H), 2.39 (s, 2H), 0.95 (s, 9H), 0.22 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 164.6, 159.6 (d, J = 243.7 Hz), 156.3, 139.8, 136.33 (d, J = 2.8 Hz), 133.5, 121.78 (d, J = 7.8 Hz), 118.3, 115.83 (d, J = 22.3 Hz), 57.6, 52.5, 40.5, 26.3, 18.9, -3.6; HRMS (ESI) calculated for C₂₄H₃₁FNO₃Si [M+H]⁺: 428.2052; found: 428.2019.**



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(4-methoxyphenyl)azetidin-2-one (3a). 85% yield; 92% *ee*; $[\alpha]_D^{20} = +41.8^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: IB-3 column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 98.5:1:0.5, t_r = 10.5, 11.3 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.27 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 4.48 (s, 1H), 4.06 (d, *J* = 1.4 Hz, 1H), 3.95 (d, *J* = 5.8 Hz, 1H), 3.79 (s, 3H), 1.26 (s, 9H), 0.72 (s, 9H), -0.03 (s, 3H), -0.32 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.9, 159.6, 151.2, 129.7, 129.1, 113.4, 93.1, 59.9, 57.7, 55.5, 54.5, 28.3, 25.7, 17.9, -4.9, -5.4; HRMS (ESI) calculated for C₂₂H₃₆NO₃Si [M+H]⁺: 390.2459; found: 390.2455.



(3S,4R)-1-(tert-Butyl)-3-[1-(tert-butyldimethylsilyloxy)vinyl]-4-

phenylazetidin-2-one (3b). Catalyzed by Rh₂(*S*-NTTL)₄ instead of Rh₂(*S*-PTTL)₄: 81% yield; 87% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.4 mL/min, hexanes:IPA = 99:1, t_r = 13.1, 14.7 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.37-7.30 (m, 2H), 7.26-7.24 (m, 3H), 4.78 (d, *J* = 5.8 Hz, 1H), 4.51-4.45 (s, 1H), 4.03 (d, *J* = 1.6 Hz, 1H), 3.98 (d, *J* = 5.8 Hz, 1H), 1.26 (s, 9H), 0.70 (s, 9H), -0.06 (s, 3H), -0.38 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.8, 150.9, 137.5, 128.0, 127.8, 93.1, 59.9, 58.1, 54.5, 28.3, 25.6, 17.8, -5.0, -5.6; HRMS (ESI) calculated for C₂₁H₃₄NO₂Si [M+H]⁺: 360.2353; found: 360.2365.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(4-chlorophenyl)azetidin-2-one (3c). 88% yield; 93% *ee*; $[\alpha]_D^{20} = +67.8^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.4 mL/min, hexanes:IPA = 98:2, t_r = 11.2, 12.4 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.31-7.25 (m, 4H), 4.76 (d, *J* = 5.8 Hz, 1H), 4.52-4.45 (m, 1H), 4.06 (d, *J* = 1.6 Hz, 1H), 3.98 (d, *J* = 5.8 Hz, 1H), 1.26 (s, 9H), 0.72 (s, 9H), -0.02 (s, 3H), -0.30 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.7, 150.7, 136.4, 133.9, 129.3, 128.1, 93.6, 60.0, 57.4, 54.8, 28.4, 25.7, 18.0, -4.9, -5.4; HRMS (ESI) calculated for C₂₁H₃₃ClNO₂Si [M+H]⁺: 394.1964; found: 394.1981.



(3S,4R)-1-(tert-Butyl)-3-[1-(triisopropylsilyloxy)vinyl]-4-(4-

chlorophenyl)azetidin-2-one (**3c'**). 84% yield; 92% *ee*; HPLC conditions for determination of enantiomeric excess: IC column, 190 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 11.1, 11.6 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71-7.01 (m, 4H), 4.78 (d, *J* = 5.9 Hz, 1H), 4.51 (d, *J* = 1.3 Hz, 1H), 4.11 (d, *J* = 1.3 Hz, 1H), 4.03 (d, *J* = 5.9 Hz, 1H), 1.28 (s, 9H), 1.01-0.92 (m, 3H), 0.90-0.84 (m, 18H); ¹³C NMR (CDCl₃, 100 MHz): 166.8, 150.8, 136.5, 134.0, 129.3, 128.2, 93.8, 60.1, 57.5, 54.8, 18.1, 17.9, 12.5; HRMS (ESI) calculated for C₂₄H₃₉ClNO₂Si [M+H]⁺: 436.2433; found: 436.2410.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(4-methylphenyl)azetidin-2-one (3d). 92% yield; 93% *ee*; $[\alpha]_D^{20} = +67.9^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 98:1:1, t_r = 10.8, 11.9 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.73 (d, *J* = 5.8 Hz, 1H), 4.44-4.43 (m, 1H), 4.01 (d, *J* = 1.4 Hz, 1H), 3.93 (d, *J* = 5.8 Hz, 1H), 2.28 (s, 3H), 1.24 (s, 9H), 0.68 (s, 9H), -0.08 (s, 3H), -0.38 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.8, 151.0, 137.6, 134.5, 128.5, 127.9, 93.0, 59.9, 57.9, 54.5, 28.3, 25.6, 21.2, 17.9, -5.0, -5.7; HRMS (ESI) calculated for C₂₂H₃₆NO₂Si [M+H]⁺: 374.2510; found: 374.2540.



(3S,4R)-1-(tert-Butyl)-3-[1-(tert-butyldimethylsilyloxy)vinyl]-4-(4-

fluorophenyl)azetidin-2-one (3e). 88% yield; 91% *ee*; $[\alpha]_D^{20} = +68.0^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 99:0.5:0.5, t_r = 9.7, 11.8 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36-7.29 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.79 (d, *J* = 5.8 Hz, 1H), 4.52-4.47 (m, 1H), 4.07 (d, *J* = 1.6 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 1H), 1.27 (s, 9H), 0.73 (s, 9H), -0.01 (s, 3H), -0.29 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.8, 162.8 (d, *J* = 246.0 Hz), 150.8, 133.5 (d, *J* = 3.1 Hz), 129.6 (d, *J* = 8.1 Hz), 114.8 (d, *J* = 21.6 Hz), 93.5, 60.0, 57.4, 54.7, 28.4, 25.6, 17.9, -5.0, -5.4; HRMS (ESI) calculated for C₂₁H₃₃FNO₂Si [M+H]⁺: 378.2259; found: 378.2243.



(3S,4R)-4-(4-Bromophenyl)-1-(tert-butyl)-3-[1-(tert-

butyldimethylsilyloxy)vinyl]azetidin-2-one (3f). 89% yield; 89% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 99:0.5:0.5, t_r = 10.3, 12.4 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.76 (d, *J* = 5.8 Hz, 1H), 4.52-4.45 (m, 1H), 4.08 (d, *J* = 1.6 Hz, 1H), 3.99 (d, *J* = 5.8 Hz, 1H), 1.28 (s, 9H), 0.73 (s, 9H), -0.01 (s, 3H), -0.28 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.7, 150.7, 136.9, 131.0, 129.7, 122.0, 93.6, 60.0, 57.4, 54.8, 28.4, 25.7, 18.0, -4.9, -5.4; HRMS (ESI) calculated for C₂₁H₃₃BrNO₂Si [M+H]⁺: 438.1458; found: 438.1443.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(4-nitrophenyl)azetidin-2-one (3g). 88% yield; 83% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 98:0.5:1.5, t_r = 11.5, 12.7 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.15 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.52-4.45 (m, 1H), 4.07-4.01 (comp, 2H), 1.26 (s, 9H), 0.69 (s, 9H), -0.05 (s, 3H), -0.34 (s, 3H).; ¹³C NMR (CDCl₃, 100 MHz): 166.3, 150.2, 147.8, 145.6, 128.7, 123.0, 94.2, 60.3, 57.0, 54.9, 28.3, 25.5, 17.8, -5.1, -5.4; HRMS (ESI) calculated for C₂₁H₃₃N₂O₄Si [M+H]⁺: 405.2204; found: 405.2235.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(4phenylphenyl)azetidin-2-one (3h). 89% yield; 91% *ee*; $[\alpha]_D^{20} = +49.5^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 0.5 mL/min, hexanes:IPA:EtOH = 98:1:1, t_r = 12.8, 14.9 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.59-7.36 (comp, 9H), 4.84 (d, *J* = 5.8 Hz, 1H), 4.56-4.50 (m, 1H), 4.08 (d, *J* = 1.6 Hz, 1H), 4.03 (d, *J* = 5.8 Hz, 1H), 1.32 (s, 9H), 0.72 (s, 9H), -0.03 (s, 3H), -0.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 166.9, 151.0, 141.2, 141.1, 136.8, 129.0, 128.5, 127.4, 127.2, 126.7, 93.2, 60.1, 57.9, 54.7, 28.4, 25.7, 18.0, -4.9, -5.5; HRMS (ESI) calculated for C₂₇H₃₈NO₂Si [M+H]⁺: 436.2666; found: 436.2690.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-[4-(dimethylamino)phenyl]azetidin-2-one (3i). 80% yield; 99% *ee*; $[\alpha]_D^{20} = +54.1^{\circ}$ (c = 1, EtOAc); HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 7.3, 10.1 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.21 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 4.72 (d, *J* = 5.7 Hz, 1H), 4.51-4.47 (m, 1H), 4.07 (d, *J* = 1.4 Hz, 1H), 3.94 (d, *J* = 5.7 Hz, 1H), 2.93 (s, 6H), 1.29 (s, 9H), 0.74 (s, 9H), -0.01 (s, 3H), -0.30 (s, 3H).; ¹³C NMR (CDCl₃, 100 MHz): 167.1, 151.5, 150.8, 128.8, 125.3, 112.3, 93.0, 59.9, 58.1, 54.4, 41.0, 28.4, 25.8, 18.0, -4.8, -5.4; HRMS (ESI) calculated for C₂₃H₃₉N₂O₂Si [M+H]⁺: 403.2775; found: 403.2789.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(3,4-dimethoxyphenyl)azetidin-2-one (3j). 81% yield; 77% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 230 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 9.6, 12.8 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.93-6.86 (comp, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.54 (d, *J* = 1.3 Hz, 1H), 4.10 (d, *J* = 1.3 Hz, 1H), 3.96 (d, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 1.28 (s, 9H), 0.70 (s, 9H), -0.01 (s, 3H), -0.31 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.8, 151.5, 149.0, 148.5, 130.2, 120.7, 111.0, 110.8, 93.1, 59.8, 58.0, 56.2, 55.8, 54.6, 28.3, 25.6, 17.9, -5.0, -5.4; HRMS (ESI) calculated for C₂₃H₃₈NO₄Si [M+H]⁺: 420.2565; found: 420.2553.



(3S,4R)-1-(tert-Butyl)-3-[1-(tert-butyldimethylsilyloxy)vinyl]-4-(3-

methoxyphenyl)azetidin-2-one (**3k**). 92% yield; 77% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 230 nm, 0.5 mL/min, hexanes:IPA:Et = 98:1:1, t_r = 11.7, 12.9 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.18 (t, J = 7.9 Hz, 1H), 6.93-6.91 (m, 2H), 6.82-6.79 (m, 1H), 4.75 (d, J = 5.8 Hz, 1H), 4.50 (d, J = 1.5 Hz, 1H), 4.07 (d, J = 1.5 Hz, 1H), 3.98 (d, J = 5.8 Hz, 1H), 3.78 (s, 3H), 1.28 (s, 9H), 0.71 (s, 9H), -0.03 (s, 3H), -0.33 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.9, 159.3, 151.1, 139.3, 129.0, 120.7, 113.7, 113.5, 93.2, 59.9, 58.2, 55.3, 54.7, 28.3, 25.7, 17.9, -5.0, -5.5; HRMS (ESI) calculated for C₂₂H₃₆NO₃Si [M+H]⁺: 390.2459; found: 390.2470.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(2methoxyphenyl)azetidin-2-one (3l). 85% yield; 25% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 230 nm, 0.5 mL/min, hexanes:IPA:Et = 98:1:1, t_r = 10.2, 11.6 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.41 (d, *J* = 7.4 Hz, 1H), 7.22-7.14 (m, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.35 (d, *J* = 5.6 Hz, 1H), 4.41 (d, *J* = 1.4 Hz, 1H), 4.01 (d, *J* = 1.4 Hz, 1H), 3.97 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 1.26 (s, 9H), 0.71 (s, 9H), -0.07 (s, 3H), -0.32 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 157.2, 151.4, 128.7, 128.6, 125.5, 119.7, 109.8, 93.2, 59.4, 55.2, 54.3, 50.3, 28.2, 25.5, 17.9, -5.0, -5.4; HRMS (ESI) calculated for C₂₂H₃₆NO₃Si [M+H]⁺: 390.2459; found: 390.2471.



TBSO (3*S*,4*R*)-1-(*tert*-Butyl)-3-[1-(*tert*-butyldimethylsilyloxy)vinyl]-4-(1naphthyl)azetidin-2-one (3m). 85% yield; 24% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 230 nm, 0.5 mL/min, hexanes:IPA:Et = 98:1:1, t_r = 10.2, 12.9 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.10 (d, *J* = 8.2 Hz, 1H), 7.88-7.81 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.73-7.66 (m, 1H), 7.52-7.41 (comp, 3H), 5.73 (d, *J* = 5.8 Hz, 1H), 4.36 (d, *J* = 1.4 Hz, 1H), 4.18 (d, *J* = 5.8 Hz, 1H), 3.94 (d, *J* = 1.4 Hz, 1H), 1.33 (s, 9H), 0.47 (s, 9H), -0.23 (s, 3H), -0.64 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 167.6, 151.0, 133.6, 132.6, 131.5, 129.0, 128.1, 126.3, 125.48, 152.46, 124.7, 122.5, 93.6, 60.5, 54.6, 53.5, 28.2, 25.4, 17.6, -5.1, -5.8; HRMS (ESI) calculated for C₂₅H₃₆NO₂Si [M+H]⁺: 410.2510; found: 410.2535.



3-[1-(tert-Butyldimethylsilyloxy)vinyl]-1-isopropyl-4,4-

dimethylazetidin-2-one (3n). 81% yield; 67% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 230 nm, 0.5 mL/min, hexanes:IPA = 98:2, $t_r = 10.3$, 12.4 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.40-4.35 (m, 1H), 4.23 (d, *J* = 1.4 Hz, 1H), 3.61-3.54 (m, 1H), 3.35 (d, *J* = 0.5 Hz, 1H), 1.43 (s, 3H), 1.37 (s, 3H), 1.31 (dd, *J* = 6.8, 1.9 Hz, 6H), 0.92 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H).; ¹³C NMR (CDCl₃, 100 MHz): 164.8, 152.6, 93.0, 65.3, 60.2, 44.2, 27.4, 25.8, 22.0, 21.9, 21.7, 18.0, -4.6, -4.7; HRMS (ESI) calculated for C₁₆H₃₂NO₂Si [M+H]⁺: 298.2197; found: 298.2162.



(3S,4R)-3-[1-(tert-butyldimethylsilyloxy)vinyl]-1-(4-

fluorophenyl)-4-(4-methoxyphenyl)azetidin-2-one (30). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.39-7.29 (m, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.95 (t, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.17 (d, J = 6.0 Hz, 1H), 4.46 (dd, J = 1.8, 0.8 Hz, 1H), 4.28 (d, J = 6.0 Hz, 1H), 4.10 (d, J = 1.8 Hz, 1H), 3.80 (s, 3H), 0.80 (s, 9H), -0.00 (s, 3H), -0.21 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 164.1, 159.9, 159.2 (d, J = 242.0 Hz), 150.5, 134.1 (d, J = 2.7 Hz), 129.0, 126.2, 118.8 (d, J = 7.8 Hz), 116.0 (d, J = 22.6 Hz), 113.9, 93.8, 61.4, 58.9, 55.5, 25.1, 18.1, -4.9, -5.3; HRMS (ESI) calculated for C₂₄H₃₁FNO₃Si [M+H]⁺: 428.2052; found: 428.2021.

Procedure for Reactions of Donor-Acceptor Cyclopropene 6 with Copper(I) and Silver(I) Catalysts



To an 10-mL oven-dried vial containing a magnetic stirring bar, $Rh_2(OAc)_4$ (1.8 mg 2.0 mol%) in DMB (1.0 mL), was added enoldiazoacetates **1c** (84 mg, 0.20 mmol) in DMB (0.5 mL) at room temperature. The reaction mixture was stirred for another 5 min, during which time the diazo compound was converted to the corresponding cyclopropene. Then the reaction mixture was passed through Celite to remove $Rh_2(OAc)_4$. After removing DMB by vacuum evaporation, the resulting cyclopropene intermediate **6c** was used for subsequent reactions.



In a two dram vial equipped with N₂, Cu(MeCN)₄PF₆ (0.02 mol) or AgSbF₆(0.02 mol) and 2,2'-isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] (0.024 mol) in DCM (0.5 mL) were stirred for 1 h under room temperature. The temperature of the solution was then cooled down to 0 °C. The cyclopropene intermediate **6c** in DCM (0.5 mL) was added dropwise to the solution under N₂ protection. The reaction mixture was stirred for another 12 h at 0 °C and then passed through Celite to remove catalyst. After removing solvent, the ratio of **2c** to **3c** was determined by ¹H NMR analysis of the corresponding reaction mixture. The resulting reaction mixture was then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 100:0 to 90:10) to give pure β-lactams **3c** and compound **2c**.

Procedure for Acidic Hydrolysis of β-Lactams 3c.



To a 10-mL oven-dried vial containing a magnetic stirring bar, β -lactams **3c** (59 mg, 1.5 mol) in THF (1.5 mL), was added HCl (2 M, 0.5 mL) at 0 °C. The reaction mixture was stirred 2-3 h under this temperature. After the reaction was finished [monitored by thin layer chromatography (TLC) until all of the material was consumed], the reaction mixture was neutralized with saturated aqueous NaHCO₃, extracted twice with ether (10 mL X 2), and the combined organic phase was dried over anhydrous Na₂SO₄. After evaporating the solvents, the residue was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 90:10 to 80:20) to give pure β -lactam **5c** in 77% yield (32 mg) with 93% *ee* and >20:1 *dr*.

(*3R*,*4R*)-3-Acetyl-1-(*tert*-butyl)-4-(4-chlorophenyl)azetidin-2-one (5c). 77% yield; 93% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 230 nm, 0.7 mL/min, hexanes:IPA = 97:3, t_r = 14.7, 19.0 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.34 (s, 4H), 5.00 (d, *J* = 2.2 Hz, 1H), 3.87 (d, *J* = 2.2 Hz, 1H), 2.28 (s, 3H), 1.23 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): 199.6, 163.0, 138.2, 134.5, 129.3, 128.1, 71.0, 55.4, 53.9, 30.2, 28.3; HRMS (ESI) calculated for C₁₅H₁₉ClNO₂ [M+H]⁺: 280.1099; found: 280.1090.

General Procedure for Enantioselective C-H Functionalization of 4a.



To a 10-mL oven-dried vial containing a magnetic stirring bar, $Rh_2(S-PTTL)_4$ (2.0 mol%, 5.0 mg) in DMB (0.5 mL), was added diazoacetamide **4a** (61 mg, 0.20 mmol) in DMB (0.5 mL) over 10 min via a syringe pump at 0 °C. The reaction mixture was stirred overnight and warmed to room temperature slowly. After the reaction was complete [monitored by thin layer chromatography (TLC) until all of the material was consumed], the reaction mixture was directly purified by column chromatography on silica gel without any further treatment (eluent: hexanes:EtOAc = 90:0 to 80:10) to give pure β-lactam **5a** in 92% yield (51 mg) with 60% *ee* and >20:1 *dr*.

(*3R*,*4R*)-3-Acetyl-1-(*tert*-butyl)-4-(4-methoxyphenyl)azetidin-2-one (5a). 92% yield; 60% *ee*; HPLC conditions for determination of enantiomeric excess: AD-H column, 210 nm, 1.0 mL/min, hexanes:IPA = 95:5, t_r = 13.2, 17.1 min. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.34 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.99 (d, *J* = 2.2 Hz, 1H), 3.92 (d, *J* = 2.2 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H), 1.26 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): 200.2, 163.3, 160.0, 131.3, 128.1, 114.5, 71.1, 55.5, 55.3, 54.3, 30.3, 28.3; HRMS (ESI) calculated for C₁₆H₂₂NO₃ [M+H]⁺: 276.1594; found: 276.1584.

References

- (a) S. Hashimoto, N. Watanabe, T. Sato, M. Shiro and S. Ikegami, *Tetrahedron lett.*, 1993, 34, 5109; (b) H. Tsutsui, T. Abe, S. Nakamura, M. Anada and S. Hashimoto, *Chem. Pharm. Bull.*, 2005, 53, 1366; (c) S. Kitagaki, M. Anada, O. Kataoka, K. Matsuno, C. Umeda, N. Watanabe and S. Hashimoto, *J. Am. Chem. Soc.*, 1999, 121, 1417.
- a) M. K. Choi, W. Yu and C. Che, *Org. Lett.*, 2005, 7, 1081; (b) M. Grohmann, and G. Maas, *Tetrahedron*, 2007, 63, 12172; (c) M. P. Doyle, M. S. Shanklin, S. M. Oon, H. Q. Pho, F. R. van der Heide and W. R. Veal, *J. Org. Chem.*, 1988, 53, 3384.

Proton NMR Spectral Observation of Cyclopropene 6c







Chemoselectivity Determination by ¹H NMR Spectrum of the Reaction Mixture





































































	File Information		#	Time	Area	Height	Width	Area%	Symmetry
LC-File	XXU-N6-NTTL-17.D		1	13.131	16628.8	507.4	0.5103	93.403	0.8
File Path	C:\CHEM32\1\DATA\XXU\		2	14.782	1174.4	42.2	0.4641	6.597	0.81
Date	13-May-14, 18:13:00								
Sample	ad-h, 99:1,0.4								
Sample Info	ad-h, 99:1,0.4								
Barcode									
Operator	XVU								
Method	PHONG.M								
Analysis Time	24.133 min								
Caralles Date	Lo oper the lockon they been developed								









































Data Collection and Structure Refinement for (3S,4R)-3i (UM-2600).



A colorless prism-like specimen of $C_{23}H_{38}N_2O_2Si$, approximate dimensions 0.41 mm \times 0.49 mm \times 0.52 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoK α sealed tube ($\lambda = 0.71073$ Å). Data collection temperature was 150 K.

The total exposure time was 5.29 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 19657 reflections to a maximum θ angle of 30.00° (0.71 Å resolution). which 6987 were of independent (average redundancy 2.813, completeness = 99.9%, R_{int} =2.53%, R_{sig} = 3.97%) and 6686 (95.69%) $2\sigma(F^2)$. The were greater than final cell constants of a = 12.0041(6) Å, b = 12.0054(6) Å, c = 16.8057(8) Å, V = 2421.9(2) Å³, are based upon the refinement of the XYZ-centroids of 9972 reflections above 20 σ (I) with 4.798° < $2\theta < 61.12^{\circ}$. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9421 and 0.9540.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{23}H_{38}N_2O_2Si$. The final anisotropic full-matrix least-squares refinement on F² with 370 variables converged at $R_1 = 3.07\%$, for the observed data and w $R_2 = 6.41\%$ for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.287 e⁻/Å³ and the largest hole was -0.153 e⁻/Å³ with an RMS deviation of 0.033 e⁻/Å³. On the basis of the final model, the calculated density was 1.104 g/cm³ and F(000), 880 e⁻.