Supplementary Information for

Trifluoroacetic Acid Adduct of Trifluoroacetate-Bridged μ-Oxo-Tetranuclear Zinc Cluster, $Zn_4(OCOCF_3)_6O•CF_3CO_2H$: Synthesis under Mild Conditions and Catalytic Transesterification and Oxazoline Formation

Yukiko Hayashi,[a] Takashi Ohshima,*[b] Yuka Fujii,[a] Yoshimasa Matsushima,[c] and Kazushi Mashima*[a]

[a] *Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

[b] *Graduate School of Pharmaceutical Sciences, Kyushu University, 3-1-1 Maidashi Higashi-ku, Fukuoka 812-8582, Japan*

[c] *Corporate Research and Development Division, Takasago International Corporation, 1-4-11 Nishi-yawata, Hiratsuka, Kanagawa, 254-0073, Japan*

E-mail: ohshima@phar.kyushu-u.ac.jp, mashima@chem.es.osaka-u.ac.jp

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Materials and methods

General: Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) spectra were measured on a Varian MERCURY300-C/H spectrometer operating at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 282 MHz (^{19}F NMR), in 5ϕ mm NMR tubes and Bruker Avace 400 Spectrometer operating at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), in 5ϕ mm NMR tubes. All ^{1}H NMR chemical shifts were reported in ppm relative to internal references of TMS at δ 0.00. All ^{13}C NMR chemical shifts were reported in ppm relative to carbon resonance in chloroform-d_1 at δ 77.00, THF-d_8 at δ 25.20. The ^{19}F NMR chemical shifts were reported in ppm relative to external reference of α,α,α-trifluorotoluene at δ –63.90. Low and high resolution mass spectra were recorded by JEOL JMS-700. IR spectra were recorded on Jasco FT/IR-410 spectrometer. Elemental analyses were conducted by Perkin-Elmer 2400II at the Faculty of Engineering Science, Osaka University. GC analyses were recorded on a Shimadzu GC-14A gas chromatograph with J&W Scientific DB-5 column. Enantiomeric excess was determined by chiral HPLC analysis with DAICEL CHIRALCEL OD-H column using a JASCO PU-2089 PLUS pump and PU-2075 PLUS UV/VIS detector. Optical rotation measurements were performed at 589 nm, on Atago AP-300 polarimeter. All catalytic reactions were carried out by the standard Schlenk techniques under an argon atmosphere. Diisopropyl ether was distilled over benzophenone ketyl. Ethyl acetate was distilled over P_2O_5. Chlorobenzene was distilled over calcium hydride. $Zn(OCOCF_3)_2 \cdot xH_2O$ was purchased from Sigma-Aldrich.

Preparation of tetranuclear zinc cluster 1a. Under an inert atmosphere of argon, zinc bistrifluoroacetate hydrate, $Zn(OCOCF_3)_2 \cdot xH_2O$, (845 mg, 2.73 mmol as a monohydrate) was heated at 120 ˚C for 4 h under reduced pressure (<0.02 mmHg) to remove water. The resulting dried powder was heated at 360 ˚C on a sand bath to sublime a μ-oxo-tetranuclear zinc cluster **1a**, which was mechanically collected and stored under an inert atmosphere (545 mg, 84%). **1a**: white solid; IR (nujol NaCl, ν/cm^{-1}) 2923, 1701, 1202, 856, 796, 730; ^{13}C NMR (75 MHz, THF-d_8, 35 ˚C) δ 117.0 (q, $J_{C\text{-}F}$ = 288 Hz, CF_3COO), 163.8 (q, $J_{C\text{-}F}$ = 38 Hz, CF_3COO); ^{19}F NMR (282 MHz, THF-d_8, 35 ˚C) δ –78.88 (s); MS (ESI) m/z (relative intensity) 933 ([$M^+ + 2H_2O + H$], 3); Elemental Anal. calcd. for $C_{12}F_{18}O_{13}Zn_4$: C15.08% found C 15.52%.

Preparation of the compound A (the mixture of tetranuclear zinc cluster 1a and its trifluoroacetate adduct 3) by Sublimation at 160 °C. Under an inert atmosphere of nitrogen, $Zn(OCOCF_3)_2 \cdot xH_2O$ (30.3 g) was heated at 120 ˚C for 1.5 h under reduced pressure (<0.02 mmHg), and then the reaction temperature was gradually raised to 160 ˚C. A white solid was sublimated during maintaining the temperature at 160 ˚C for 30 min. The starting mononuclear zinc material

was completely consumed within 6 h. The resulting white solid was collected and stored under an inert atmosphere (24.7 g, 98% yield based on zinc). The zinc content of the compound **A** was determined to be 25.2% by titration with EDTA solution using XO indicator. Thus, the compound **A** was a mixture of **1a** and its trifluoroacetate adduct **3** in 28:72 ratio. White solid; IR (KBr) 1708, 1629, 1439, 1203, 851, 799, 729, 520, 427; ^{1}H NMR (500 MHz, DMSO-d_6, 47 ˚C) δ 10.25 (br-s, CF_3CO_2H); ^{13}C NMR (125 MHz, DMSO-d_6, 47 ˚C) δ 116.6 (q, $J_{C\text{-}F}$ = 294.72 Hz, CF_3CO), 158.87 (q, $J_{C\text{-}F}$ = 33.96 Hz, CF_3CO); ^{19}F NMR (470 MHz, DMSO-d_6, 47 ˚C) δ –74.27 (s); MS (ESI) *m*/*z* 1062 [$Zn_4(OCOCF_3)_6O + CF_3CO_2^-$]; HRMS (ESI) *m*/*z* calcd. for $C_{14}F_{21}O_{15}Zn_4$ 1062.6073 found 1062.6074.

Preparation of the compound B (the mixture of tetranuclear zinc cluster 1 and its trifluoroacetate adduct 2) in small scale by refluxing in toluene. $Zn(OCOCF_3)_2 \cdot xH_2O$ (9.70 g) was dissolved in 270 mL of toluene at 60 ˚C, and then the solution was refluxed. The fraction contained toluene and water after refluxing for 30 min showed strong acidity due to CF_3CO_2H (pH ≈ 1). After refluxing the solution for 4 h, the solution became turbid due to the formation of an insoluble clusters. The product was filtrated after cooling to room temperature, washed with toluene, and dried in vacuum for 2 h to remove residual solvent to give white solid (6.37 g, 93% yield based on zinc). The zinc content of the compound **B** was determined to be 25.6% by titration with EDTA solution using XO indicator. Thus, the compound **B** was a mixture of **1** and its trifluoroacetate adduct **2** in 41:59 ratio.

Preparation of the compound B (the mixture of tetranuclear zinc cluster 1a and its trifluoroacetate adduct 3) in large scale by refluxing in toluene. $Zn(OCOCF_3)_2 \cdot xH_2O$ (Zn content 18wt%, H_2O content 19wt%, 2.00 kg) was dissolved in 7 L of toluene at 60 ˚C under N_2 atmosphere, and then the solution was refluxed. After refluxing the solution for 4 h, about 4 L of an azeotropic mixture of toluene, water, and TFA was removed form the reaction mixture and the solution became turbid due to the formation of an insoluble clusters. The product was filtrated after cooling to room temperature, washed with toluene, and dried in vacuum (<5 mmHg) at 75˚C to remove residual solvent to give white solid (1.08 kg). The zinc content of the compound **B** was determined to be 25.5% by titration with EDTA solution using XO indicator.

General procedure for the transesterification catalyzed by the zinc clusters. Catalyst (23.8 mg, 0.0250 mmol, calculated as $Zn_4(OCOCF_3)_6O$), methyl ester **4** (2.0 mmol), and alcohol **5** (2.4 mmol) in diisopropyl ether (3.4 mL, 0.6 M) were refluxed for periodic time under an argon atmosphere. The resulting mixture was concentrated and purified by silica gel column chromatography.

General procedure for the acetylation of alcohol 5b catalyzed by the zinc clusters. Catalyst (23.8 mg, 0.0250 mmol, calculated as $Zn_4(OCOCF_3)_6O$), alcohol **5b** (2.0 mmol), and ethyl acetate (3.4 mL, 0.6 M) were refluxed for 18 h under an argon atmosphere. The resulting mixture was concentrated and purified by silica gel column chromatography.

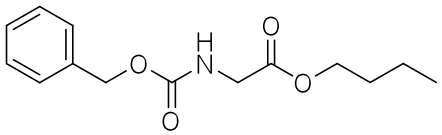
General procedure for the oxazoline formation catalyzed by the zinc clusters. Catalyst (35.8 mg, 0.0375 mmol, calculated as $Zn_4(OCOCF_3)_6O$), methyl benzoate (**4c**, 1.5 mmol), and (*S*)–valinol (**5c**, 1.8 mmol) in chlorobenzene (2.5 mL) were refluxed for 12 h under an argon atmosphere. The resulting mixture was concentrated and purified by silica gel column chromatography.

Computational Methods

Geometry optimizations and energies were calculated with the Gaussian 03 package (Revision D.01)[S-1] using B3LYP[S-2] hybrid density functional theory with LANL2DZ basis set for Zn and 6-31G(d,p) basis set for all other atoms.

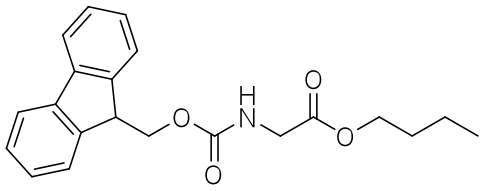
Characterization data for the isolated compounds

Butyl *N*-benzyloxycalbonylglycinoate (Cbz-Gly-O^{n}Bu) (9aa)



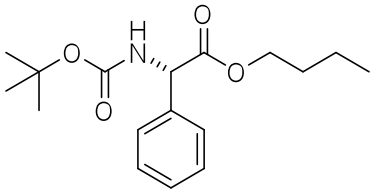
Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); colorless oil; IR ($CHCl_3$, ν/cm^{-1}) 3441, 3379, 3024, 2963, 2878, 1744, 1705, 1528, 1512, 1458, 1404, 1358, 1273, 1188, 1057, 995; ^{1}H NMR (400 MHz, $CDCl_3$, 35 ˚C) δ 7.36-7.25 (m, 4H, *aromatic*), 5.22 (br s, 1H, N*H*), 5.13 (s, 2H, PhCH_2), 4.16 (t, J = 6.7 Hz, 2H, OCH_2CH$_2$), 3,97 (d, J = 5.4 Hz, 2H, NHCH_2), 1.66-1.56 (m, 2H, *methylene*), 1.42-1.33 (m, 2H, *methylene*), 0.93 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 35 ˚C) δ 170.0, 156.2, 136.3, 128.4, 128.1, 128.0, 67.0, 65.2, 42.7, 30.5, 18.9, 13.5; MS (EI) m/z (relative intensity) 265 ([M$^+$], 34), 108 (89), 91 (100); HRMS (EI) m/z calcd. for $C_{14}H_{19}NO_4$ 265.1314 found 265.1316.

Butyl *N*-9-fluorenylmethyloxycalbonylglycinoate (Fmoc-Gly-O^{n}Bu) (9ba)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 10/1 to 4/1); colorless oil; IR ($CHCl_3$, ν/cm^{-1}) 3441, 3063, 3024, 2963, 2878, 1736, 1721, 1520, 1451, 1404, 1358, 1204, 1057, 1003; ^{1}H NMR (400 MHz, $CDCl_3$, 35 ˚C) δ 7.75 (d, J = 7.4 Hz, 2H, *fluorenyl*), 7.59 (br d, J = 7.4 Hz, 2H, *fluorenyl*), 7.38 (t, J = 7.4 Hz, 2H, *fluorenyl*), 7.29 (dt, J = 1.0, 7.4 Hz, 2H, *fluorenyl*), 5.32 (br s, 1H, N*H*), 4.40 (d, J = 7.1 Hz, 2H, fluorenylCH_2), 4.22 (t, J = 7.1 Hz, 1H, *fluorenyl*), 4.16 (t, J = 6.7 Hz, 2H, OCH_2CH$_2$), 3.97 (d, J = 5.2 Hz, 2H, NHCH_2), 1.66-1.59 (m, 2H, *methylene*), 1.42-1.32 (m, 2H, *methylene*), 0.92 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 35 ˚C) δ 170.0, 156.2, 143.8, 141.3, 127.7, 127.0, 125.0, 119.9, 67.2, 65.3, 47.1, 42.8, 30.5, 19.0, 13.6; MS (EI) m/z (relative intensity) 353 ([M$^+$], 1), 178 (88), 165 (25), 71 (4); HRMS (EI) m/z calcd. for $C_{21}H_{23}NO_4$ 353.1627 found 353.1643.

(*S*)-butyl *N*-*tert*-butoxycalbonylphenylglycinoate (Boc-Phg-O^{n}Bu) (9ca)



Purified by flush column chromatography (silica gel, Hexane/EtOAc = 15/1 to 4/1); colorless oil; IR ($CHCl_3$, ν/cm^{-1}) 3441, 3063, 3024, 2963, 2940, 2878, 1805, 1721, 1505, 1474, 1366, 1319, 1242, 1165, 1126, 1057, 1026; ^{1}H NMR (400 MHz, $CDCl_3$, 35 ˚C) δ 7.37-7.29 (m, 5H, *aromatic*), 5.57 (br s, 1H, N*H*), 5.30 (d, 1H, J = 5.3 Hz, NHC*H*), 4.11 (dt, J = 6.6, 1.6 Hz, 2H, OCH_2CH$_2$), 1.58-1.51 (m, 2H, *methylene*), 1.43 (s, 9H, C(CH_3)$_3$), 1.29-1.20 (m, 2H, *methylene*),

0.84 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 35 ˚C) δ 171.1, 154.8, 137.2, 128.7, 128.2, 127.0, 80.0, 65.5, 57.7, 30.4, 28.3, 18.8, 13.5; MS (EI) m/z (relative intensity) 307 ([M^+], 1), 206 (40), 150 (97), 106 (100), 57 (77); HRMS (ESI) m/z calcd. for $C_{17}H_{25}NO_4Na$ 330.1675 found 330.1699; $[\alpha]_{589}^{24}$ +103.2 (c 0.96 in $CHCl_3$). The enantiomeric excess (%ee) was determined to be 95% by HPLC using ChiralPAK OD-H column (5% i-PrOH/ hexanes, 1 mL/min, 254 nm): t_R (minor, 5.2 min), t_R (major, 5.5 min).

Spectral data of **6aa**,[S-3] **6ba**,[S-3] **6ac**,[S-3] **7**,[S-4] and **12**[S-5] were described in previous reports.

References for the Supplementary Information

S-1 Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

S-2 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

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S-4 T. Iwasaki, Y. Maegawa, Y. Hayashi, T. Ohshima and K. Mashima, *Synlett*, 2009, 1659.

S-5 T. Ohshima, T. Iwasaki and K. Mashima, *Chem. Commun.*, 2006, 2711.

Cartesian Coordinates

TFA

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.687718	-2.242156	3.240174
2	6	0	1.890031	-0.668409	5.079307
3	6	0	1.853120	-2.063208	4.417723
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7	9	0	3.078133	-0.468412	5.675722
8	1	0	2.000735	-3.871762	4.885008

$Zn_4(OCOCF_3)_6O$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.601258	-0.412494	2.452787
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4	8	0	1.268949	3.213101	0.605759
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6	8	0	-0.991944	3.317257	0.636799
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46	9	0	-0.767138	-5.548884	-0.076341
47	9	0	-0.871638	-5.092514	-2.199654

$Zn_4(OCOCF_3)_6O{\bullet}CF_3CO_2H$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.475114	0.274170	2.749955
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5	6	0	0.345803	4.160162	0.193613
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43	9	0	1.234724	5.941310	1.460969
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45	9	0	-0.761447	6.232501	0.641667
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52	9	0	-0.237387	-0.616377	6.083182
53	9	0	0.346451	0.277406	4.185807
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