Supporting Information

Stereocontrol in solid-phase radical reactions: Radical addition to oxime ether anchored to polymer support

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General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 200 or 300 MHz and at 50 or 125 MHz, respectively. IR spectra were recorded using FTIR apparatus. Mass spectra were obtained by EI, CI, or SIMS methods. Preparative TLC separations were carried out on precoated silica gel plates (E. Merck $60F_{254}$). Flash column chromatography was performed using E. Merck Kieselgel 60 (230-400 mesh).

2-(Benzyloxyamino)butanoic acid (3). To a suspension of oxime ether **1** (0.83 mmol/g, 220 mg, 0.18 mmol) in CH_2Cl_2 (6.0 mL) was added Et_2Zn (1.0 M in hexane, 0.93 mL, 0.93 mmol) under a nitrogen atmosphere at -78 °C. After the reaction mixture was stirred at the same temperature for 30 min, the resin was filtered, washed well with CH_2Cl_2, AcOEt followed by MeOH and then dried in vacuo. To a flask with the resulting resin **2** was added TFA/CH_2Cl_2 (1:5, v/v, 5.0 mL) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 30 min, the reaction mixture was filtered and washed with MeOH/$CHCl_3$ (1:11, v/v, 60 mL), and the filtrate was concentrated at reduced pressure. Purification of the residue by Amberlite IR-120B (eluting with MeOH) followed by preparative TLC (MeOH/$CHCl_3$ 1:10, v/v) afforded the α-amino acid derivative **3** (34 mg, 89%) as a white solid: ^{1}H NMR

(CD_3OD) _ 7.34-7.26 (5H, m), 4.68 (2H, s), 3.50 (1H, br t, *J*=10.2 Hz), 1.58 (2H, m), 0.95 (3H, t, *J*=11.1 Hz); ^{13}C NMR (CD_3OD) _ 177.2, 138.9, 129.4, 129.1, 128.7, 76.9, 66.1, 23.6, 10.7; HRMS calcd for $C_{11}H_{15}NO_3$ (M^+) 209.1051, found 209.1064.

4-(*t*-Butyldimethylsiloxymethyl)phenylmethanol (4). To a solution of *p*-xylyene glycol (1.0 g, 7.2 mmol) and imidazole (1.2 g, 18 mmol) in DMF (3 mL) was added dropwise a solution of *t*-butyldimethylsilyl chloride (1.1 g, 7.3 mmol) in DMF (5 mL) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 3 h, the reaction mixture was diluted with Et_2O. The organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by flash chromatography (hexane/AcOEt 5:1) afforded **4** (1.1 g, 62%) as a colorless oil and 1,4-di(*t*-butyldimethylsiloxymethyl)benzene (0.26 g, 10%) as a white solid. **4**: IR ($CHCl_3$) 3608, 3447, 2930, 1514, 1471 cm^{-1}; ^1H NMR ($CDCl_3$) __7.29 (4H, m), 4.73 (2H, s), 4.62 (2H, br s), 0.94 (9H, s), 0.09 (6H, s); ^{13}C NMR ($CDCl_3$) _ 140.7, 139.4, 126.8, 126.1, 65.0, 64.6, 25.8, 18.2, -5.4; HRMS calcd for $C_{14}H_{24}O_2Si$ (M^+) 252.1544, found 252.1554. 1,4-di(*t*-butyldimethylsiloxymethyl)benzene

: IR ($CHCl_3$) 2956, 1472 cm^{-1}; ^1H NMR ($CDCl_3$) __7.28 (4H, m), 4.73 (4H, s), 0.94 (18H, s), 0.09 (12H, s); ^{13}C NMR ($CDCl_3$) _ 140.0, 125.9, 64.8, 25.8, 18.3, -5.4; HRMS calcd for $C_{20}H_{38}O_2Si_2$ (M^+) 366.2408, found 366.2419.

***N*-[4-(*t*-Butyldimethylsiloxymethyl)benzyloxy]phthalimide (5).** To a solution of **4** (7.3 g, 29 mmol) and Et_3N (4.4 mL, 32 mmol) in CH_2Cl_2 (40 mL) was added dropwise mesyl chloride (2.5 mL, 32 mmol) under a nitrogen atmosphere at 0 °C. After the reaction mixture was stirred at the same temperature for 1 h, Et_3N (4.4 mL, 32 mmol) and *N*-hydroxyphthalimide (5.9 g, 58 mmol) were added at 20 °C. After being heated at reflux for 8 h, the solvent was evaporated at reduced pressure. After to the resulting

residue was added AcOEt, the organic phase was washed with 1*N* NaOH, saturated aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by recrystallization (hexane/AcOEt) afforded **5** (9.0 g, 79%) as colorless crystals: mp 82-84 °C (hexane/AcOEt); IR ($CHCl_3$) 2956, 1733, 1469 cm^{-1}; ^1H NMR ($CDCl_3$) __7.68-7.81 (4H, m), 7.50, 7.33 (each 2H, d, *J*=8.0 Hz), 5.20, 4.74 (each 2H, s), 0.93 (9H, s), 0.08 (6H, s); ^{13}C NMR ($CDCl_3$) _ 163.3, 142.6, 134.2, 132.1, 129.7, 128.7, 125.9, 123.3, 79.5, 64.5, 25.7, 18.2, -5.5; HRMS calcd for $C_{22}H_{27}NO_4Si$ (M^+) 397.1708, found 397.1711. Anal. Calcd for $C_{22}H_{27}NO_4Si$: C, 66.47; H, 6.85; N, 3.52. Found: C, 66.30; H, 6.82; N, 3.38.

Methyl (*E*)-2-[4-(*t*-Butyldimethylsiloxymethyl)benzyloxyimino]ethanate (6). To a solution of **5** (12 g, 30 mmol) in MeOH (200 mL) was added a solution of hydrazine monohydrate (1.7 g, 33 mmol) in MeOH (10 mL) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 1 h, a solution of 2-hydroxy-2-methoxyacetic acid methyl ester (7.2 g, 60 mmol) in MeOH (10 mL) was added to the reaction mixture at 20 °C. After being stirred at the same temperature for 8 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated at reduced pressure. Purification of the residue by flash chromatography (hexane/AcOEt 10:1) afforded **6** (9.4 g, 93%) as a colorless oil: IR ($CHCl_3$) 2956, 1737, 1600, 1467 cm^{-1}; ^1H NMR ($CDCl_3$) __7.54 (1H, s), 7.33 (4H, m), 5.28, 4.74 (each 2H, s), 3.85 (3H, s), 0.94 (9H, s), 0.10 (6H, s); ^{13}C NMR ($CDCl_3$) _ 162.3, 141.8, 140.7, 134.3, 128.4, 126.1, 77.9, 64.5, 52.3, 25.8, 18.2, -5.4; HRMS calcd for $C_{17}H_{27}NO_4Si$ (M^+) 337.1708, found 337.1698.

***N*-[(*E*)-2-(4-(Hydroxymethyl)benzyloxyimino)ethanonyl]bornane-10,2-sultam (7)** To a solution of (1*R*)-(+)-2,10-camphorsultam (2.0 g, 9.3 mmol) and glyoxylic oxime ether **6** (3.8 g, 11 mmol) in CH_2ClCH_2Cl (40 mL) was added Me_3Al (1.0 M in hexane,

11 mL, 11 mmol) under a nitrogen atmosphere at 20 °C. After being heated at reflux for 24 h, the reaction mixture was diluted with 1*N* HCl and then extracted with CH_2Cl_2. The organic phase was washed with water, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by flash chromatography (hexane/AcOEt 4:1) afforded the silylated sultam derivative (4.8 g, quantitative) as a colorless oil: $[\alpha]^{22}_D$ +61.9 (*c* 2.3, $CHCl_3$); IR ($CHCl_3$) 2959, 1693, 1585, 1463 cm^{-1}; ^1H NMR ($CDCl_3$) __8.19 (1H, s), 7.33 (4H, m), 5.29, 4.74 (each 2H, s), 3.98 (1H, dd, *J*=7.1, 5.3 Hz), 3.51, 3.45 (each 1H, d, *J*=13.7 Hz), 2.20-2.00 (2H, m), 1.95-1.82 (3H, m), 1.48-1.28 (2H, m), 1.15, 0.97 (each 3H, s), 0.94 (9H, s), 0.10 (6H, s); ^{13}C NMR ($CDCl_3$) _ 158.9, 141.6, 140.7, 134.2, 128.5, 126.0, 78.0, 65.0, 64.5, 52.8, 48.7, 47.6, 44.5, 38.1, 32.7, 26.1, 25.7, 20.7, 19.6, 18.2, -5.5; HRMS calcd for $C_{26}H_{40}N_2O_5SSi$ (M^+) 520.2425, found 520.2421. To a solution of the silylated sultam derivative (4.8 g, 9.2 mmol) in EtOH (60 mL) was added pyridinium *p*-toluenesulfonate (4.6 g, 18 mmol) under a nitrogen atmosphere at 20 °C. After being heated at 60 °C for 2 h, the solvent was evaporated at reduced pressure. After to the resulting residue was added CH_2Cl_2, the organic phase was washed with saturated aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by flash chromatography (hexane/AcOEt 1:1) afforded sultam derivative (3.3 g, 89%) as colorless crystals: mp 139-142 °C (hexane/AcOEt); $[\alpha]^{21}_D$ +80.0 (*c* 1.09, $CHCl_3$); IR ($CHCl_3$) 3606, 2964, 1693, 1586, 1458 cm^{-1}; ^1H NMR ($CDCl_3$) __8.20 (1H, s), 7.37 (4H, m), 5.30, 4.69 (each 2H, s), 3.98 (1H, dd, *J*=7.2, 5.8 Hz), 3.51, 3.46 (each 1H, d, *J*=13.8 Hz), 2.12-2.05 (2H, m), 1.96-1.87 (3H, m), 1.47-1.26 (2H, m), 1.15, 0.97 (each 3H, s); ^{13}C NMR ($CDCl_3$) _ 158.9, 141.1, 140.8, 135.0, 128.7, 126.9, 77.9, 65.0, 64.7, 52.9, 48.7, 47.7, 44.5, 38.1, 32.7, 26.2, 20.7, 19.7; HRMS calcd for $C_{20}H_{26}N_2O_5S$ (M^+) 406.1561, found 406.1560. Anal. Calcd for $C_{20}H_{26}N_2O_5S$: C, 59.09; H, 6.45; N, 6.89; S, 7.89. Found: C, 59.04; H, 6.69; N,

6.90; S, 7.96.

Attachment of oxime ether 7 to Carboxypolystyrene HL resin.

To a suspension of Carboxypolystyrene HL resin (1.18 mmol/g, 12 g, 14 mmol) in CH_2Cl_2 (200 mL) were added oxime ether **7** (8.1 g, 20 mmol), DCC (8.5 g, 41 mmol) and DMAP (0.83 g, 6.8 mmol) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 1 h and then stood for 11 h, the resin was filtered, washed well with CH_2Cl_2, AcOEt followed by MeOH and then dried in vacuo.

Attachment of the sultam derivative to Wang resin. To a solution of **7** (7.2 g, 18 mmol) in pyridine (15 mL) was added glutaric anhydride (2.0 g, 18 mmol) under a nitrogen atmosphere at 20 °C and the reaction mixture was then heated at 80 °C for 1 h. After glutaric anhydride (2.0 g, 18 mmol) was added to the reaction mixture, which was then heated at 80 °C for 1 h, glutaric anhydride (2.0 g, 18 mmol) was added to the reaction mixture. After being heated at 80 °C for 2 h, the reaction mixture was diluted with AcOEt and then was washed with 5% HCl, water, brine, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by flash chromatography (hexane/AcOEt 3:2) afforded the acid derivative (9.1 g, 99%) as a colorless oil: $[\alpha]^{21}_D$ +67.1 (*c* 0.92, $CHCl_3$); IR ($CHCl_3$) 3684, 2969, 1732, 1586, 1519 cm^{-1}; ^1H NMR ($CDCl_3$) __8.20 (1H, s), 7.40-7.31 (4H, m), 5.31, 5.11 (each 2H, s), 3.98 (1H, dd, *J*=6.8, 5.6 Hz), 3.52, 3.46 (each 1H, d, *J*=14.0 Hz), 2.45-2.36 (4H, m), 2.13-1.90 (7H, m), 1.48-1.36 (2H, m), 1.16, 0.98 (each 3H, s); ^{13}C NMR ($CDCl_3$) _ 178.1, 172.5, 159.0, 140.9, 135.9, 128.7, 128.3, 77.7, 65.8, 65.1, 52.9, 48.8, 47.7, 44.6, 38.1, 33.0, 32.8, 26.2, 20.7, 19.73, 19.67; HRMS calcd for $C_{25}H_{32}N_2O_8S$ (M^+) 520.1877, found 520.1903. To a suspension of Wang resin (0.83 mmol/g, 6.0 g, 5.0 mmol) in CH_2Cl_2 (100 mL) were added the acid derivative (5.2 g, 10 mmol), DCC (5.1 g, 25 mmol) and DMAP (0.3 g,

2.5 mmol) under a nitrogen atmosphere at 20 °C. After the reaction mixture was stirred at the same temperature for 1 h and then stood for 11 h, the resin was filtered, washed well with CH_2Cl_2, AcOEt followed by MeOH and then dried in vacuo.

***N*-[(*2R*)-2-(4-(Hydroxymethyl)benzyloxyamino)butanonyl]bornane-10,2-sultam (10).** To a suspension of oxime ether **8** (0.77 mmol/g, 250 mg, 0.19 mmol) in CH_2Cl_2 (6.0 mL) was added Et_3B (1.0 M in hexane, 1.5 mL, 1.5 mmol) under a nitrogen atmosphere at -78 °C. After the reaction mixture was stirred at the same temperature for 30 min, the resin was filtered, washed well with CH_2Cl_2 and AcOEt and then dried in vacuo. To a flask with the resulting resin in THF/MeOH (2:1, 12 mL) was added K_2CO_3 (207 mg, 1.5 mmol) under a nitrogen atmosphere at 20 °C. After being stirred at the same temperature for 1.5 h, the reaction mixture was filtered and washed with MeOH, and the filtrate was concentrated at reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 1:1) afforded the α-amino acid derivative **10** (4 mg, 5%) as a colorless oil: $[\alpha]^{20}_D$ +137.37 (*c* 0.99, $CHCl_3$); IR ($CHCl_3$) 3640, 2966, 1693, 1458 cm^{-1}; ^1H NMR ($CDCl_3$) __7.38-7.24 (4H, m), 4.68, 4.63 (each 1H, d, *J*=11.7 Hz), 4.62 (3H, s), 4.26 (1H, dd, *J*=7.9, 4.8 Hz), 3.91 (1H, br t, *J*=6.2 Hz), 3.454, 4.451 (each 1H, d, *J*=14.0 Hz), 2.05 (2H, br d, *J*=6.5 Hz), 1.95-1.75 (3H, m), 1.72-1.28 (4H, m), 1.11, 0.95 (each 3H, s), 0.94 (3H, t, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) _ 173.8, 140.2, 136.9, 128.7, 126.7, 75.2, 64.7, 64.1, 52.7, 48.4, 47.5, 44.3, 38.0, 32.5, 26.1, 23.7, 20.5, 19.6, 10.3; HRMS calcd for $C_{22}H_{32}N_2O_5S$ (M^+) 436.2030, found 436.2032.

Ethyl radical addition to oxime ether 9. To a suspension of oxime ether **9** (0.83 mmol/g, 200 mg, 0.166 mmol) in CH_2Cl_2 (10 mL) was added Et_3B or Et_2Zn (1.0 M in hexane, 0.83 mL, 0.83 mmol) under a nitrogen atmosphere at -78 °C. After the reaction mixture was stirred at the same temperature for 30 min, the resin was filtered, washed well with CH_2Cl_2 and AcOEt, and then dried in vacuo. To a flask with the resulting resin

was added TFA/CH_2Cl_2 (1:5, v/v, 5.0 mL) under a nitrogen atmosphere at 20 °C. After being stirred at the same temperature for 30 min, the reaction mixture was filtered and washed with CH_2Cl_2 (50 mL), and the filtrate was concentrated at reduced pressure. After the resulting residue was added CH_2Cl_2, the organic phase was washed with diluted aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 2:3, 2-fold development) afforded the α-amino acid derivative **11a** (68 mg, 74%) in the case of Et_3B or (61 mg, 67%) in the case of Et_2Zn. $[\alpha]^{19}_D$ +70.0 (*c* 0.97, $CHCl_3$); IR ($CHCl_3$) 2965, 1731, 1457 cm^{-1}; ^1H NMR ($CDCl_3$) __7.36, 7.30 (each 2H, br d, *J*=7.5 Hz), 5.10 (2H, s), 4.72, 4.66 (each 1H, d, *J*=11.7 Hz), 4.28 (1H, dd, *J*=7.8, 4.8 Hz), 3.96 (1H, br t, *J*=6.3 Hz), 3.51, 3.48 (each 1H, d, *J*=14.1 Hz), 2.48-2.36 (4H, m), 2.13-1.80 (7H, m), 1.75-1.23 (4H, m), 1.12, 0.97 (each 3H, s), 0.95 (3H, t, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) _ 178.2, 173.7, 172.5, 137.8, 135.0, 128.6, 127.9, 75.1, 66.0, 64.8, 64.1, 52.8, 48.4, 47.6, 44.4, 38.1, 33.0, 32.7, 32.5, 26.2, 23.7, 20.5, 19.7, 19.6, 10.3; SIMS calcd for $C_{27}H_{38}N_2O_8S$ - H (negative, M^+ - H) 549.3332, found 549.3320.

Alkyl radical addition to oxime ether 9. To a suspension of oxime ether **9** (0.83 mmol/g, 200 mg, 0.166 mmol) in RI/toluene (4:1,.v/v, 5 mL) was added Et_3B or Et_2Zn (1.0 M in hexane, 0.83 mL, 0.83 mmol) under a nitrogen atmosphere at 0 °C. After the reaction mixture was stirred at the same temperature for 15 min, Et_3B or Et_2Zn (1.0 M in hexane, 0.83 mL, 0.83 mmol) was added to the reaction mixture. After the reaction mixture was stirred at the same temperature for 15 min, the resin was filtered, washed well with CH_2Cl_2 and AcOEt, and then dried in vacuo. To a flask with the resulting resin was added TFA/CH_2Cl_2 (1:5, v/v, 5.0 mL) under a nitrogen atmosphere at 20 °C. After being stirred at the same temperature for 30 min, the reaction mixture was filtered and washed with CH_2Cl_2 (50 mL), and the filtrate was concentrated at reduced pressure.

After to the resulting residue was added CH_2Cl_2, the organic phase was washed with diluted aqueous $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated at reduced pressure. Purification of the residue by preparative TLC (hexane/AcOEt 3:2, 3-fold development) afforded the α-amino acid derivative **11b** or **11c**. **11b**, $[\alpha]^{19}_{D}$ +59.1 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2966, 1732, 1456 cm^{-1}; ^1H NMR ($CDCl_3$) __7.36, 7.30 (each 2H, br d, *J*=7.8 Hz), 5.10 (2H, s), 4.69, 4.62 (each 1H, d, *J*=12.0 Hz), 4.14 (1H, br d, *J*=5.1 Hz), 3.97 (1H, br t, *J*=6.3 Hz), 3.51, 3.47 (each 1H, d, *J*=13.5 Hz), 2.48-2.37 (4H, m), 2.14-1.82 (8H, m), 1.48-1.28 (2H, m), 1.12, 0.97 (each 3H, s), 1.00, 0.86 (each 3H, d, *J*=6.9 Hz); ^{13}C NMR ($CDCl_3$) _ 178.4, 174.0, 172.5, 137.9, 134.9, 128.7, 127.9, 75.0, 67.9, 66.0, 64.9, 52.9, 48.2, 47.5, 44.4, 38.3, 33.0, 32.7, 32.6, 30.0, 26.2, 20.5, 19.7, 19.6, 17.6; HRMS calcd for $C_{28}H_{40}N_2O_8S$ + H (M^+ + H) 565.2582, found 565.2572. **11c**, $[\alpha]^{19}_{D}$ +50.0 (*c* 0.98, $CHCl_3$); IR ($CHCl_3$) 2933, 1731, 1451 cm^{-1}; ^1H NMR ($CDCl_3$) __7.35, 7.29 (each 2H, br d, *J*=8.1 Hz), 5.10 (2H, s), 4.68, 4.61 (each 1H, d, *J*=12.0 Hz), 4.14 (1H, m), 3.97 (1H, br t, *J*=6.3 Hz), 3.51, 3.46 (each 1H, d, *J*=14.4 Hz), 2.48-2.37 (4H, m), 2.17-1.79 (7H, m), 1.78-0.95 (13H, m), 1.13, 0.97 (each 3H, s); ^{13}C NMR ($CDCl_3$) _ 178.2, 173.9, 172.5, 138.0, 134.9, 128.7, 127.9, 74.9, 67.7, 66.0, 64.9, 52.9, 48.2, 47.5, 44.4, 39.7, 38.3, 33.0, 32.7, 32.6, 29.6, 28.6, 26.2, 26.1, 26.0, 25.8, 20.4, 19.8, 19.6; HRMS calcd for $C_{31}H_{44}N_2O_8S$ + H (M^+ + H) 605.2894, found 605.2900.