Supporting Information for

Reductive amidation of alkyl tosylates with isocyanates
by Ni/Co-dual catalytic system

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1. General information

All reactions were performed on oven- and flame-dried glassware under argon using standard Schlenk techniques. Flash-column chromatography was performed with silica-gel 60 (KANTO Chemical Co. Inc., 40–50 nm). TLC monitoring was carried out with silica-gel aluminum sheets (Merck, type 60 F 254). Gas chromatography (GC) monitoring was carried out on Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were recorded with Varian-400 (1H NMR: 400 MHz; 13C NMR: 101 MHz) spectrometer or Varian-500 (1H NMR: 500 MHz; 13C NMR: 126 MHz) spectrometers, calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for 1H NMR spectra and at 77.0 ppm for 13C NMR spectra, respectively. Low-resolution mass spectrum (LRMS) was recorded on Shimadzu GCMS-QP2010SE (EI, 70 eV). High-resolution mass spectrum (HRMS) was performed by the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

2. Materials

All nickel catalysts were synthesised based on the reported method.1 Vitamin B12 and methylcobalamin were purchased from Nacalai tesque, Inc. (Product No.: 36323-54) and TCI Co. LTD. (Product No: M2742), respectively. All solvents were dried over activated MS 4Å, distilled and stored with activated MS 4Å under argon. Unless otherwise noted, commercially available reagents were used as received without further purification.

3. Synthetic methods for alkyl tosylates

Unless otherwise noted, alkyl tosylates were prepared in one of the following methods.

**General procedure 1:** The alcohol (1.0 equiv.), dichloromethane (DCM, 0.45 mol/L), Et3N (1.3 equiv.) and N,N-dimethylaminopyridine (DMAP, 2 mol%) were added to a round-bottom flask and the mixture was cooled to 0 °C. TsCl (1.1 equiv.) was added and the reaction mixture was stirred overnight at rt. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The combined organic phases were washed with saturated NaHCO3 (aq., 1 M HCl aq.) and brine. The obtained organic phase was dried over anhydrous MgSO4. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography or recrystallisation.
**General procedure 2:** alcohol (1.0 equiv.) and pyridine (1 mol/L) were added and cooled to 0 ºC. TsCl (1.5 equiv.) was added to a round-bottom flask and the mixture was stirred overnight at rt. After completion of the reaction, water was added to the reaction mixture and the aqueous phases were extracted with DCM. The combined organic phase was washed with 1 M HCl aq. and brine and dried over MgSO₄. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography or recrystallisation.

**1u.** was prepared by the general procedure 1. Isolated as a white solid (Mp. 138.0 – 138.5 ºC) in 88% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.44 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.20 (dt, J = 6.3, 3.9 Hz, 1H), 5.10 – 5.03 (m, 1H), 4.16 (dd, J = 10.2, 4.7 Hz, 1H), 4.09 (dd, J = 10.2, 5.7 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.57 – 2.35 (m, 2H), 2.43 – 2.37 (m, 4H), 2.30 (dd, J = 16.0, 3.6 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 175.9, 165.8, 145.4, 133.5, 132.2, 130.1, 129.6, 129.2, 128.5, 127.9, 84.0, 69.1, 51.7, 40.2, 38.3, 35.6, 21.6. HRMS calcd for C₂₂H₂₆NO₇S [M+NH₄]⁺: 448.14300, found 448.14245.

**Synthesis of alkyl ditosylate 3**

![Diagram of the synthesis of alkyl ditosylate 3](image)

1,2,6-Hexanetriol (1.21 g, 9.04 mmol, 1.0 equiv.), DCM (5 mL), and Et₃N (3.78 mL, 27.1 mmol, 3.0 equiv.) were added to a round-bottom flask and the mixture was cooled to -20 ºC. TsCl (3.79 g, 19.9 mmol, 2.2 equiv.) in DCM (15 mL) was added slowly and the reaction mixture was stirred overnight at -20 ºC. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The combined organic phases were washed with 1 M HCl aq. and brine. The obtained organic phase was dried over
anhydrous Na₂SO₄. After filtration and removing the solvent, the residue was purified by silica-gel column chromatography (hexane/DCM = 3:7) to obtain the hydroxyl ditosylate as a white solid in 73% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.74 (m, 4H), 7.40 – 7.31 (m, 4H), 4.06 – 3.95 (m, 3H), 3.90 – 3.83 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 1.71 – 1.52 (m, 2H), 1.47 (dt, J = 10.6, 8.6, 8.1, 5.6 Hz, 1H), 1.53 – 1.30 (m, 4H).

The ditosylate (2.0 g, 4.52 mmol, 1.0 equiv.), DCM (13 mL), DMAP (27.6 mg, 0.226 mmol, 5 mol%) and imidazole (769.3 mg, 11.3 mmol, 2.5 equiv.) were added to a round-bottom flask and the mixture was cooled to 0 ºC. TBSCI (817.5 mg, 5.42 mmol, 1.2 equiv.) was added and the reaction mixture was stirred overnight at rt. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The obtained organic phase was dried over anhydrous Na₂SO₄. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (hexane/DCM = 1:1) to obtain 3 as a colorless oil in 90% yield; ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.71 (m, 4H), 7.39 – 7.30 (m, 4H), 4.07 (dd, J = 7.0, 5.5 Hz, 2H), 3.99 – 3.89 (m, 1H), 3.85 (dd, J = 9.9, 5.5 Hz, 1H), 3.80 (dd, J = 9.9, 5.0 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 1.89 – 1.64 (m, 2H), 0.77 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 145.0, 144.9, 132.8, 132.6, 129.9, 129.9, 127.9, 127.9, 72.5, 66.4, 66.3, 33.3, 25.6, 21.6, 21.6, 17.8, -4.7, -5.2. HRMS calcd for C₂₆H₄₄NO₇S₂Si [M+NH₄]⁺: 574.23285, found 574.23236.

4. General procedure for the Ni/Co-catalysed reductive amidation of alkyl tosylates

In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with NiCl₂(6,6'-Me₂bpy) (10 mol%), vitamin B₁₂ (VB₁₂, 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, dodecyl tosylate (1a, 85.1 mg, 0.25 mmol, 1.0 equiv.) and t-Bu-isocyanate (47 µL, 0.375 mmol, 1.5 equiv.) were added into
the solution. The reaction mixture was stirred at 30 °C for 24 h. The obtained mixture was quenched by saturated NH₄Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over MgSO₄. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the product 2a as a white solid (Mp. 45.0 – 45.5 °C) in 91% yield; ¹H NMR (400 MHz, CDCl₃) δ 5.21 (s, 1H), 2.07 (t, J = 7.6 Hz, 2H), 1.34 (s, 9H), 1.32 – 1.22 (m, 19H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.5, 51.0, 37.8, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 25.8, 22.7, 14.1. HRMS calcd for C₁₇H₃₆NO [M+H]⁺: 270.27269, found 270.27939.

5. Characterisation of alkyl amides

2b. Isolated as a white solid (Mp.: 76.5 – 77.0 °C); ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.20 (s, 1H), 7.09 (t, J = 7.5 Hz, 1H), 2.35 (t, J = 7.6 Hz, 2H), 1.72 (p, J = 7.5 Hz, 2H), 1.47 – 1.14 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.4, 137.9, 129.0, 124.1, 119.7, 37.9, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.6, 22.7, 14.1. HRMS calcd for C₁₉H₃₂NO [M+H]⁺: 290.24839, found 290.24805.

2c. Isolated as a white solid (Mp.: 104.5 – 105.0 °C); ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 8.9 Hz, 2H), 7.19 (s, 1H), 6.84 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 2.32 (t, J = 7.6 Hz, 2H), 1.71 (p, J = 7.5 Hz, 2H), 1.39 – 1.16 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.3, 156.3, 131.1, 121.7, 114.1, 55.4, 37.6, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.7, 22.7, 14.1. HRMS calcd for C₂₀H₃₄NO₂ [M+H]⁺: 320.25895, found 320.25833.
2d. Isolated as a white solid (Mp.: 69.5 – 70.0 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 5.18 (s, 1H), 2.64 (t, J = 7.4 Hz, 2H), 2.12 – 2.02 (m, 2H), 2.01 – 1.88 (m, 2H), 1.34 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 172.0, 141.6, 128.5, 128.3, 125.9, 51.1, 36.8, 35.1, 28.8, 27.1. HRMS calcd for C₁₄H₂₂NO [M+H]⁺: 220.17014, found 220.16975.

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2e. Isolated as a white solid (Mp.: 61.5 – 62.0 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 5.19 (s, 1H), 2.61 (t, J = 7.7 Hz, 2H), 2.07 (t, J = 7.5 Hz, 2H), 1.63 (tt, J = 9.1, 6.6 Hz, 3H), 1.40 – 1.28 (m, 11H); ¹³C NMR (126 MHz, CDCl₃) δ 172.2, 142.3, 128.4, 128.3, 125.7, 51.0, 37.5, 35.7, 31.0, 28.8, 25.4. HRMS calcd for C₁₅H₂₄NO [M+H]⁺: 234.18579, found 234.18550.

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2f. Isolated as a white solid (Mp.: 44.5 – 45.0 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 5.19 (s, 1H), 2.62 (t, J = 7.1 Hz, 2H), 2.10 (t, J = 7.2 Hz, 2H), 1.71 – 1.59 (m, 6H), 1.33 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 172.2, 142.3, 128.4, 128.3, 125.7, 51.0, 37.5, 35.7, 31.0, 28.8, 25.4. HRMS calcd for C₁₆H₂₆NO [M+H]⁺: 248.20144, found 248.20103.

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2g. Isolated as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 5.22 (s, 1H), 3.88 – 3.78 (m, 1H), 2.26 – 2.02 (m, 2H), 1.82 – 1.71 (m, 1H), 1.69 – 1.52 (m, 2H), 1.34 (s, 9H), 1.13 (d, J = 6.1 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.4, 67.8, 51.0, 35.2, 33.6, 28.8, 25.9, 23.8, 18.1, -4.3, -4.7. HRMS calcd for C₁₅H₂₄NO₂Si [M+H]⁺: 288.23588, found 288.23569.

S6
2h. Isolated as a colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.28 (s, 1H), 5.10 – 5.02 (m, 1H), 2.19 – 1.85 (m, 4H), 1.66 (s, 3H), 1.58 (s, 3H), 1.32 (m, 13H), 1.20 – 1.03 (m, 1H), 0.86 (d, $J = 6.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 172.7, 131.2, 124.7, 51.0, 36.8, 35.4, 32.7, 32.1, 28.8, 25.7, 25.4, 19.3, 17.6. HRMS calcd for C$_{15}$H$_{30}$NO [M+H]$^+$: 240.23247, found 240.23203.

2i. Isolated as a colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.58 (s, 1H), 2.44 (tt, $J = 6.8$, 2.3 Hz, 2H), 2.25 (t, $J = 7.0$ Hz, 2H), 2.17 – 2.09 (m, 2H), 1.51 – 1.28 (m, 13H), 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.9, 81.5, 78.6, 51.1, 37.0, 31.0, 28.8, 21.9, 18.3, 15.4, 13.6. HRMS calcd for C$_{13}$H$_{24}$NO [M+H]$^+$: 210.18579, found 210.18541.

2j. Isolated as a colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.30 (s, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 2.27 (t, $J = 7.5$ Hz, 2H), 2.06 (t, $J = 7.5$ Hz, 2H), 1.66 – 1.54 (m, 4H), 1.31 (s, 9H), 1.23 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.7, 172.2, 60.4, 60.2, 60.0, 51.0, 37.3, 34.1, 34.1, 29.6, 29.0, 28.8, 28.7, 28.5, 28.4, 25.5, 25.3, 25.1, 24.7, 24.6, 24.4, 14.4, 14.3, 14.1, 14.0. HRMS calcd for C$_{13}$H$_{26}$NO$_3$ [M]$^+$: 244.19127, found 244.19107.

2k. Isolated as a white solid (Mp.: 91.5 – 92.0 ºC); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 9.1$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 5.29 (s, 1H), 3.97 (t, $J = 6.0$ Hz, 2H), 2.29 (t, $J = 7.2$ Hz, 2H), 2.14 – 2.02 (m, 2H), 1.32 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.4, 157.5, 129.3,

2l. Isolated as a white solid (Mp.: 95.5 – 96.0 °C); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 5.30 (s, 1H), 4.02 (t, J = 5.9 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 2.10 (p, J = 6.3 Hz, 2H), 1.33 (s, 12H), 1.31 (s, 9H); ^13C NMR (126 MHz, CDCl_3) δ 171.6, 161.4, 136.5, 113.8, 83.6, 66.6, 51.2, 33.8, 29.6, 28.8, 25.2, 24.8. HRMS calcd for C_{20}H_{33}BNO_4 [M+H]^+: 362.25026, found 362.25043.

2m. Isolated as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.34 (s, 1H), 3.65 – 3.44 (m, 2H), 3.44 – 3.35 (m, 1H), 3.35 – 3.21 (m, 1H), 2.80 – 2.63 (m, 1H), 2.20 – 1.94 (m, 2H), 1.44 (s, 9H), 1.34 (s, 9H); ^13C NMR (126 MHz, CDCl_3) δ 170.2, 154.4, 79.4, 51.3, 48.6, 37.3, 36.4, 28.7, 28.4, 27.9. HRMS calcd for C_{19}H_{27}N_{2}O_3 [M+H]^+: 271.20217, found 271.20157.

2n. Isolated as a white solid (Mp.: 104.5 – 105.0 °C); ^1H NMR (400 MHz, CDCl_3) δ 5.21 (s, 1H), 1.94 (tt, J = 11.7, 3.4 Hz, 1H), 1.86 – 1.72 (m, 4H), 1.68 – 1.61 (m, 1H), 1.51 – 1.34 (m, 2H), 1.33 (s, 9H), 1.31 – 1.12 (m, 3H); ^13C NMR (126 MHz, CDCl_3) δ 175.6, 50.8, 46.3, 29.8, 28.9, 25.8. HRMS calcd for C_{11}H_{22}NO [M+H]^+: 184.17014, found 184.16972.

2o. Isolated as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.20 (s, 1H), 1.98 (d, J = 7.0 Hz, 2H), 1.89 – 1.77 (m, 1H), 1.34 (s, 6H), 1.34 (s, 9H), 1.30 – 1.19 (m, 16H); ^13C NMR (126 MHz, CDCl_3) δ...
MHz, CDCl$_3$ δ 172.3, 51.0, 42.9, 35.4, 33.8, 33.4, 31.8, 29.6, 28.8, 28.7, 28.2, 26.5, 23.0, 22.6, 14.1. HRMS calcd for C$_{17}$H$_{36}$NO [M+H]$^+$: 270.27969, found 270.27939.

![BocN](image1)

**2p.** Isolated as a white solid (Mp.: 111.5 – 112.0 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.38 (s, 1H), 3.68 – 3.20 (m, 4H), 2.90 (d, J = 30.3 Hz, 2H), 2.79 – 2.64 (m, 1H), 2.16 – 1.93 (m, 2H), 1.43 (s, 9H), 1.33 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.6, 154.6, 79.1, 51.3, 51.1, 50.7, 45.5, 44.9, 40.4, 40.7, 35.9, 35.1, 31.5, 30.7, 28.8, 28.5. HRMS calcd for C$_{15}$H$_{23}$N$_2$O$_3$ [M+H]$^+$: 285.21782, found 285.21760.

![2q](image2)

**2q.** Isolated as a white solid (Mp.: 115.5 – 116.0 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 5.20 (s, 1H), 1.93 (d, J = 6.9 Hz, 2H), 1.81 – 1.61 (m, 6H), 1.34 (s, 9H), 1.32 – 1.21 (m, 2H), 1.19 – 1.06 (m, 1H), 0.97 – 0.86 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 171.8, 51.1, 45.9, 35.4, 33.1, 28.9, 26.3, 26.1. HRMS calcd for C$_{12}$H$_{24}$NO [M+H]$^+$: 198.18579, found 198.18542.

![2r](image3)

**2r.** Isolated as a white solid (Mp.: 143.5 – 144.0 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 5.22 (s, 1H), 3.76 (d, J = 11.5 Hz, 2H), 2.43 (s, 3H), 2.37 (td, J = 12.0, 2.4 Hz, 2H), 1.96 (d, J = 6.7 Hz, 2H), 1.79 – 1.65 (m, 3H), 1.38 – 1.21 (m, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.5, 143.5, 132.9, 129.6, 127.7, 51.3, 46.3, 44.0, 32.6, 31.2, 28.8, 21.5. HRMS calcd for C$_{18}$H$_{28}$N$_2$O$_3$S [M+H]$^+$: 353.18989, found 353.18994.
2s. Isolated as a white solid (Mp.: 88.5 – 89.0 °C); ¹H NMR (400 MHz, CDCl₃) δ 5.23 (s, 1H), 3.94 (ddt, J = 11.7, 4.5, 1.2 Hz, 2H), 3.40 (td, J = 11.9, 2.1 Hz, 2H), 2.12 – 1.92 (m, 3H), 1.68 – 1.58 (m, 2H), 1.34 (s, 9H), 1.33 – 1.22 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 170.8, 67.9, 51.3, 45.0, 32.8, 32.5, 28.8. HRMS calcd for C₁₁H₂₂NO₂[M+H]⁺: 200.16505, found 200.16406.

2t. Isolated as a white solid (Mp.: 103.5 – 104.0 °C); ¹H NMR (400 MHz, CDCl₃) δ 5.19 (s, 1H), 1.93 (d, J = 6.9 Hz, 2H), 1.79 – 1.65 (m, 6H), 1.34 (s, 9H), 1.28 – 1.07 (m, 6H), 0.99 – 0.84 (m, 7H); ¹³C NMR (126 MHz, CDCl₃) δ 171.8, 51.1, 45.9, 37.5, 37.0, 35.6, 33.0, 32.0, 29.2, 28.9, 23.0, 14.1. HRMS calcd for C₁₆H₃₂NO [M+H]⁺: 254.24839, found 254.24814.

2u. Isolated as a colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 8.02 – 7.96 (m, 2H), 7.55 (ddt, J = 8.7, 7.0, 1.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 5.67 (s, 1H), 5.21 (dt, J = 6.1, 4.1 Hz, 1H), 5.05 (td, J = 6.4, 1.9 Hz, 1H), 2.89 (d, J = 12.2 Hz, 2H), 2.65 – 2.56 (m, 1H), 2.56 – 2.43 (m, 2H), 2.40 – 2.21 (m, 2H), 2.14 (dd, J = 14.8, 8.5 Hz, 1H), 1.33 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 176.8, 169.3, 166.3, 133.4, 129.7, 128.5, 83.8, 79.4, 51.5, 49.2, 42.8, 39.6, 37.8, 35.8, 28.7. HRMS calcd for C₂₀H₂₆NO₅[M+H]⁺: 360.18110, found 360.18005.

2v. Isolated as a white solid (Mp.: 100.5 – 101.0 °C); ¹H NMR (500 MHz, CDCl₃) δ 4.64 (s, 1H), 3.96 – 3.83 (m, 1H), 3.34 (d, J = 9.8 Hz, 1H), 3.10 (d, J = 9.8 Hz, 1H), 2.38 (d, J = 16.6 Hz, 1H), 2.11 (d, J = 16.6 Hz, 1H), 1.38 (s, 9H), 1.32 (s, 9H), 1.13 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 173.5, 154.6, 54.8, 53.9, 50.4, 43.4, 35.1, 29.6, 28.9, 27.7, 23.5. HRMS calcd for C₁₅H₂₉N₂O₃[M+H]⁺: 285.21782, found 285.21759.
2w. Isolated as a colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta \) 5.30 (s, 1H), 2.32 – 2.23 (m, 2H), 1.87 – 1.78 (m, 2H), 1.44 (s, 9H), 1.30 (s, 6H), 0.96 (s, 9H), 0.17 (s, 6H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta \) 172.9, 72.9, 51.0, 40.4, 32.7, 29.7, 28.8, 28.2, 25.9, 18.1, -2.1. HRMS calcd for C\(_{16}\)H\(_{36}\)NO\(_2\)Si [M+H]\(^+\): 302.25153, found 302.25125.

6. Regioselective functionalisation of the alkyl ditosylate 3

6-1. Ni/Co-catalysed regioselective amidation of alkyl ditosylate 3

In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 °C for 3 min under vacuum. After cooling, the Schlenk tube was charged with NiCl\(_2\)(6,6'-Me\(_2\)bpy) (7.8 mg, 0.025 mmol, 10 mol%), vitamin B\(_{12}\) (VB\(_{12}\), 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, ditosylate 3 (139.2 mg, 0.25 mmol, 1.0 equiv.) and tBu-isocyanate (47 µL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 °C for 24 h. The obtained mixture was quenched by saturated NH\(_4\)Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over MgSO\(_4\). After filtration and removing the solvent, the residue was purified by silica-gel column chromatography (chloroform) to give the product 4 as a colorless oil in 87% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.78 (d, \(J = \) 8.3 Hz, 2H), 7.34 (d, \(J = \) 7.9 Hz, 2H), 5.21 (s, 1H), 3.90 – 3.77 (m, 3H), 2.45 (s, 3H), 2.04 (t, \(J = \) 7.5 Hz, 2H), 1.70 – 1.07 (m, 16H), 0.82 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta \) 172.0, 144.8, 132.9, 129.8, 127.9, 73.0, 69.8, 51.1, 37.4, 33.8, 28.8, 25.7, 25.6, 24.4, 21.6, 18.0, -4.6, -4.8. HRMS calcd for C\(_{24}\)H\(_{43}\)NO\(_2\)SSi [M+H]\(^+\): 486.27095, found 486.27023.

6-2. Cyanation of compound 4
This reaction was carried out following the literature.\(^2\) To a solution of 4 (102.0 mg, 0.21 mmol) in 3 mL of DMSO was added KCN (27.4 mg, 0.42 mmol, 2.0 equiv.), and the mixture was stirred at 60 °C for 12 h. After the reaction, the reaction mixture was extracted with Et\(_2\)O. The ethereal layer was washed with brine, dried over MgSO\(_4\) and evaporated to remove solvent. The residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the product 5 as a colorless oil in 82% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.23 (s, 1H), 3.97 – 3.89 (m, 1H), 2.45 (dd, \(J = 5.5, 4.8\) Hz, 2H), 2.09 (t, \(J = 7.4\) Hz, 2H), 1.69 – 1.53 (m, 5H), 1.34 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.9, 117.7, 68.1, 51.1, 37.3, 36.7, 28.8, 26.0, 25.7, 25.4, 24.5, 17.9, -4.7, -4.7. HRMS calcd for C\(_{18}\)H\(_{37}\)N\(_2\)O\(_2\)Si [M+H]\(^+\): 341.26243, found 341.26221.

6.3. Thiophenylation of compound 4

This reaction was carried out following the literature.\(^3\) To a solution of 4 (100 mg, 0.21 mmol) in EtOH (2.5 mL) was added NaOH (12.6 mg, 0.315 mmol, 1.5 equiv.). After the reaction mixture became homogeneous upon heating (40 °C), thiophenol (32 μL, 0.135 mmol, 1.5 equiv.) was added. The reaction mixture was heated (50 °C) for 24 h. After cooling to rt, the reaction mixture was concentrated in vacuo and diluted with H\(_2\)O. The aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with brine, filtered, and concentrated in vacuo. Purification of the resultant residue by silica-gel chromatography (Hexane/EtOAc = 5:1) afforded the product 6 as a colorless oil in 68% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.28 (m, 2H), 7.31 – 7.21 (m, 2H), 7.19 – 7.11 (m, 1H), 5.26 (s, 1H), 3.80 (t, \(J = 6.6, 4.9\) Hz, 1H), 3.05 – 2.86 (m, 2H), 2.06 (t, \(J = 7.5\) Hz, 2H), 1.73 – 1.46 (m, 4H), 1.44 – 1.24 (m, 11H), 0.86 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 172.2, 136.9, 129.1, 128.8, 125.8, 71.2, 51.0, 40.7, 37.6, 35.9, 28.8, 25.8, 25.7, 24.5, 18.0, -4.5, -4.6. HRMS calcd for C\(_{23}\)H\(_{41}\)NNaO\(_2\)Si [M+Na]\(^+\): 446.25250, found 446.25217.

7. Reductive amidation of ditosylate 3 by Martin’s method using NiBr\(_2\)(6-MePy) catalyst\(^4\)

![Diagram of the reaction](https://via.placeholder.com/150)

Starting materials: TsO\(_2\)OTBS, TsO\(_3\)OTs

**Reaction conditions:**
- NiBr\(_2\)(6-MePy) (3 mol%)  (3 mol%)
- Mn (1.5 equiv.)
- DMF, 30 °C, 24 h
- then H\(^+\)

**Products:** TsO\(_2\)OTBS (4), 0%
In a flame dried Schlenk tube, Mn powder (20.6 mg, 0.375 mmol, 1.5 equiv.) was added and heated at 400 °C for 3 min under vacuum. After cooling, the Schlenk tube was charged with NiBr₂(6-Mebp) (2.9 mg, 0.0075 mmol, 3 mol%), DMF (0.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, ditosylate 3 (139.2 mg, 0.25 mmol, 1.0 equiv.) and 4-Bu-isocyanate (47 µL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 °C for 24 h. The obtained mixture was quenched by saturated NH₄Cl aq. and diluted with EtOAc. The organic phase was analysed by GC using mesitylene as an internal standard. As a result, the reaction afforded complex mixture, in which a part of ditosylate 3 remained unchanged (Figure S1, a).

**Figure S1.** (a) A GC chart of the reaction mixture in the amidation of ditosylate 3 by NiBr₂(6-Mebp) under Martin’s conditions. (b) A GC chart of the mono-amidation product 4.
8. Effect of counter anions in the reductive amidation of alkyl tosylates

As shown in Table S1, careful selection of counter anion on nickel catalysts is essential in the present amidation because alkyl tosylates would be converted into alkyl halides via a tosylate–halogen exchange reaction with the anion. Thus, NiBr₂(6-Me bpy) catalyst gave alkyl amide 2e in the amidation of alkyl tosylate 1e in 18% yield with 32% conversion of 1e (Entry 1, Table S1). In contrast, NiCl₂(6-Me bpy) and NiCl₂(6,6′-Me₂bpy) catalysts afforded a negligible amount of 2e, in which most of 1e remained unchanged (Entries 2 and 3). These results would indicate that Br anion on NiBr₂ or in-situ generated MnBr₂ displaced TsO group to Br during reaction. Additionally, low-reactivities of NiCl₂ complexes were repeated in the cases of alkyl tosylates 1d and 1f (Entries 5 and 7), whereas NiCl₂(6,6′-Me₂bpy)/VB₁₂-dual catalytic system led to complete conversion of 1 and good product yields in all cases (Entries 4, 6 and 8).

Table S1 Examination for the effect of the counter anions

<table>
<thead>
<tr>
<th>Entry</th>
<th>1 (n)</th>
<th>Ni-Cat.</th>
<th>Co-Cat.</th>
<th>Conv. of 1 (%)</th>
<th>2 and yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1e (2)</td>
<td>NiBr₂(6-Me bpy)</td>
<td>none</td>
<td>32</td>
<td>2e</td>
</tr>
<tr>
<td>2</td>
<td>1e (2)</td>
<td>NiCl₂(6-Me bpy)</td>
<td>none</td>
<td>&lt;1</td>
<td>2e</td>
</tr>
<tr>
<td>3</td>
<td>1e (2)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>none</td>
<td>&lt;1</td>
<td>2e</td>
</tr>
<tr>
<td>4</td>
<td>1e (2)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>VB₁₂</td>
<td>100</td>
<td>2e</td>
</tr>
<tr>
<td>5</td>
<td>1d (1)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>none</td>
<td>&lt;1</td>
<td>2d</td>
</tr>
<tr>
<td>6</td>
<td>1d (1)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>VB₁₂</td>
<td>100</td>
<td>2d</td>
</tr>
<tr>
<td>7</td>
<td>1f (3)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>none</td>
<td>&lt;1</td>
<td>2f</td>
</tr>
<tr>
<td>8</td>
<td>1f (3)</td>
<td>NiCl₂(6,6′-Me₂bpy)</td>
<td>VB₁₂</td>
<td>100</td>
<td>2f</td>
</tr>
</tbody>
</table>

*Yields were determined by GC using mesitylene as an internal standard. Isolated yields.

9. Stoichiometric reactions of cobalt complexes with alkyl tosylates

In order to investigate a relationship between the steric hindrance of cobalt catalysts and alkyl tosylates, we carried out stoichiometric reactions of cobalt catalysts with alkyl tosylates.
(Eq. 1). That is, in a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 °C for 3 min. under vacuum. After cooling, the Schlenk tube was charged with cobalt catalyst (VB$_{12}$ or salcomine), DMF (1.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, alkyl tosylate 1 (1a: 0.25 mmol or 1o: 0.25 mmol) and mesitylene (0.25 mmol) as an internal standard were added into the solution. The recovery of alkyl tosylates was monitored by GC measurement. These results were graphically showed in Figure S2. As a result, the rate of reaction progress in the two S$_{N}$2-type oxidative addition (S$_{N}$2-type OA) between cobalt complexes and alkyl tosylates was quite similar. These results indicate that the S$_{N}$2-type OA would not be the rate-determining step in the present amidation and that the transalkylation between alkyl-Co(III) and Ni(0) might be the rate-determining step.
10. Mechanistic investigation

In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 °C for 3 min under vacuum. After cooling, the Schlenk tube was charged with NiCl₂(6,6'-Me₂-bpy) (7.8 mg, 0.025 mmol, 10 mol%), Me-cobalamin (16.8 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, dodecyl tosylate (1a, 85.1 mg, 0.25 mmol, 1.0 equiv.) and tBu-isocyanate (47 µL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 °C for 24 h. The obtained mixture was quenched by saturated NH₄Cl aq. and diluted with EtOAc. The organic phase was taken up and analysed by GC using mesitylene as an internal standard.
In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with NiCl$_2$(6,6'-Me$_2$bp) (7.8 mg, 0.025 mmol, 10 mol%), vitamin B$_{12}$ (VB$_{12}$, 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 µL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, cyclopropylmethyl tosylate (7, 56.6 mg, 0.25 mmol, 1.0 equiv.) and 4-anisyl isocyanate (55.9 mg, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH$_4$Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over MgSO$_4$. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the mixture of isomers 8 as a colorless oil.

The $^1$H NMR data is consistent with the literature: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 9.0$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 5.88 (ddt, $J = 16.8$, 10.2, 6.1 Hz, 1H), 5.26 – 4.89 (m, 2H), 3.79 (s, 3H), 2.65 – 2.33 (m, 4H).

![Chemical structures and NMR spectra](image)
11. Spectral data for products

2a

S18
12. References


