Recyclable Copper Catalysts Based on Imidazolium-Tagged C_2-Symmetric Bis(oxazoline) and Their Application in D–A Reactions in Ionic Liquids

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Supplementary data

1. Preparation of ligands

Synthesis of 4-iodobutoxy-(*tert*-butyl)dimethylsilane **4**

TBSCl 6.000 g, NaI 12.000 g, and 80 mL of dry acetonitrile were added to a oven dried flask under N_2 atmosphere, 28 mL of dry THF was added dropwise to the stirring solution, the mixture was heated at 55°C for 10 h, after which the solution was allowed to cool to room temperature and 120 mL of H_2O was added, extracted with a mixture of pentane/ether(9:1, 3×40 mL), the organic layer were combined, washed with a solution of sat $Na_2S_2O_3$, dried over Na_2SO_4, the solvent removed under vacuum to afford a colorless oil. Yield: 10.000 g (84%)

Synthesis of 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,9-di(*tert*-butyl)dimethylsilane **5b**

Compound **5b** was prepared according to the procedure described above for **5a** and isolated as a pale yellow oil in a yield of 71% after purification by column chromatography. $[\alpha]_D^{20}$ = -92.3 (*c* = 0.15, MeOH). ^{1}H NMR(400MHz, $CDCl_3$): δ = 4.11-4.07 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-CH_aH$_b$O), 4.02-3.98 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-CH$_a$$H_b$O), 3.86-3.81 (t, *J* = 8.4 Hz, 2H, oxazoline-C*H*N), 3.59-3.56（m, 4H, CH_2CH_2O), 2.03-2.00 (m, 4H, CCH_2CH_2), 1.98-1.87 (m, 4H, $CH_2CH_2CH_2$), 1.55-1.48 (m, 4H, $CH_2CH_2CH_2$), 1.30-1.22 (m, 36H, *tBu*), 0.02 (s,12H,OSi(CH_3)$_2$). ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.4, 75.6, 68.6, 63.2, 46.2, 34.3, 33.4, 32.8, 26.1, 20.6, 20.7, -5.0. MS (ESI): *m*:*z* = 639.5 [M^{+1}]. Anal. Calc. for $C_{35}H_{70}N_2O_4Si_2$: C, 65.77; H, 11.04; N, 4.38; found: C, 65.75; H, 11.18; N, 4.52.

Synthesis of 5,5-bis[(4*S*,5*R*)-4,5-dihydro-4,5-diphenyloxazol-2-yl]nonane-1,9-di(*tert*-butyl)dimethylsilane **5c**

Compound **5c** was prepared according to the procedure described above for **5a** and isolated as

a pale yellow oil in a yield of 55% after purification by column chromatography. $[\alpha]_D^{20}$ = -197.3 (*c* = 0.21, MeOH). ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.06-6.88 (m, 20H, oxazoline-*ph*), 5.95-5.93 (d, *J* = 10.0 Hz, 2H, oxazoline-C*H*O), 5.57-5.54 (t, *J* = 10.0 Hz, 2H, oxazoline-C*H*N), 3.71-3.67 (m, 4H, CH_2CH_2O), 2.46-2.23 (m, 4H, CCH_2CH_2), 1.67-1.54 (m, 8H, $CH_2CH_2CH_2$), 0.88 (s, 18H, $OSiC(CH_3)_3$), 0.06 (m,12H,$OSi(CH_3)_2$). MS (ESI): *m*:*z* = 831.5 [M^{+1}]. Anal. Calc. for $C_{51}H_{70}N_2O_4Si_2$: C, 73.69; H, 8.49; N, 3.37; found: C, 71.97; H, 8.80; N, 4.09.

Synthesis of 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,9-diol **6b**

Compound **6b** was prepared according to the procedure described above for **6a** and isolated as a yellow oil in a yield of 82% after purification by column chromatography. $[\alpha]_D^{20}$ = -108.5 (*c* = 0.20, MeOH)。^{1}HNMR(400MHz, $CDCl_3$): δ = 4.11-4.07 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-C$H_a$$H_b$O), 4.02-3.98 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-C$H_a$$H_b$O), 3.86-3.81 (t, *J* = 8.4 Hz, 2H, oxazoline-C*H*N), 3.59-3.56（m, 4H, CH_2CH_2O), 2.03-2.00 (m, 4H, CCH_2CH_2), 1.98-1.87 (m, 4H, $CH_2CH_2CH_2$), 1.55-1.48 (m, 4H, $CH_2CH_2CH_2$), 1.30-1.22 (s, 18H, *tBu*). ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.6, 75.2, 68.6, 61.5, 46.3, 33.8, 32.5, 31.4, 25.8, 20.5. MS (ESI): *m*:*z* = 411.3 [M^{+1}]. Anal. Calc.for $C_{23}H_{42}N_2O_4$: C, 67.28; H, 10.31; N, 6.82; found: C, 63.29; H, 10.43; N, 6.51.

Synthesis of 5,5-bis[(4*S*,5*R*)-4,5-dihydro-4,5-diphenyloxazol-2-yl]nonane-1,9-diol **6c**

Compound **6c** was prepared according to the procedure described above for **6a** and isolated as an yellow oil in a yield of 56% after purification by column chromatography. $[\alpha]_D^{20}$ = -372.2 (*c* = 1.46, MeOH), ^{1}HNMR (500MHz, $CDCl_3$): δ = 7.29-6.93(m, 20H, oxazoline-*ph*), 5.99-5.98 (d, *J* = 10.5 Hz, 2H, oxazoline-C*H*O), 5.61-5.59 (d, *J* = 10.5 Hz, 2H, oxazoline-C*H*N), 3.71-3.69 (m, 4H, CH_2CH_2O), 2.46-2.28 (m, 4H, CCH_2CH_2), 1.70-1.62 (m, 8H, $CH_2CH_2CH_2$). ^{13}CNMR (125MHz, $CDCl_3$): δ = 169.3, 137.1, 135.7, 127.8, 127.6, 127.6, 127.4, 127.0, 126.6, 86.2, 73.4, 61.7, 47.0, 32.9, 32.2, 20.4. MS (ESI): *m*:*z* = 603.3 [M^{+1}]. Anal. Calc. for $C_{39}H_{42}N_2O_4$: C, 77.71; H, 7.02; N, 4.65, found: C, 75.33; H, 7.32; N, 4.25.

Synthesis of 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,9- ditosylate **7b**

To a solution of **6b** (0.280 g, 0.68 mmol) in 10 mL of dichloromethane, TsCl (0.520 g, 2.7 mmol) and Et_3N (0.280 g, 2.7 mmol) were added at 0°C under N_2 atmosphere, the mixture was warmed to room temperature and stirred for 8 h. After which, the reaction mixture was quenched by addition of brine (10 mL), organic layer was washed with water (3×10 mL), dried over Na_2SO_4 and the solvent removed under vacuum to afford the crude product, which was purified by column chromatography (SiO_2, EtOAc/PE 1/1) to afford **7b** yield: 0.420 g (86%). mp: 100~102°C $[\alpha]_D^{20}$ = -46.7 (*c* = 0.20, MeOH). ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.77-7.76 (d, *J* = 8.0 Hz, 4H, OTs-ph-C*H*), 7.34-7.33(d, *J* = 8.0 Hz, 4H, OTs-ph-C*H*), 4.12-4.07 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-C$H_a$$H_b$O), 4.01-3.97 (m, 6H, oxazoline-C*H*N + CH_2CH_2O), 3.97-3.80 (dd, *J* = 8.4 Hz and 1.6 Hz, 2H, oxazoline-C$H_a$$H_b$O), 2.44 (s, 6H, OTs-C$H_3$), 1.91 (m, 4H, CCH_2CH_2), 1.66-1.62 (m, 4H, $CH_2CH_2CH_2$), 1.25-1.21 (m, 4H, $CH_2CH_2CH_2$), 0.85 (m, 18H, *tBu*). ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.8, 144.8,

133.3, 130.0, 128.0, 75.7, 70.5, 68.7, 46.3, 34.1, 32.4, 29.3 , 26.0, 21.8, 20.3, MS (ESI): *m*:*z* = 719.3 [M^{+1}]. Anal. Calc. for $C_{37}H_{54}N_2O_8S_2$: C, 61.81; H, 7.57; N, 3.90; found: C, 61.77; H, 7.72; N, 3.91.

Synthesis of 5,5-bis[(4*S*,5*R*)-4,5-dihydro-4,5-diphenyloxazol-2-yl]nonane-1,9- ditosylate **7c**

Compound **7c** was prepared according to the procedure described above for **7b** and isolated as an yellow oil in a yield of 85% after purification by column chromatography. mp: 100~102°C $[\alpha]_D^{20}$ = -172.3(*c* = 0.40, MeOH) ^{1}HNMR (400MHz, $CDCl_3$): δ = 7.80-7.78 (d, *J* = 7.6 Hz, 4H, OTs-ph-C*H*)， 7.31-7.29 (d, *J* = 7.6 Hz, 4H, OTs-ph-C*H*)，7.04-6.90 (m, 20H, ph-C*H*), 5.98-5.95 (d, *J* = 10.5 Hz, 2H, oxazoline-C*H*O), 5.58-5.55 (d, *J* = 10.5 Hz, 2H, oxazoline-C*H*N), 4.12-4.09 (m, 4H, CH_2OTs), 2.40 (s, 6H, OTs-CH_3), 2.04-1.76 (m, 4H, CCH_2CH$_2$), 1.53(m, 4H, CH$_2$CH_2CH$_2$), 1.27-1.24 (m, 4H, CH$_2$CH_2CH$_2$). ^{13}CNMR (100MHz, $CDCl_3$): δ = 168.6, 144.9, 137.4, 137.3, 135.9, 130.1, 128.1, 128.0, 127.8, 127.7, 127.2, 126.9, 86.5, 73.7, 70.3, 46.7, 32.6, 29.2, 21.8, 20.3. MS (ESI): *m*:*z* = 911.3 [M^{+1}]. Anal. Calc. for $C_{53}H_{54}N_2O_8S_2$: C, 69.87; H, 5.97; N, 3.07; found: C, 69.27; H, 6.11; N, 3.05.

Synthesis of (*S*)-2- { 1,9-dichloro-5-[(*R*)-4,5-dihydro-4-phenyloxazol-2-yl]nonan-5-yl } -4,5-dihydro-4-phenyloxazole **8**

PPh_3 (1.150 g, 4.40 mmol) and CCl_4 (1 mL) were added to a solution of 6a(0.500 g, 1.10 mmol) in 10 mL of dichloromethane under N_2 atmosphere, the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum to afford the crude product as a brown oil, which was purified by column chromatography (SiO_2, EtOAc/PE 5/1) to afford **8**, yield: 0.410 g (76%). $[\alpha]_D^{20}$ = +108.5 (*c* = 1.50, MeOH), ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.37-7.27 (m, 10H, oxazoline-ph-C*H*), 5.29-5.24 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH_aH$_b$O), 4.72-4.67 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH$_a$$H_b$O), 4.18-4.14 (t, *J* = 8.0 Hz, 2H, oxazoline-C*H*N), 3.60-3.57 (t, *J* = 8.0 Hz, 4H, CH$_2$CH_2Cl), 2.18-2.12 (m, 4H, CCH_2CH$_2$), 1.86-1.83 (m, 4H, CH$_2$CH_2CH$_2$), 1.55-1.49 (m, 4H, CH$_2$CH_2CH$_2$).^{13}C NMR (100MHz, $CDCl_3$): δ = 168.7, 142.3, 128.9, 127.8, 126.9, 75.3, 69.8, 44.9, 32.6, 32.0, 21.4. MS (ESI): *m*:*z* = 488.4 [M^{+1}].

Synthesis of 1,1'- {5,5-bis[(*R*)-4,5-dihydro-4-phenyloxazol-2-yl]nonane-1,9} bis-(1*H*-imidazole) **9**

7a (3.250 g, 4.30 mmol **)** and imidazole (0.750 g, 10.30 mmol) were dissolved in 20 mL of DMF under N_2 atmosphere, Cs_2CO_3 (3.350 g, 10.30 mmol) was added to the solution and stirred for 14 h. After which, 60 mL of dichloromethane was added, organic layer was washed with sat NH_4Cl aqueous liquid (3×60 mL), and then sat Na_2CO_3 (3×60 mL) , dried over Na_2SO_4. The solvent was removed under vacuum to afford a yellow oil, which was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 15/1) to afford **9**, yield: 1.700 g (72%). mp: 61~64°C $[\alpha]_D^{20}$ = +132.1 (*c* = 0.29, CH_2Cl_2), ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.41 (m, 2H, imidazole-C*H*), 7.29-7.23 (m, 10H, oxazoline-ph-C*H*), 7.02 (s, 2H, imidazole-C*H*), 6.85(s, 2H, imidazole-C*H*), 5.22-5.18 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH_aH$_b$O), 4.65-4.60 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH$_a$$H_b$O), 4.13-4.09 (t, *J* = 8.0 Hz,

2H, oxazoline-C*H*N), 3.95-3.92 (t, *J* = 8.0 Hz, 4H, CH_2CH_2mim), 2.11-2.03 (m, 4H, CCH_2CH_2), 1.82-1.78 (m, 4H, $CH_2CH_2CH_2$), 1.28-1.23 (m, 4H, $CH_2CH_2CH_2$). ^{13}CNMR (100MHz, $CDCl_3$): δ = 168.4, 142.2, 137.4, 129.7, 129.0, 127.9, 126.9, 118.9, 75.3, 69.7, 46.5, 46.1, 32.6, 31.1, 21.1. MS (ESI): *m*:*z* = 581.4 [M^{+1}].

Synthesis of 1,1'- { 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,9 } bis-(1,2-dimethyl-1*H*-imidazole) diOTs **10b**

Compound **10b** was prepared according to the procedure described above for **10a** from **7b** in a yield of 93%. $[\alpha]_D^{20}$ = -17.1 (*c* = 0.60, MeOH) ^{1}HNMR(400MHz, $CDCl_3$): δ = 7.68-7.66 (d, *J*=8.0 Hz, 4H, OTs-ph-C*H*), 7.41(s, 4H, imidazole-C*H*), 7.11-7.09 (d, *J* = 8.0 Hz, 4H, OTs-ph-C*H*), 4.14-4.09 (m, 2H, oxazoline-CH_aH_bO), 4.01-3.97 (m, 6H, oxazoline-C*H*N + CH_2CH_2mim), 4.09-4.06 (m, 2H, oxazoline-CH_aH_bO), 3.98-3.96 (s, 6H, imidazole-CH_3)，2.59 (s, 6H, imidazole-CH_3), 2.31 (s, 6H, OTs- CH_3), 1.98-1.80 (m, 4H, CCH_2CH_2), 1.73-1.69 (m, 4H, $CH_2CH_2CH_2$), 1.66-1.26 (m, 4H, $CH_2CH_2CH_2$), 0.88 (m, 18H, *tBu*). ^{13}CNMR (100MHz, $CDCl_3$): δ = 166.9, 144.2, 143.9, 139.2, 128.7, 126.0, 122.9, 121.4, 75.6, 68.8, 48.4, 45.7, 35.5 34.0, 32.0, 29.9, 21.4, 21.0. MS (ESI)：*m*:*z* = 284.3 [M^{2+}], *m*:*z* = 171.0 [M^-]. HRMS (ESI): calc. for $C_{33}H_{56}N_6O_2^{2+}$:284.2226; found: 284.2225.

Synthesis of 1,1'- { 5,5-bis[(4*S*,5*R*)-4,5-dihydro-4,5-diphenyloxazol-2-yl]nonane-1,9 } bis-(1,2-dimethyl-1*H*-imidazole) diOTs **10c**

Compound 10c was prepared according to the procedure described above for 10a from 7c in a yield of 89%. $[\alpha]_D^{20}$ = -209.9 (*c* = 0.86, MeOH), ^{1}H NMR (400MHz, DMSO): δ = 7.69~6.89 (m, 32H, Ph+imidazole-C*H*), 6.05~6.02 (d, *J* = 10.0 Hz, 2H, oxazoline-C*H*O), 5.62~5.60 (d, *J* =10.0 Hz, 2H, oxazoline-C*H*O), 4.17~4.15 (m, 4H, CH_2CH_2-imidazole), 3.67 (s, 6H, OTs-CH_3), 2.59 (s, 6H, imidazol-CH_3), 2.27 (s, 6H, imidazol-CH_3), 1.85~1.28(m, 12H, $(CH_2)_3CH_2$-imidazole). ^{13}CNMR (100MHz, $CDCl_3$): δ = 169.3, 144.9, 144.5, 138.2, 128.7, 128.4, 128.1, 127.9, 127.5, 127.1, 126.9, 126.1, 122.9, 121.5, 85.9, 73.1, 35.3, 30.1, 21.5. HRMS (ESI): calc. for $C_{49}H_{56}N_6O_2^{2+}$: 380.2226, found: 380.2226.

Synthesis of 1,1'- { 5,5-bis[(*R*)-4,5-dihydro-4-phenyloxazol-2-yl]nonane-1,9 } bis-(3-methyl-1*H*-imidazole) diI **10d**

9 (0.070 g, 0.13 mmol) and CH_3I (0.145 g, 1.00 mmol) were dissolved in dry Et_2O and stirred for 24 h at room temperature. The solvent was removed under vacuum to afford **10d**, yield: 0.094 g (86%). $[\alpha]_D^{20}$ = +56.5 (*c* = 0.12, MeOH), ^{1}HNMR (400MHz， DMSO): δ = 9.11 （s, 2H, imidazole-C*H*）7.70 (s, 2H, imidazole-C*H*), 7.71 (s, 2H, imidazole-C*H*), 7.67-7.16 (m, 10H，oxazoline-ph-C*H*), 5.24-5.20 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH_aH_bO), 4.69-4.65 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH_aH_bO), 4.57-4.20 (t, *J* = 8.0 Hz, 4H, CH_2CH_2mim), 4.13-3.97(oxazoline-C*H*N), 3.81 (s, 6H, imidazole-CH_3), 2.00-1.98(m, 4H, CCH_2CH_2), 1.86-1.83 (m, 4H, $CH_2CH_2CH_2$), 1.33-1.32 (m, 4H, $CH_2CH_2CH_2$). ^{13}CNMR (100MHz, DMSO): δ = 167.5, 142.7, 136.6, 128.6, 127.4, 126.6, 123.6, 122.4, 74.6, 69.6, 64.6, 48.6, 45.7, 35.9, 32.8, 30.8, 20.5. MS (ESI): *m*:*z* = 967.6 [$M+I^{+1}$], *m*:*z* = 707.3 [$M-I]^-$.

Synthesis of 1,1'-｛5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,9｝bis-(1,2-dimethyl-1*H*-imidazole) dihexafluorophosphate **10f**

Compound **10f** was prepared according to the procedure described above for **10e** from **10b** in a yield of 95%. mp: 121~124°C $[\alpha]_D^{20}$ = -50 (*c* = 0.10, MeOH) ^{1}HNMR(300 MHz, DMSO): δ = 7.60 (s, 4H, imidazole-C*H*), 4.13-4.05 (m, 8H, oxazoline-CH_aH$_b$O + oxazoline-C*H*N + CH_2CH_2mim), 3.78 (m, 8H, oxazoline-CH$_a$$H_b$O + imidazole-C$H_3$), 2.56 (s, 6H, imidazole-CH_3), 1.90-1.68 (m, 8H, $CH_2CH_2CH_2$), 1.20 (m, 4H, $CH_2CH_2CH_2$), 0.81 (m, 18H, *tBu*). ^{13}CNMR (75MHz, DMSO): δ = 165.8, 144.1, 122.2, 120.8, 74.6, 68.0, 48.4, 45.2, 40.1, 34.6, 33.3, 32.7, 29.3, 25.5, 20.5, HRMS (ESI): calc. for $C_{33}H_{56}N_6O_2^{2+}$: 284.2226, found: 284.2225, calc. for PF_6^-: 144.9641; found: 144.9809.

Synthesis of 1,1'-｛5,5-bis[(*R*)-4,5-dihydro-4-phenyloxazol-2-yl]nonane-1,9｝bis-(1,2-dimethyl-1*H*-imidazole) diCl **10g**

8 (0.380 g, 0.79 mmol) and 1,2-dimethyl-1*H*-imidazole (0.303 g, 3.16 mmol) were dissolved in 3 mL of Et_2O, the solution was stirred for 24 h under N_2 atmosphere. Et_2O was removed under high vacuum. Residue was washed with hexane (3×10 mL) to afford a yellow solid, yield: 0.49 g (91%). $[\alpha]_D^{20}$ = +91.8 (*c* = 1.00, MeOH), ^{1}HNMR (400MHz， DMSO): δ = 7.36-7.30 (m, 10H，oxazoline-ph-C*H*), 7.04 (s, 2H, imidazole-C*H*), 6.71 (s, 2H, imidazole-C*H*), 5.25-5.21 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH_aH$_b$O), 4.69-4.65 (dd, 2H, *J* = 8.0 Hz and 2.0 Hz, 2H, oxazoline-CH$_a$$H_b$O), 4.04-4.00 (t, *J* = 8.0 Hz, 6H, oxazoline-C*H*N + CH_2CH_2mim), 3.66-3.53 (m, 4H, CCH_2CH_2), 2.25(s, 6H, imidazole-CH_3), 2.01-1.73 (m, 4H, $CH_2CH_2CH_2$), 1.44-1.40(m, 4H, $CH_2CH_2CH_2$). ^{13}CNMR (100MHz, $CDCl_3$): δ = 168.2, 143.4, 129.7, 127.9, 127.4, 75.3, 69.7, 46.3, 45.9, 32.8, 32.7, 21.6. HRMS (ESI): calc. for $C_{37}H_{48}N_6O_2^{2+}$:304.1919; found: 304.1914

Synthesis of 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]pentan-1-(*tert*-butyl)dimethylsilane **11**

A solution of **3b** (1.000 g, 3.80 mmol) in 20 mL of dry THF was cooled to -78°C under N_2 atmosphere, *n*-BuLi (1.3 mL, 2.9 M in hexane, 3.80 mmol) was added to the solution dropwise, the resulting mixture was stirred at 0°C for 1 h, **4** (1.410 g , 0.15mmol) was added slowly to the mixture, after which the ice bath was removed and the solution left to warm to room temperature and stirred for a further 12 h. After this time, the reaction mixture was quenched by addition of water (15 mL) and extracted with dichloromethane (3×15mL). The organic fractions were combined washed with brine (1×20 mL) and H_2O (1×20 mL), dried over Na_2SO_4 and the solvent removed under vacuum to afford a thick dark oily residue, which was purified by column chromatography (SiO_2, PE/EtOAc, 10/1) to afford **11**, yield: 1.100g (65%). $[\alpha]_D^{20}$ = -57.13(*c* = 0.40, MeOH). ^{1}H NMR(500MHz, $CDCl_3$): δ = 4.20-4.16 (m, 2H, CH_2-OTBS), 4.11-4.05 (m, 2H, oxazoline-CH_aH$_b$O), 3.90-3.87 (m, 2H, oxazoline-CH$_a$$H_b$O), 3.62-3.59 (t, *J* = 6.5 Hz, 2H, oxazoline-C*H*N), 3.48-3.45（t, *J* = 7.8 Hz, 1H, bridge-C*H*), 2.00-1.88 (m, 2H, CCH_2CH_2), 1.58-1.55 (m, 2H, $CH_2CH_2CH_2$), 1.44-1.41 (m, 2H, $CH_2CH_2CH_2$), 0.92-0.89 (m, 27H, *tBu*), 0.04-0.01 (s, 6H, OTBS-CH_3). ^{13}C NMR (125MHz, $CDCl_3$): δ = 164.7, 164.4, 75.6, 75.5, 68.8, 68.8, 62.9, 39.8, 33.8, 33.7, 32.5, 29.7, 25.9, 23.9,

18.3, -5.3.

Synthesis of 5,5-bis((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)pentan-1-ol **12**

A solution of **11** (1.000 g, 2.14 mmol) in 10 mL of dry THF was cooled to 0°C under N_2 atmosphere, TBAF (0.560 g, 2.14 mmol) in 1.5 mL of THF were added to the solution dropwise, the resulting mixture was warmed to room temperature and stirred for 8 h. After which, the reaction mixture was quenched by addition of water (10 mL), washed with EtOAc (10 mL) and then with brine (10 mL), extracted with EtOAc (2×10 mL). The organic fractions dried over Na_2SO_4 and the solvent removed under vacuum to afford the crude product, which was purified by column chromatography (SiO_2, PE/EtOAc 2/1 to EtOAc) to afford **12** as an yellow oil; yield: 0.640 g (86%). $[\alpha]_D^{20}$ = -81.9 (*c* = 0.10, MeOH), ^{1}H NMR(500MHz, $CDCl_3$): δ = 4.22-4.18 (m, 2H, oxazoline-CH_aH$_b$O), 4.11-4.07 (m, 2H, oxazoline-CH$_a$$H_b$O), 3.92-3.87(t, *J* = 6.5 Hz, 2H, oxazoline-C*H*N), 3.70(s, 2H, CH_2-OH), 3.47-3.44（t, *J* = 7.8 Hz, 1H, bridge-C*H*), 2.65 (s, 2H, O*H*), 2.00-1.92 (m, 2H, CCH_2CH$_2$), 1.65-1.51 (m, 4H, CH_2CH_2CH$_2$), 0.94 (s, 18H, *tBu*). ^{13}C NMR (100MHz, $CDCl_3$): δ=164.9, 164.6, 75.4, 68.9, 61.8, 39.5, 33.7, 31.5, 28.5, 25.7, 23.3. MS (ESI): *m*:*z* = 339.5 [M^{+1}]

Synthesis of 5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]pentyl-1-tosylate **13**

To a solution of **12** (0.500 g, 1.48 mmol) in 10 mL of dichloromethane, TsCl (0.340 g, 1.77 mmol) and Et_3N (0.180 g, 1.77 mmol) were added at 0°C under N_2 atmosphere, the mixture was stirred for 8 h. After which, the reaction mixture was quenched by addition of brine (10 mL), organic layer was washed with water (3×10 mL), dried over Na_2SO_4 and the solvent removed under vacuum to afford the crude product, which was purified by column chromatography (SiO_2, EtOAc/PE 1/1) to afford **13** yield: 0.540 g (74%). mp: 46~48°C $[\alpha]_D^{20}$ = -41.2 (*c* = 0.10, MeOH), ^{1}H NMR(500MHz, $CDCl_3$): δ = 7.80-7.79 (d, *J* = 7.5 Hz, 2H, OTs-ph-C*H*), 7.37-7.35 (d, *J* = 7.5 Hz, 2H, OTs-ph-C*H*), 4.19-4.01 (m, 6H, CH_2-OTs + oxazoline-CH$_a$$H_b$O + oxazoline-C$H_aH_b$O), 3.88-3.87(t, *J* = 6.5 Hz, 2H, oxazoline-C*H*N), 3.39（t, *J* = 7.8 Hz, 1H, bridge-C*H*), 2.50 (s, 3H, OTs-CH_3), 1.96 (m, 2H, CCH_2CH$_2$), 1.71-1.68 (m, 2H, CH$_2$CH_2CH$_2$), 1.43-1.42 (m, 2H, CH$_2$CH_2CH$_2$), 0.89 (s, 18H, *tBu*). ^{13}C NMR (100MHz, $CDCl_3$): δ=164.9, 164.6, 129.8, 127.9, 75.6, 75.5, 70.1, 68.9, 68.9, 39.5, 33.7, 29.1, 28.5, 25.8, 23.4, 21.7.

Synthesis of 1-｛5,5-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]pentyl｝-(1,2-dimethyl-1*H*-imidazole) OTs **14**

Compound **14** was prepared according to the procedure described above for **10a** from **13** in 93% yield. ^{1}HNMR(400MHz, DMSO): δ = 7.61 (d, *J* = 2.5 Hz, 1H, imidazole-C*H*), 7.60 (d, *J* = 2.5 Hz, 1H, imidazole-C*H*), 7.47-7.45 (d, *J* = 10.0 Hz, 2H, OTs-ph-C*H*), 7.11-7.09 (d, *J* = 10.0 Hz, 2H, OTs-ph-C*H*), 4.16-3.97 (m, 6H, CH_2-OTs + oxazoline-CH$_a$$H_b$O + oxazoline-C$H_aH_b$O), 3.73-3.70(t, 2H, oxazoline-C*H*N), 3.70(s, 3H, imidazole-CH_3), 3.38（t, 1H, bridge-C*H*), 2.55 (s, 3H, OTs-CH_3), 2.28(s, 3H, imidazole-CH_3), 1.80 (m, 2H, CCH_2CH$_2$), 1.60 (m, 2H, CH_2CH_2CH$_2$), 1.30-1.28 (m, 2H, CH_2CH_2CH$_2$), 0.83 (s, 18H, *tBu*). ^{13}CNMR (100MHz, DMSO): 166.3, 166.1, 146.3, 145.0, 138.0, 128.5, 125.9, 123.4, 118.4, 76.7, 75.4,

69.8, 63.8, 48.6, 35.1, 34.5, 34.3, 26.0, 25.1, 21.2, 10.8. MS (ESI)：*m*:*z* = 321.3 [M-mim$^+$] *m*:*z* = 171.1 [M$^-$]. Anal. Calc. for $C_{41}H_{42}N_2O_8S_2$: C, 63.65; H, 8.51; N, 9.28; found: C, 63.59; H, 8.53; N, 9.48.

Synthesis of 2,2-bis((S)-4-tert-butyl-4,5-dihydrooxazol-2-yl)propane-1,3-diol **18**

18 was synthesized according to reference[1]. To a solution of **3b** (1.040 g, 4.0 mmol) in 15 mL of dichloromethane, $(CH_2O)n$ (0.340 g, 1.10 mmol) , 1,4-Dioxane (3.8 mL) and H_2O (0.7 mL) were added, Et_3N (1.54 mL) in 11 mL of THF were added at room temperature during 30 mins , the mixture was stirred for 3days. After which, the reaction mixture was poured to cooled pentane, the white solid appeared was recrystallized from EtOAc/PE yield: 1.090 g (83.7%). mp: 124~126°C $[\alpha]_D^{20}$= -88.2 (*c* = 0.12, CH_2Cl_2), ^{1}H NMR(500MHz, DMSO): δ = 4.66 (s, 2H, O*H*), 4.06 (dd, *J* = 9.0 Hz and 8.5 Hz, 2H, oxazoline-CH_aH$_b$O), 3.95 (dd, *J* = 9.0 Hz and 8.5 Hz, 2H, oxazoline-CH$_a$$H_b$O,), 3.91-3.880 (m, 4H, CCH_2OH), 3.73（dd, *J* = 8.5 Hz and 9.0 Hz, 2H, oxazoline-C*H*N), 0.79 (s, 18H, *tBu*). ^{13}C NMR (125MHz, DMSO): δ = 164.0, 75.1, 67.9, 60.4, 50.0, 34.0, 25.9.

Synthesis of 2,2-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]
propane-1,3-ditrifluoromethanesulfonate **19**

To a solution of **18** (0.330 g, 1.0 mmol) in 10 mL of dry dichloromethane, 1,2-dimethyl-1*H*-imidazole(0.190 g, 2.0 mmol) was added, the mixture was cooled to -78°C,Tf_2O(0.35 mL, 2.0 mmol) was added dropwise. The temperature of reaction solution was kept below -40°C for 2h, then 10mL of cold water was added, organic layer was separated, washed with 10 mL of brine, solvent was removed under vacuum, the crude product was purified by column chromatography (SiO_2, EtOAc/PE 5/1). Yield: 0.180 g (32%). mp: 91~93°C $[\alpha]_D^{20}$= -31.7 (*c* = 0.21, CH_2Cl_2), ^{1}H NMR(500MHz, $CDCl_3$): δ = 5.05 (s, 4H, CCH_2OTf), 4.27 (dd, *J* = 8.5 Hz and 8.5 Hz, 2H, oxazoline-CH_aH$_b$O), 4.14 (dd, *J* = 8.5 Hz and 8.5 Hz, 2H, oxazoline-CH$_a$$H_b$O), 3.94(dd, *J* = 8.5 Hz and 8.5 Hz, 2H, oxazoline-C*H*N), 0.89 (s, 18H, *tBu*), ^{13}C NMR (125MHz, $CDCl_3$): δ = 158.5, 119.8, 77.0, 75.9, 71.4, 69.4, 33.7, 25.7. MS (ESI): *m*:*z* = 591.1 [M^{+1}]

Synthesis of 1,1'-｛2,2-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,3｝
bis-(1,2-dimethyl-1*H*-imidazole) diOTf **20a**

19 (0.180 g, 0.31 mmol) and 1,2-dimethyl-1*H*-imidazole (0.300 g, 3.10 mmol) were dissolved in 2 mL of CH_3CN, the solution was heated to 70°C for 24 h under N_2 atmosphere. CH_3CN was removed under high vacuum. Residue was washed with Et_2O (3×10 mL) until it changed to light yellow solid, yield: 0.120 g (49%). $[\alpha]_D^{20}$ = -39.15 (*c* = 0.06, MeOH), ^{1}H NMR(500MHz, DMSO): δ = 7.53(s, 2H, imidazole-C*H*),7.47(s, 2H, imidazole-C*H*), 4.90 (m, 4H, CCH_2mim), 4.30 (dd, *J* = 9.5 Hz and 9.5 Hz, 2H, oxazoline-CH_aH$_b$O), 4.03 (dd, *J* = 9.5 Hz and 9.5 Hz, 2H, oxazoline-CH$_a$$H_b$O), 3.88(dd, *J* = 9.5 Hz and 9.5 Hz, 2H, oxazoline-C*H*N), 3.76(s, 6H, imidazole-CH_3)， 2.56(s, 6H, imidazole-CH_3), 0.80 (s, 18H, *tBu*), ^{13}C NMR (125MHz, DMSO): δ = 161.4, 146.8, 122.9, 121.8, 118.1, 75.5, 69.6, 49.8, 48.3, 40.2, 35.4, 33.8, 25.9. HRMS (ESI): calc. for $C_{27}H_{45}N_6O_2^{2+}$: 242.1762; found: 242.1754; calc. for OTf$^-$:

148.9514; found: 148.9517.

Synthesis of 1,1'- { 2,2-bis[(*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl]nonane-1,3 } bis-(1,2-dimethyl-1*H*-imidazole) dihexafluorophosphate **20b**

Compound **20b** was prepared according to the procedure described above for **10e** from **10b** in 89% yield. mp: 107~109°C $[\alpha]_D^{20}$ = -25.24 (*c* = 0.07, $CHCl_3$), ^{1}H NMR(500MHz, DMSO): δ = 7.65(s, 2H, imidazole-C*H*),7.57(s, 2H, imidazole-C*H*), 4.86 (m, 4H, CCH_2mim), 4.27 (dd, *J* = 10.0 Hz and 9.5 Hz, 2H, oxazoline-CH_aH$_b$O), 4.01(dd, *J* = 10.0 Hz and 9.5 Hz, 2H, oxazoline-CH$_a$$H_b$O), 3.87(dd, *J* = 10.0 Hz and 9.5 Hz, 2H, oxazoline-C*H*N), 3.77(s, 6H, imidazole-CH_3)， 2.62(s, 6H, imidazole-CH_3), 0.83 (s, 18H, *tBu*), ^{13}C NMR (125MHz, DMSO): δ = 161.3, 146.8, 122.8, 122.6, 75.5, 69.6, 49.8, 48.3, 40.1, 35.4, 33.8, 25.9. HRMS (ESI): calc. for $C_{27}H_{45}N_6O_2^{2+}$: 242.1755; found: 242.1754; calc. for PF_6^-: 144.9641; found: 144.9809.

2. Theoretical calculations results of 10b-Cu-15a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.922571	-3.110542	-0.583677
2	6	0	0.026377	-4.862309	-1.144233
3	6	0	1.178105	-3.933100	-1.588671
4	1	0	0.172029	-5.167353	-0.099952
5	1	0	0.118579	-5.786338	-1.726546
6	6	0	1.774313	-3.112742	-0.448159
7	1	0	1.991314	-4.563829	-1.967823
8	1	0	0.860431	-3.313479	-2.428783
9	1	0	1.482608	-3.498678	0.526183

10	6	0	-3.490704	-3.196961	-0.572854
11	6	0	-4.223260	-2.099975	0.218348
12	1	0	-3.746040	-4.176495	-0.159548
13	1	0	-3.815552	-3.197496	-1.616432
14	6	0	-5.647083	-1.865403	-0.312246
15	1	0	-4.263346	-2.389168	1.275439
16	1	0	-3.681384	-1.152149	0.177103
17	6	0	-6.453988	-0.996093	0.660298
18	1	0	-5.584497	-1.356837	-1.281187
19	1	0	-6.159793	-2.824234	-0.473597
20	1	0	-6.621100	-1.518687	1.607910
21	1	0	-5.913608	-0.070101	0.875356
22	7	0	-7.788759	-0.648964	0.126935
23	7	0	-9.460697	0.447694	-0.725386
24	6	0	-10.291871	1.528585	-1.268230
25	1	0	-10.422186	2.317540	-0.524300
26	1	0	-9.837308	1.939515	-2.172129
27	1	0	-11.267536	1.112438	-1.519110
28	6	0	-8.834539	-1.545080	-0.020160
29	1	0	-8.744775	-2.579219	0.272172
30	6	0	-9.879981	-0.861384	-0.552402
31	1	0	-10.875865	-1.180924	-0.816148
32	6	0	-7.364074	1.806473	-0.316183
33	1	0	-7.947614	2.645784	-0.697727

34	1	0	-7.015248	2.049973	0.693010
35	1	0	-6.459601	1.683398	-0.927801
36	6	0	5.248131	-3.234945	0.409175
37	1	0	6.132824	-3.366974	1.010893
38	6	0	3.941153	-3.299266	0.734328
39	1	0	3.456511	-3.500452	1.673143
40	7	0	3.204996	-3.036810	-0.429522
41	7	0	5.322077	-2.933693	-0.940714
42	6	0	6.563217	-2.669997	-1.682557
43	1	0	6.555908	-1.619659	-1.989192
44	1	0	7.402994	-2.870099	-1.017838
45	1	0	6.625372	-3.331661	-2.549741
46	6	0	3.842651	-2.508951	-2.882371
47	1	0	2.783176	-2.475394	-3.115621
48	1	0	4.282982	-1.529157	-3.102075
49	1	0	4.316242	-3.267079	-3.517704
50	6	0	4.094234	-2.811534	-1.450662
51	6	0	-8.181685	0.565926	-0.305594
52	6	0	-1.438566	-3.099242	0.851122
53	6	0	-0.578142	-2.623492	2.861382
54	6	0	-1.336654	-3.977335	2.916279
55	1	0	0.477853	-2.768235	3.117312
56	1	0	-0.685174	-4.841546	3.070887
57	1	0	-2.150624	-4.009889	3.639839

58	6	0	-1.488947	-1.866988	-1.359377
59	6	0	-0.510748	-0.029730	-2.316749
60	6	0	-1.961264	-0.199237	-2.814453
61	1	0	-0.462235	0.831238	-1.651376
62	1	0	-2.638989	0.592533	-2.494505
63	1	0	-2.046294	-0.378720	-3.886528
64	8	0	-2.430065	-1.415897	-2.159632
65	8	0	-1.930516	-4.109252	1.591572
66	7	0	-0.342087	-1.247072	-1.412911
67	7	0	-0.649090	-2.263054	1.416077
68	6	0	-1.132992	-1.521341	3.819048
69	6	0	-2.611848	-1.196703	3.541278
70	1	0	-2.981458	-0.494963	4.296680
71	1	0	-2.750859	-0.719142	2.567096
72	1	0	-3.251352	-2.086342	3.596773
73	6	0	-0.310031	-0.231177	3.654731
74	1	0	-0.670552	0.531093	4.353969
75	1	0	0.749272	-0.408017	3.881230
76	1	0	-0.409300	0.173742	2.643438
77	6	0	-0.962935	-2.033526	5.265636
78	1	0	-1.572080	-2.920524	5.474685
79	1	0	0.082847	-2.283439	5.485116
80	1	0	-1.273571	-1.259601	5.975199
81	6	0	0.531525	0.153320	-3.450663

82	6	0	0.136442	1.435509	-4.221172
83	1	0	0.892212	1.657608	-4.981810
84	1	0	-0.825390	1.338645	-4.737361
85	1	0	0.078256	2.299548	-3.549770
86	6	0	1.921473	0.381654	-2.842355
87	1	0	1.968665	1.297093	-2.249534
88	1	0	2.219815	-0.439965	-2.183568
89	1	0	2.687024	0.462748	-3.619886
90	6	0	0.557685	-1.030696	-4.435031
91	1	0	0.793989	-1.978711	-3.937990
92	1	0	-0.394066	-1.168009	-4.959820
93	1	0	1.321097	-0.862642	-5.202079
94	29	0	0.932603	-1.274756	0.012207
95	6	0	4.245316	0.784740	3.273316
96	6	0	3.437838	1.857647	2.512981
97	1	0	4.208112	0.887886	4.357372
98	1	0	5.270586	0.709144	2.916098
99	1	0	2.886432	2.525778	3.178513
100	1	0	4.061289	2.427701	1.823247
101	8	0	3.594788	-0.482088	2.944530
102	7	0	2.497044	1.026831	1.739633
103	6	0	2.737341	-0.299432	1.970131
104	8	0	2.161661	-1.282253	1.457601
105	6	0	1.555058	1.488122	0.837687

106	6	0	1.379985	2.934092	0.708396
107	1	0	2.221426	3.572227	0.950568
108	6	0	0.193265	3.424628	0.319547
109	1	0	0.036977	4.495981	0.238190
110	1	0	-0.650870	2.768536	0.112660
111	8	0	0.824288	0.684693	0.223531
112	6	0	-1.414038	-4.383606	-1.350298
113	1	0	-2.067203	-5.208579	-1.051161
114	1	0	-1.602837	-4.216624	-2.417590
115	1	0	-2.459538	8.211184	-0.557709
116	6	0	-2.972428	7.814750	0.324339
117	6	0	-3.122873	6.313809	0.252802
118	1	0	-3.953275	8.305010	0.376600
119	1	0	-2.411417	8.121488	1.213067
120	6	0	-3.211243	5.542149	1.421686
121	6	0	-3.216083	5.656066	-0.982605
122	6	0	-3.387946	4.160367	1.364895
123	1	0	-3.151071	6.033225	2.390236
124	6	0	-3.393638	4.274355	-1.054440
125	1	0	-3.159218	6.235519	-1.901114
126	6	0	-3.475328	3.527357	0.122391
127	1	0	-3.475230	3.573227	2.273434
128	1	0	-3.486881	3.776568	-2.014381
129	16	0	-3.618096	1.734602	0.047357

130	8	0	-2.217184	1.195482	0.068412
131	8	0	-4.406861	1.340119	1.250751
132	8	0	-4.310328	1.423100	-1.246623
133	8	0	5.216829	0.163536	-1.975317
134	16	0	5.014190	0.842348	-0.661426
135	8	0	4.856512	-0.159466	0.457055
136	8	0	3.916068	1.853860	-0.661981
137	6	0	6.515784	1.756400	-0.292986
138	6	0	7.527945	1.176326	0.472579
139	6	0	6.679343	3.040961	-0.820963
140	6	0	8.705017	1.887363	0.711378
141	1	0	7.389695	0.181667	0.884893
142	6	0	7.860025	3.736274	-0.576645
143	1	0	5.883004	3.488975	-1.406206
144	6	0	8.893820	3.173495	0.189618
145	1	0	9.490146	1.435346	1.312423
146	1	0	7.983649	4.735738	-0.986715
147	6	0	10.171245	3.939369	0.435708
148	1	0	10.715813	4.108182	-0.501291
149	1	0	9.967631	4.925271	0.869541
150	1	0	10.838296	3.402665	1.116400

References

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