Supporting Information

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General Information

Dry CH_2Cl_2 was purchased from Kanto Chemical Company. *O*-Allylhydroxylamine-HCl and quinoline-4-carbaldehyde were purchased from Tokyo Chemical Industry Company, Ltd., and Wako Pure Chemicals Industries, Ltd., respectively. Precoated silica gel plates with a fluorescent indicator (Merck 60 F254) were used for analytical TLC. Flash column chromatography was carried out with Kanto Chemical silica gel (Kanto Chemical Company; Silica gel 60N, spherical neutral, 0.040–0.050 mm; catalog no. 37563-84). ^{1}H-NMR spectra was recorded at 500 MHz, and ^{13}C-NMR spectra were recorded at 125 MHz on JEOL ECA-500. The chemical shifts are expressed in parts per million downfield from internal solvent peaks $CHCl_3$ (7.26 ppm, ^{1}H-NMR), $CDCl_3$ (77.0 ppm, ^{13}C-NMR), and *J* values are given in hertz. The coupling patterns are expressed by s (singlet), d (doublet), t (triplet), and m (multiplet). The infrared spectra were measured on a Horiba FT-210 spectrometer with Jasco ATR-diamond prism equipment. High-resolution mass spectra were measured on a JEOL JMS-AX505 HA spectrometer.

Preparation of the 4-Quinolylformyl-*O*-Allyloxime (5)

To a solution of quinoline-4-carbaldehyde (50.1 mg, 0.319 mmol) in CH_2Cl_2 (3.2 mL) was added *O*-allylhydroxylamine-HCl (52.4 mg, 0.478 mmol) at room temperature, and the resultant mixture was stirred for 2 h. Then, the reaction mixture was diluted with additional CH_2Cl_2 (5 mL) and washed with saturated NaCl aqueous solution (10 mL × 1), dried over Na_2SO_4, filtered, and concentrated to afford crude product. The flash chromatography (hexane:EtOAc = 2:1) furnished the title compound **5** (34.2 mg, 51%, inseparable mixture *E*:*Z* = ∼10:1) as a colorless oil: IR (Diamond prism) ν cm^{-1} 1,576, 1,508, 1,421, 1,039, 1,024, 928, 845, 756, 611; for major product *E*-5, ^{1}H-NMR (500 MHz, $CHCl_3$) δ 8.92 (d, *J* = 4.6 Hz, 1H), 8.71 (s, 1H), 8.43 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.75 (apparently t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 4.6 Hz, 1H), 7.61 (apparently t, *J* = 7.5 Hz, 1H), 6.10 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 9.8 Hz, 1H), 4.81 (d, *J* = 5.8 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.9, 148.6, 146.1, 136.1, 133.5, 130.1, 129.6, 127.5, 125.2, 124.2, 119.7, 118.5, 75.8; HR-MS (FAB, Peg400 matrix) *m*/*z* 213.1028 [M+H]$^+$, calculated for $C_{13}H_{13}ON_2$ 213.1028 [M+H].

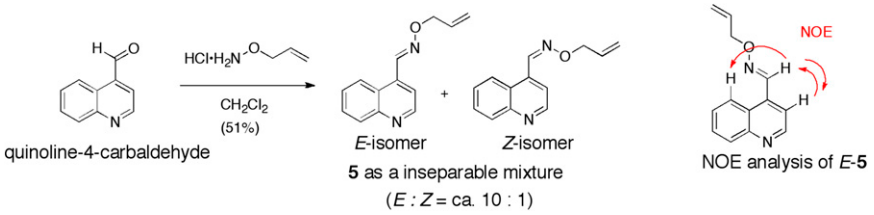

Fig. S1. Preparation of **5**.

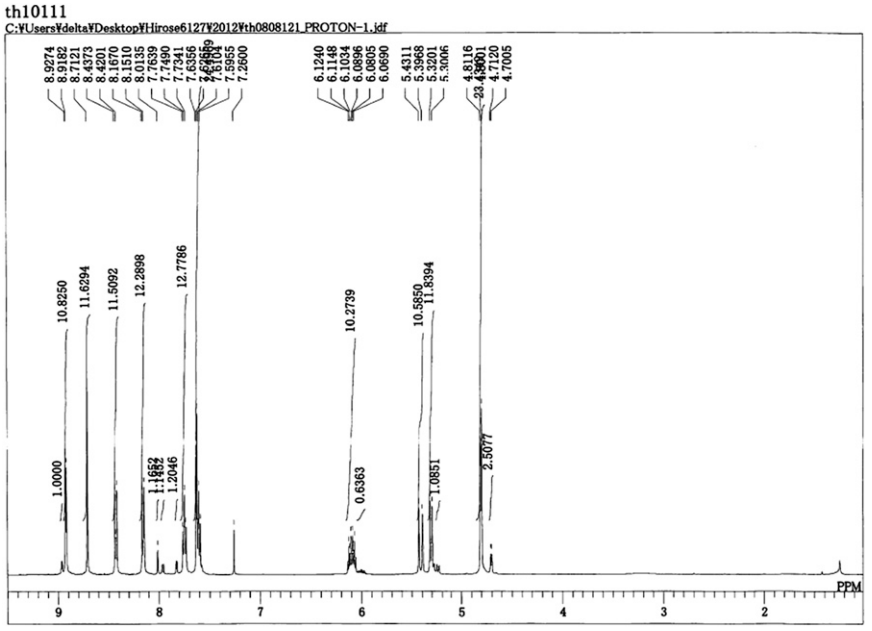

Fig. S2. ^{1}H-NMR spectra of **5** (500 MHz, $CDCl_3$).

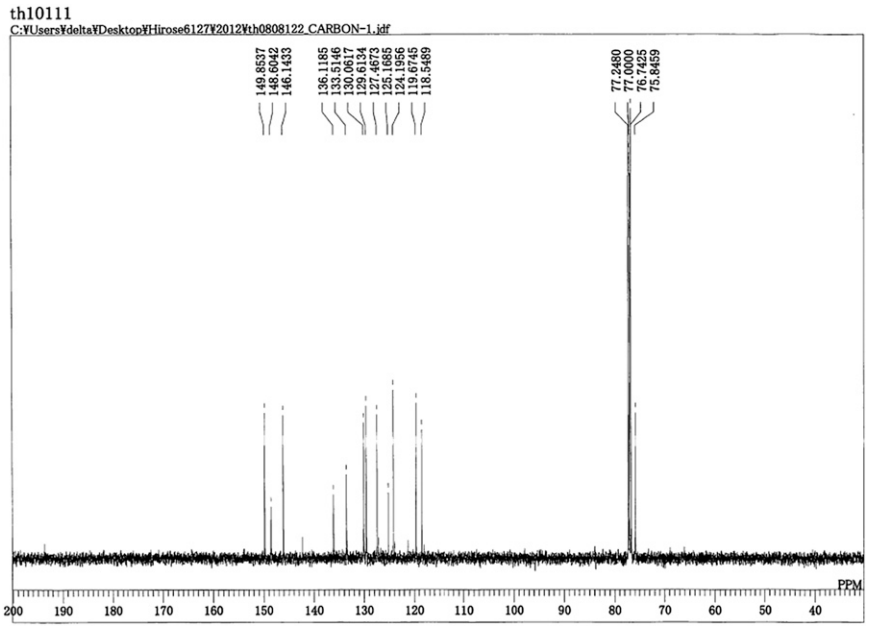

Fig. S3. ^{13}C-NMR spectra of **5** (125 MHz, CDCl3).

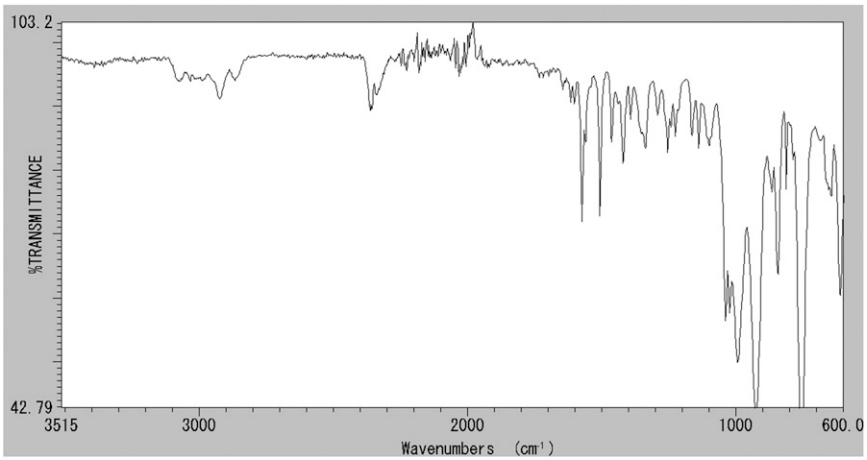

Fig. S4. IR spectra (diamond prism).

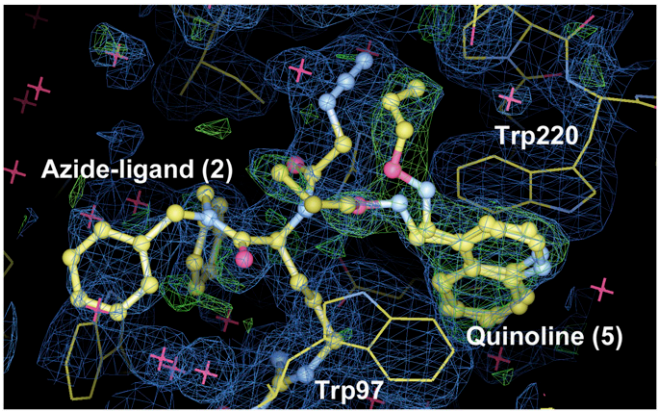

Fig. S5. Electron density maps of 2mFo-DFc (>1σ, blue) and omit map (>2.4σ, green) at active site of crystal of [*Sm*ChiB]-[**2**]-[**5**]. Omit map was calculated without quinoline molecule.

Table S1. Statistics of diffraction data collection and refinement

Crystal	Apo	*Syn*-triazole **4**	Azide **2**	Azide **2**/**5** (mimic of alkyne **3**), low dose	Azide **2**/**5** (mimic of alkyne **3**), high dose
Ligands	—				
Ligands incorporation method	—	Soaking	Cocrystallization	Soaking	Soaking
Final concentration in drops, μM	—	26.0	400	12.5/125	250/1250
Data collection					
Space group	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$	$P4_32_12$
Unit cell *a*, *c*, Å	98.13, 197.51	97.76, 197.75	97.44, 197.10	97.69, 197.40	97.45, 197.53
X-ray source	PF-AR NW12A	PF-AR NE3A	PF BL-17A	PF BL-5A	PF-AR NW12A
Wavelength, Å	1.0000	1.0000	0.9800	1.0000	1.0000
Resolution range, Å	30–1.7 (1.76–1.7)	40–2.3 (2.37–2.3)	40–2.2 (2.28–2.2)	40–2.3 (2.28–2.2)	40–2.0 (2.07–2.0)
Observed reflections	1,948,112	662,724	644,281	795,647	947,126
Unique reflections	106,499	43,256	49,003	49,388	65,168
Redundancy	18.3 (11.9)	15.3 (15.2)	13.1 (13.1)	16.1 (15.8)	14.5 (14.4)
Completeness, %	99.6 (100)	100 (100)	100 (100)	100 (100)	100 (100)
$\langle I\rangle/\langle\sigma(I)\rangle$	33.9 (5.9)	25.8 (5.2)	29.9 (6.1)	27.4 (4.55)	36.8 (7.9)
R_{sym}*, %	8.3 (42.9)	11.4 (70.4)	8.7 (47.1)	10.2 (45.4)	7.4 (39.2)
Wilson-*B*, Å^2	20.2	35.6	33.9	24.6	22.8
Refinement					
Resolution range, Å	30–1.7	40–2.3	40–2.2	40–2.2	40–2.0
No. of reflections (work/free)	101,067/5,311	41,001/2,176	46,269/2,478	46,875/2,501	61,598/3,285
R_{work}/R_{free}†, %	16.9/18.2	18.6/22.6	17.0/20.2	16.9/19.8	16.7/19.0
$\langle B\rangle$, Å^2, protein/water/ligand	21.0/32.2/44.3	38.7/39.5/59.9	28.4/57.5/38.6	19.9/45.9/28.9	23.0/52.2/33.6
Rmsd deviations					
Bond lengths, Å	0.009	0.020	0.011	0.011	0.013
Bond angles, °	1.250	1.976	1.401	1.397	1.425
Ramachandran plot‡, %					
Most favored	98.6	97.8	98.0	97.8	98.6
Additionally allowed	1.4	2.2	2.0	2.2	1.4
Outliers	0	0	0	0	0
PDB ID code	3WD0	3WD1	3WD2	3WD3	3WD4

Values in parentheses correspond to the outer shell.

*$R_{sym} = \Sigma_{hkl}\ |I_i - \langle I_i\rangle|/\Sigma_{hkl}\ I_i$, where I_i is the observed intensity and $\langle I_i\rangle$ is the average intensity obtained from multiple observations of symmetry-related reflections.

†$R_{work} = \Sigma_{hkl}\ ||F_{obs}| - |F_{calc}||/\Sigma_{hkl}\ |F_{obs}|$. Five percent of the reflections were excluded for R_{free} calculation.

‡Analyzed with RAMPAGE (1).

1. Lovell SC, et al. (2003) Structure validation by Cα geometry: ϕ,ψ and Cβ deviation. *Proteins* 50(3):437–450.