Supporting Information: Gold Catalyzed Intermolecular Amidation of Benzylic C-H Bonds

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Contents:

1. General

All reactions were carried out in air. ^{1}H NMR spectra of solutions in CDCl$_3$ were on 300 MHz NMR spectrometers. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvents signals. Abbreviations for signal couplings are: s, singlet: d, doublet: t, triplet: m, multiplet.

2. Complex synthesis

2.1 Synthesis of gold complex 1 [AubpyCl$_2$]Cl[1]

Dipyridine (312 mg, 2 mmol) in water (20 mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398 mg, 1 mmol) in 20 mL of water. After 3 hours, the resulting solution was filtered through celite. The yellow precipitate rinsed with water (15 mL) and eluted with CH_3CN. Concentration *in vacuo* provided the desired gold(III) complex **1** as a yellow powder (320 mg, 65% yield). ^{1}H NMR (300 MHz, CH_3CN-d_3) δ 9.45-9.44 (m, 2H), 8.66-8.60 (m, 4H), 8.09-8.06 (m, 2H).

2.2 Synthesis of gold complex 2 [AuPy$_2$Cl$_2$]Cl[2]

Pyridine (316 mg, 4 mmol) in water (20 mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398 mg, 1 mmol) in 20 mL of water. After 3 hours, the resulting solution was filtered through celite. The yellow precipitate rinsed with water (15 mL) and eluted with CH_3CN. Concentration *in vacuo* provided the desired gold(III) complex **2** as a yellow powder (369 mg, 80% yield). ^{1}H NMR (300 MHz, CH_3CN-d_3) δ 8.55-8.51(m, 4H), 7.84-7.76 (m, 2H), 7.42-7.36 (m, 4H).

2.3 Synthesis of gold complex 3 PicAuCl$_2$[3]

2-picolinic acid (246 mg, 2 mmol) in water (20 mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398 mg, 1 mmol) in 20 mL of water. After 3 hours, the resulting solution was filtered through celite. The yellow precipitate rinsed with water (15 mL) and eluted with acetone. Concentration *in vacuo* provided the desired dichloro(pyridine-2-carboxylato)gold(III) complex ($PicAuCl_2$) as a yellow powder (268 mg, 70% yield). ^{1}H NMR (300 MHz, acetone-d_6) δ 9.30-9.28 (m, 1H), 8.71-8.66 (m, 1H), 8.27-8.23 (m, 1H), 8.20-8.17 (m, 1H).

3. Gold-catalyzed amidation of benzylic sp^{3}C-H bond: Optimization of conditions

A 25 mL round-bottom flask equipped with magnetic stirrer was charged with ethylbenzene

(0.5 mmol), *p*-toluenesulfonamide (0.5 mmol), solvent (3 ml), oxidant (0.5 mmol) and gold catalyst (10 mol %). The resulting mixture was continuously stirred for 8-13 h. At the end of the reaction, the mixture was filtered and the filtrate was extracted with ethyl acetate (3-10 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and the fraction was collected and concentrated to give the desired product.

4. Gold-bipy/NBS catalyzed amidation of benzylic sp^3C-H bonds with sulphonamides

4.1 General procedure for amidation of benzylic sp^3C-H bonds with sulfonamides

A 25 mL round-bottom flask equipped with magnetic stirrer was charged with benzylic reagent (1 mmol), sulfonylamide (0.5 mmol), acetonitrle (3 ml), *N*-bromosuccinide (NBS) (0.5 mmol) and gold-complex **1** (3mol %). The resulting mixture was continuously stirred at 70 ^{o}C. At the end of the reaction, the mixture was filtered and the filtrate was extracted with ethyl acetate (3-10 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and the fraction was collected and concentrated to give the desired product.

4.2 Characterization of products

***N*-benzhydryl-4-methylbenzenesulfonamide (4a)**[4]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.58-7.56 (m, 2H, ArH), 7.22-7.19 (m, 6H, ArH), 7.15-7.09 (m, 6H, ArH), 5.59-5.58 (m, 1H, NH), 5.28-5.26 (m, 1H, CH).

***N*-benzhydryl-4-nitrobenzenesulfonamide (4b)**[5]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.18 (d, J = 9 Hz, 2H, ArH), 7.75 (d, J = 9 Hz, ArH), 7.24-7.22 (m, 6H, ArH), 7.13-7.01 (m, 4H, ArH), 5.74 (m, 1H, NH), 7.41-7.39 (m, 1H, CH).

4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (4c)[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66-7.63 (m, 2H, ArH), 7.17-7.14 (m, 7H, ArH), 5.60-5.57 (m, 1H, NH), 4.51-4.42 (m, 1H, CH), 2.38 (s, 3H, CH_3), 1.41 (d, J = 6.9 Hz, 3H, CH_3).

4-nitro-*N*-(1-phenylethyl)benzenesulfonamide (4d)[7]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.41-8.38 (m, 1H, ArH), 8.16-8.13 (m, 2H, ArH), 7.79-7.79 (m, 2H, ArH), 7.18-7.15 (m, 2H, ArH), 7.06-7.04 (m, 2H, ArH), 4.94-4.91 (m, 1H, NH), 4.67-4.58 (m, 1H, CH), 1.51-1.49 (m, 3H, CH_3).

4-nitro-*N*-tritylbenzenesulfonamide (4e)[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.00-7.98 (m, 2H, ArH), 7.35-7.31 (m, 8H, ArH), 7.22-7.19 (m, 9H, ArH), 6.02 (s, 1H, NH).

4-methyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide (4f)[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.85-7.82 (m, 2H, ArH), 7.42-7.39 (m, 2H, ArH), 7.18-7.01 (m, 3H, ArH), 6.51-6.49 (m, 1H, ArH), 4.89-4.88 (m, 1H, NH), 4.49-4.48 (m, 1H, CH), 3.07-2.74 (m, 2H, CH_2), 2.51 (s, 3H, CH_3), 2.47-2.37 (m, 2H, CH_2), 2.15-1.63 (m, 2H, CH_2).

4-nitro-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)benzenesulfonamide (4g)[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.47-8.44 (m, 2H, ArH), 8.17-8.14 (m, 2H, ArH), 7.24-7.21 (m, 1H, ArH), 7.15-7.09 (m, 2H, ArH), 6.69-6.67 (m, 1H, ArH), 5.10-5.08 (m, 1H, NH), 4.68-4.57 (m, 1H, CH), 3.13-2.84 (m, 2H, CH_2), 2.41-2.15 (m, 2H, CH_2), 1.26-0.89 (m, 2H, CH_2).

***N*-(9*H*-fluoren-9-yl)-4-methylbenzenesulfonamide (4h)**[3]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99-7.96 (m, 2H, ArH), 7.65-7.62 (m, 2H, ArH),

7.44-7.37 (m, 5H, ArH), 7.27-7.20 (m, 3H, ArH), 5.41 (d, 1H, *J* = 9.6 Hz, NH), 4.80 (d, 1H, *J* = 9.6 Hz, CH), 2.52 (s, 3H, CH_3).

4-methyl-*N*-(1-*p*-tolylethyl)benzenesulfonamide (4i)[3]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66-7.63 (m, 2H, ArH), 7.20-7.17 (m, 2H, ArH), 7.01-6.98 (m, 4H, ArH), 5.29-5.26 (m, 1H, NH), 4.44-4.39 (m, 1H, CH), 2.40 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 1.40 (d, 3H, *J* = 6.9 Hz, CH_3).

4-nitro-*N*-(1-*p*-tolylethyl)benzenesulfonamide (4j)[11]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.15-8.12 (m, 2H, ArH), 7.79-7.76 (m, 2H, ArH), 6.93-6.92 (m, 4H, ArH), 5.12-5.10 (m, 1H, NH), 4.60-4.54 (m, 1H, CH), 2.25 (s, 3H, CH_3), 1.49 (d, 3H, *J* = 6.9 Hz, CH_3).

***N*-(2,3-dihydro-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (4k)**[12]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.88-7.83 (m, 2H, ArH), 7.36-7.20 (m, 6H, ArH), 4.88-4.80 (m, 1H, CH), 4.73-4.70 (m, 1H, NH), 2.90-2.69 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 2.37-1.07 (m, 2H, CH_2).

***N*-(2,3-dihydro-1*H*-inden-1-yl)-4-nitrobenzenesulfonamide (4l)**[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.42-8.39 (m, 2H, ArH), 8.16-8.13 (m, 2H, ArH), 7.44-7.42 (m, 1H, ArH), 7.18-7.09 (m, 3H, ArH), 5.28-5.24 (m, 1H, NH), 4.96-4.92 (m, 1H, CH), 2.94-2.77 (m, 2H, CH_2), 2.54-2.33 (m, 2H, CH_2).

***N*-(bis(4-fluorophenyl)methyl)-4-methylbenzenesulfonamide (4m)**[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.55-7.52 (m, 2H, ArH), 7.13-6.93 (m, 7H, ArH), 6.89-6.83 (m, 3H, ArH), 6.11 (d, 1H, *J* = 7.8 Hz, ArH), 5.54 (d, 1H, *J* = 7.8 Hz, CH), 2.38 (s, 3H, CH_3).

***N*-(1-(4-methoxyphenyl)ethyl)-4-nitrobenzenesulfonamide (4n)**[7]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.17-8.15 (m, 2H, ArH), 7.80-7.77 (m, 2H, ArH), 6.98-6.95 (m, 2H, ArH), 6.69-6.62 (m, 2H, ArH), 4.98-4.93 (m, 1H, NH), 4.60-4.54 (m, 1H, CH), 3.73 (s, 3H, OCH_3), 1.47 (d, J = 6.9 Hz, 3H, CH_3).

4-methyl-*N*-(1-phenylpropyl)benzenesulfonamide (4o)[14]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.56-7.54 (m, 2H, ArH), 7.14-7.09 (m, 5H, ArH), 7.03-7.01 (m, 2H, ArH), 6.30-6.28 (m, 1H, NH), 4.27-4.07 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.84-1.68 (m, 2H, CH_2), 0.81-0.76 (m, 3H, CH_3).

4-nitro-*N*-(1-phenylpropyl)benzenesulfonamide (4p)[15]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08-8.07 (m, 2H, ArH), 7.73-7.71 (m, 2H, ArH), 7.12-7.10 (m, 3H, ArH), 6.98-6.95 (m, 2H, ArH), 5.41-5.39 (m, 1H, NH), 4.36-4.28 (m, 1H, CH), 1.83-1.69 (m, 2H, CH_2), 0.88-0.83 (m, 3H, CH_3).

5. Gold-bipy/NBS catalyzed amidation of benzylic sp^3C-H bonds with carboxamides

5.1 General procedure for amidation of benzylic sp^3C-H bonds with carboxamides

A 25 mL round-bottom flask equipped with magnetic stirrer was charged with benzylic reagent (1 mmol), carboxamide (0.5 mmol), acetonitrile (3 ml), *N*-bromosuccinide (NBS) (0.5 mmol) and gold-complex **1** (3 mol %). The resulting mixture was continuously stirred at 70 ^{o}C. At the end of the reaction, the mixture was filtered and the filtrate was extracted with ethyl acetate (3-10 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and the fraction was collected and concentrated to give the desired product.

5.2 Characterization of products

***N*-benzhydrylbenzamide (4q)**[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84-7.81 (m, 2H, ArH), 7.51-7.33 (m, 13H, ArH), 6.88-6.86 (m, 1H, NH), 6.48-6.46 (m, 1H, CH).

_N_-benzhydryl-4-nitrobenzamide (4r)[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.29 (d, J = 9.0 Hz, 2H, ArH), 7.97 (d, J = 9.0 Hz, 2H, ArH), 7.35-7.27 (m, 11H, ArH), 6.79-6.77 (m, 1H, NH), 6.47-6.44 (m, 1H, CH).

_N_-(1-phenylethyl)benzamide (4s) [16]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.77 (m, 2H, ArH), 7.50-7.29 (m, 8H, ArH), 6.42-6.41 (m, 1H, NH), 5.38-5.33 (m, 1H, CH), 1.63-1.61 (m, 3H, CH_3).

4-nitro-_N_-(1-phenylethyl)benzamide (4t)[17]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30-8.27 (d, J = 9.0 Hz, 2H, ArH), 7.95-7.92 (d, J = 9.0 Hz, 2H, ArH), 7.41-7.36 (m, 5H, ArH), 6.40-6.37 (m, 1H, NH), 5.40-5.30 (m, 1H, CH), 1.66-1.04 (m, 3H, CH_3).

4-fluoro-N-(1-phenylethyl)benzamide (4u)[17]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99-7.96 (m, 2H, ArH), 7.64-7.60 (m, 1H, ArH), 7.54-7.52 (m, 2H, ArH), 7.38-7.30 (m, 4H, ArH), 4.93-4.91 (m, 1H, NH), 4.73-4.72 (m, 1H, CH), 1.53-1.50 (m, 3H, CH_3).

_N_-tritylbenzamide (4v)[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86-7.84 (m, 2H, ArH), 7.54-7.46 (m, 3H, ArH), 7.36-7.30 (m, 16H, ArH+NH).

4-nitro-_N_-tritylbenzamide (4w)[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30-8.28 (m, 2H, ArH), 7.98-7.95 (m, 2H, ArH), 7.34-7.28 (m, 16H, ArH+NH).

***N*-(1,2,3,4-tetrahydronaphthalen-1-yl)benzamide (4x)**[19]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.77 (m, 2H, ArH), 7.51-7.34 (m, 4H, ArH), 7.22-7.16 (m, 3H, ArH), 6.38-6.36 (m, 1H, NH), 5.44-5.38 (m, 1H, CH), 2.85-2.83 (m, 2H, CH_2), 2.18-1.88 (m, 4H, $2CH_2$).

4-nitro-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)benzamide (4y)[20]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30-8.29 (m, 2H, ArH), 7.97-7.94 (m, 2H, ArH), 7.35-7.32 (m, 1H, ArH), 7.22-7.17 (m, 3H, ArH), 6.41-6.33 (m, 1H, ArH), 5.43-5.40 (m, 1H, CH), 2.89-2.85 (m, 2H, CH_2), 2.17-2.16 (m, 2H, CH_2), 1.93-1.91 (m, 2H, CH_2).

***N*-(9*H*-fluoren-9-yl)benzamide (4z)**[21]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84-7.81 (m, 2H, ArH), 7.75-7.73 (m, 2H, ArH), 7.67-7.64 (m, 2H, ArH), 7.53-7.51 (m, 1H, ArH), 7.48-7.41 (m, 4H, ArH), 7.38-7.30 (m, 2H, ArH), 6.50-6.48 (m, 1H, CH), 6.41-6.33 (m, 1H, NH).

***N*-(1-*p*-tolylethyl)benzamide (4aa)**[22]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.78-7.75 (m, 2H, ArH), 7.50-7.42 (m, 3H, ArH), 7.31-7.27 (m, 2H, ArH), 7.19-7.17 (m, 2H, ArH), 6.31-6.29 (m, 1H, NH), 6.36-6.29 (m, 1H, CH), 2.35 (s, 3H, CH_3), 1.60 (d, 3H, J = 6.9 Hz, CH_3).

***N*-(2,3-dihydro-1*H*-inden-1-yl)benzamide (4bb)**[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.81-7.79 (m, 2H, ArH), 7.52-7.38 (m, 5H, ArH), 7.29-7.25 (m, 2H, ArH), 6.37-6.34 (m, 1H, NH), 5.76-5.68 (m, 1H, CH), 3.05-2.89 (m, 2H, CH_2), 2.78-1.90 (m, 2H, CH_2).

***N*-(2,3-dihydro-1*H*-inden-1-yl)-4-fluorobenzamide (4cc)**[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.82-7.79 (m, 2H, ArH), 7.38-7.35 (m, 1H, ArH), 7.29-7.22 (m, 2H, ArH), 7.14-7.08 (m, 3H, ArH), 6.31-6.29 (m, 1H, NH), 5.73-5.66 (m, 1H,

CH), 3.09-2.91 (m, 2H, CH_2), 2.75-1.91 (m, 2H, CH_2).

_N_-(bis(4-fluorophenyl)methyl)benzamide (4dd)[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.77 (m, 2H, ArH), 7.33-7.29 (m, 2H, ArH), 7.24-7.21 (m, 2H, ArH), 7.04-7.00 (m, 7H, ArH), 6.39-6.38 (m, 1H, NH), 5.79-5.76 (m, 1H, CH).

4-fluoro-_N_-(1-(4-methoxyphenyl)ethyl)benzamide (4ee)[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80-7.75 (m, 2H, ArH), 7.34-7.31 (m, 2H, ArH), 7.13-7.07 (m, 2H, ArH), 6.92-6.89 (m, 2H, ArH), 6.28-6.13 (m, 1H, NH), 5.30-5.28 (m, 1H, CH), 3.81 (s, 3H, OCH_3), 1.60 (d, J = 6.9 Hz, 3H, CH_3).

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