Supporting Information

Cobalt-Rhodium Heterobimetallic Nanoparticle-Catalyzed Synthesis of α,β -Unsaturated Amides from Internal Alkynes, Amines, and Carbon Monoxide

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I. General

Workup procedures were done in air. Toluene was freshly distilled from sodium to use. Liquid was transferred via a syringe or a cannula. Unless otherwise noted, all commercial materials were used without purification. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. TLC plates were visualized by ultraviolet light and treated with acidic *p*-anisaldehyde stain followed by gentle heating. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on a Bruker 300MHz spectrometer. Chemical shifts were referenced to CDCl_3 . High Resolution Mass spectrum was measured at the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. Compounds **3a**,¹ **3i**,² **3j**,³ **3n**,³ **3o**,³ **3p**,¹ and **4a**¹ were known compounds.

Immobilization of Metal Nanoparticles on Charcoal

To a two-neck flask were added *o*-dichlorobenzene (24 ml), oleic acid (0.2 ml), and trioctylphosphine oxide (0.4 g). While the solution was heated at 180°C, a solution of metal carbonyl, $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ (1.0 g), $\text{Co}_4(\text{CO})_{12}$ (1.19 g), or $\text{Rh}_4(\text{CO})_{12}$ (0.89 g) in 6 ml *o*-dichlorobenzene was injected into the flask. The resulting solution was heated to 180°C for 2 h and then concentrated to a volume of 5 ml. The concentrated solution was cooled to room temperature. To the cooled solution were added 25 ml of THF. After the solution was well stirred for 10 min, flame-dried charcoal (2.0 g) was added to the solution. After the resulting solution had been refluxed for 12 h, the precipitates were filtered and washed with diethyl ether (20 ml), dichloromethane (20 ml), acetone (20 ml), and methanol (20 ml). Vacuum drying gave a black solid.

General procedure for Co_2Rh_2 catalyzed aminocarbonylation

Aminocarbonylations were performed in a 100 ml stainless steel autoclave equipped with a stirring bar and the followings were placed in the autoclave in the order, alkyne

(1.5 mmol), amine (1.0 mmol), molecular sieves, toluene (4 mL), and 5 mol % Co_2Rh_2 (0.09 g of the immobilized Co_2Rh_2). The reactor was charged with 5 atm of CO and heated at 130 °C for 24h. After the reactor was cooled to room temperature, the solution was filtered and concentrated, and the product isolated by chromatography on a silica gel column, eluting with hexane and ethyl acetate (v/v, 4 : 1).

II. Characterization data of α,β -Unsaturated Amides

(E)-N-butyl-2-propylhex-2-enamide (3b)

IR: 3448, 1737, 1662, 1632, 1512, 1417 cm^{-1} ; **^1H NMR (300 MHz)** δ 0.92 (m, 9 H), 1.41 (m, 8 H), 2.10 (dd, 2 H, $J = 7.3$ Hz, $J = 14.7$ Hz), 2.27 (t, 2 H, $J = 7.9$ Hz), 3.29 (dd, 2 H, $J = 6.8$ Hz, $J = 13.1$ Hz), 5.94 (s, 1 H), 6.14 (t, 1 H, $J = 7.3$ Hz) ppm; **^{13}C NMR (75 MHz)** δ 13.8, 13.9, 14.0, 20.2, 22.3, 22.4, 29.3, 30.2, 31.9, 39.4, 134.4, 137.2, 170.0 ppm; **Exact Mass** for ($\text{C}_{13}\text{H}_{25}\text{NO}$, EI): 211.1936 (calc), 211.1932 (found)

(E)-N-butyl-2-ethylpent-2-enamide (3c)

IR: 3448, 1737, 1662, 1632, 1512, 1417 cm^{-1} ; **^1H NMR (300 MHz)** δ 0.93 (t, 3 H, $J = 7.3$ Hz), 1.02 (q, 6 H, $J = 7.4$ Hz), 1.36 (qd, 2 H, $J = 7.0$ Hz, $J = 14.0$ Hz), 1.53 (m, 2 H), 2.14 (p, 2 H, $J = 7.5$ Hz), 2.31 (q, 2 H, $J = 7.5$ Hz), 3.30 (dd, 1 H, $J = 7.1$ Hz, $J = 12.9$ Hz), 5.93 (s, 1 H), 6.11 (t, 1 H, $J = 7.3$ Hz) ppm; **^{13}C NMR (75 MHz)** δ 13.8, 13.9, 20.2, 20.5, 21.3, 31.9, 39.5, 135.6, 138.0 ppm; **Exact Mass** for ($\text{C}_{11}\text{H}_{21}\text{NO}$, EI): 183.1623 (calc), 183.1623 (found)

(3d)

(3d')

(E)-2-benzylidene-N-butylbutanamide (3d),

(E)-N-butyl-2-phenylpent-2-enamide (3d')

IR: 3440, 1741, 1706, 1661, 1619, 1510, 1418 cm^{-1} ; **^1H NMR (300 MHz)** δ 0.85 (t, 3.3 H, $J =$

7.2 Hz), 0.96 (dd, 6 H, $J = 6.7$ Hz, $J = 13.4$ Hz), 1.12 (t, 3.3 H, $J = 7.4$ Hz), 1.23 (dd, 2.2 H, $J = 7.3$ Hz, $J = 14.8$ Hz), 1.38 (m, 4.2 H), 1.58 (m, 2 H), 1.95 (p, 2 H, $J = 7.4$ Hz, 3d'), 2.55 (q, 2.2 H, $J = 7.4$ Hz, 3d), 3.23 (dd, 2 H, $J = 6.4$ Hz, $J = 13.1$ Hz, 3d'), 3.37 (dd, 2.2 H, $J = 6.5$ Hz, $J = 13.2$ Hz, 3d), 5.39 (s, 1 H, 3d'), 6.54 (s, 1.2 H, 3d), 6.98 (t, 1 H, $J = 7.7$ Hz, 3d'), 7.14 (m, 3.2 H), 7.34 (m, 8.4 H) ppm; ^{13}C NMR (75 MHz) δ 13.4, 13.5, 13.7, 13.8, 19.9, 20.1, 21.1, 22.5, 31.5, 31.7, 39.5, 127.5, 128.0, 128.3, 128.4, 128.8, 129.6, 131.5, 135.3, 135.8, 136.2, 140.2, 142.2, 166.7, 169.8 ppm; **Exact Mass** for ($\text{C}_{15}\text{H}_{21}\text{NO}$, EI): 231.1623 (calc), 231.1623 (found)

(E)-2-benzylidene-N-butylhexanamide (3e),

(E)-N-butyl-2-phenylhept-2-enamide (3e')

IR: 3440, 1742, 1705, 1661, 1619, 1507, 1417 cm^{-1} ; ^1H NMR (300 MHz) δ 0.78-0.97 (m, 15 H), 1.19-1.62 (m, 20 H), 1.94 (m, 2H, 3e'), 2.51 (m, 3 H, 3e), 3.23 (m, 2H, 3e'), 3.36 (dd, 3 H, $J = 6.4$ Hz, $J = 13.5$ Hz, 3e), 5.35 (t, 1 H, $J = 5.4$ Hz, 3e'), 6.31 (s, 1.5 H, 3e), 7.01 (dt, 1H, $J = 1.4$ Hz, $J = 7.7$ Hz, 3e'), 7.09 (s, 1.5 H, 3e), 7.14-7.41 (m, 12.5 H) ppm; ^{13}C NMR (75 MHz) δ 13.8, 13.8, 13.9, 20.1, 20.2, 22.4, 22.8, 27.8, 29.0, 31.0, 31.1, 31.6, 31.8, 39.6, 127.6, 128.0, 128.4, 128.5, 128.9, 129.8, 131.7, 135.7, 136.0, 136.3, 139.4, 141.2, 166.7, 170.2 ppm; **Exact Mass** for ($\text{C}_{17}\text{H}_{25}\text{NO}$, EI): 259.1936 (calc), 259.1936 (found)

(E)-N-butyl-3-(4-methoxyphenyl)-2-phenylacrylamide (3f),

(E)-N-butyl-2-(4-methoxyphenyl)-3-phenylacrylamide (3f')

IR: 3424, 1738, 1651, 1600, 1507, 1418 cm^{-1} ; ^1H NMR (300 MHz) δ 0.88 (dt, 6.6 H, $J = 4.2$ Hz, $J = 7.2$ Hz), 1.27 (dt, 4.4 H, $J = 6.9$ Hz, $J = 14.0$ Hz), 1.43 (m, 4.4 H), 3.29 (m, 4.4 H), 3.70 (s, 3 H, f), 3.84 (s, 3.6 H, f'), 5.46 (s, 1 H, f), 5.60 (s, 1.2 H, f'), 6.62 (s, 1 H), 6.65 (s, 1.2 H), 6.97 (m, 7.6 H), 7.14 (m, 5.6 H), 7.26 (dd, 2.2 H, $J = 6.0$ Hz, $J = 7.8$ Hz), 7.44 (d, 2.2 H, $J = 7.0$ Hz), 7.81 (s, 2.2 H) ppm; ^{13}C NMR (75 MHz) δ 13.8, 20.1, 31.6, 39.9, 55.2, 55.3, 113.6, 115.0, 127.7, 128.0, 128.1, 128.3, 128.4, 129.7, 130.0, 130.3, 131.1, 132.0, 132.2, 134.2, 135.3, 136.5, 136.6, 136.7, 159.7, 159.8, 167.2, 167.4 ppm; **Exact Mass** for ($\text{C}_{20}\text{H}_{23}\text{NO}_2$, EI): 309.1729 (calc),

309.1729 (found)

(E)-N-octyl-2,3-diphenylacrylamide (3g)

IR: 3424, 1744, 1664, 1614, 1510, 1417 cm^{-1} ; **^1H NMR (300 MHz)** δ 0.87 (t, 3 H, $J = 6.1$ Hz), 1.23 (m, 10 H), 1.43 (quin, 2 H, $J = 6$ Hz), 3.28 (dd, 2 H, $J = 6.6$ Hz, $J = 13.4$ Hz), 5.52 (t, 1 H, $J = 4.3$ Hz), 6.97 (m, 2 H), 7.09 (m, 3 H), 7.24 (m, 2 H), 7.42 (m, 3 H), 7.85 (s, 1 H) ppm; **^{13}C NMR (75 MHz)** δ 14.2, 22.7, 26.8, 26.9, 29.2, 29.5, 31.8, 40.2, 128.1, 128.4, 128.5, 129.6, 129.9, 130.3, 134.6, 135.0, 136.4, 136.9, 167.0 ppm; **Exact Mass** for ($\text{C}_{23}\text{H}_{29}\text{NO}$, EI): 335.2249 (calc), 335.2249 (found)

(E)-N-octyl-2-propylhex-2-enamide (3h)

IR: 3440, 1737, 1660, 1632, 1510, 1419 cm^{-1} ; **^1H NMR (300 MHz)** δ 0.90 (m, 9 H), 1.28 (m, 10 H), 1.42 (m, 4 H), 1.51 (m, 2 H), 2.10 (dd, 2 H, $J = 7.3$ Hz, $J = 14.8$ Hz), 2.30 (t, 2 H, $J = 7.3$ Hz), 3.27 (dd, 2 H, $J = 6.6$ Hz, $J = 13.4$ Hz), 6.16 (t, 1 H, $J = 7.3$ Hz), 6.23 (t, 1 H, $J = 5.3$ Hz) ppm; **^{13}C NMR (75 MHz)** δ 13.8, 13.9, 14.0, 22.2, 22.3, 22.6, 27.0, 29.1, 29.2, 29.3, 29.6, 30.1, 31.8, 39.6, 134.3, 137.0, 169.8 ppm; **Exact Mass** for ($\text{C}_{17}\text{H}_{33}\text{NO}$, EI): 267.2562 (calc), 267.2562 (found)

(E)-N-benzyl-2,3-diphenylacrylamide (3k)

IR: 3424, 1782, 1660, 1606, 1510 cm^{-1} ; **^1H NMR (300 MHz)** δ 4.52 (d, 2 H, $J = 5.9$ Hz), 5.81 (s, 1 H), 6.99 (dd, 2 H, $J = 1.7$ Hz, $J = 7.8$ Hz), 7.20 (m, 10 H), 7.40 (m, 3 H), 7.91 (s, 1 H) ppm; **^{13}C NMR (75 MHz)** δ 44.1, 127.4, 128.3, 128.7, 130.0, 130.5, 134.3, 135.0, 136.1, 137.7,

138.4, 167.2 ppm; **Exact Mass** for (C₂₂H₁₉NO, EI): 313.1467 (calc), 313.1467 (found)

(E)-N-benzyl-2-propylhex-2-enamide (3l)

IR: 3440, 1662, 1622, 1507, 1451, 1419 cm⁻¹; **¹H NMR (300 MHz)** δ 0.91 (dt, 6 H, *J* = 4.8 Hz, *J* = 7.3 Hz), 1.42 (m, 4 H), 2.10 (q, 2 H, *J* = 7.4 Hz), 2.30 (m, 2 H), 4.45 (d, 2 H, *J* = 5.8 Hz), 6.18 (t, 1 H, *J* = 7.3 Hz), 6.31 (s, 1 H), 7.26 (m, 5 H) ppm; **¹³C NMR (75 MHz)** δ 13.9, 14.0, 22.3, 22.4, 29.3, 30.2, 43.7, 127.3, 127.7, 128.6, 135.0, 137.0, 138.9, 169.8 ppm; **Exact Mass** for (C₁₆H₂₃NO, EI): 245.1780(calc), 245.1780 (found)

(E)-N-phenethyl-2,3-diphenylacrylamide (3m)

IR: 3416, 1664, 1612, 1512, 1416 cm⁻¹; **¹H NMR (300 MHz)** δ 2.76 (t, 2 H, *J* = 6.8 Hz), 3.54 (q, 2 H, *J* = 6.7 Hz), 5.50 (t, 1 H, *J* = 5.1 Hz), 6.96 (m, 2 H), 7.03-7.24 (m, 10 H), 7.35 (m, 1 H), 7.85 (s, 1 H) ppm; **¹³C NMR (75 MHz)** δ 35.5, 41.4, 126.5, 128.2, 128.5, 128.6, 128.7, 128.8, 129.6, 129.9, 130.5, 134.4, 135.0, 136.1, 137.0, 138.8, 167.0 ppm; **Exact Mass** for (C₂₃H₂₁NO, EI): 327.1623 (calc), 327.1626 (found)

N-benzyl-2-methyleneoctanamide (3q)

IR: 3360, 1654, 1592, 1547, 1416 cm⁻¹; **¹H NMR (300 MHz)** δ 0.87 (t, 3 H, *J* = 6.6 Hz), 1.28 (m, 6 H), 1.45 (m, 2 H), 2.33 (t, 2 H, *J* = 7.5 Hz), 4.50 (d, 2 H, *J* = 5.7 Hz), 5.27 (s, 1 H), 5.59 (s, 1 H), 7.32 (m, 5 H) ppm; **¹³C NMR (75 MHz)** δ 14.3, 22.8, 28.2, 29.1, 31.8, 32.6, 43.9, 117.5, 127.7, 128.0, 128.9, 138.5, 145.9, 169.0 ppm; **Exact Mass** for (C₁₆H₂₃NO, EI): 245.1780 (calc), 245.1781 (found)

III. References

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-3b-

-3c-

-3d+3d'-

-3f+3f'-

-3g-

-3h-

-3k-

-31-

-3m-

-3q-