-Electronic Supplementary Information (ESI)-

Gold-complexes Catalyzed Oxidative α-Cyanation of Tertiary Amines

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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 (7.24 and 7.70 ppm). Abbreviations for signal couplings are: s, singlet: d, doublet: t, triplet: m, multiplet.

Materials. Commercially available tertiary amines were used as received. N, N-dimethyl-*p*-anisidine,[S1] 1-phenylpiperdine,[S2] 2-phenyl-1,2,3,4-tetrahydroisoquin oline[S2] were prepared according to literature procedures. Trimethylsilyl cyanide (98%) and *tert*.-butyl hydroperoxide (5.5 M solution in decane) were purchased.

General procedure for the synthesis of gold complexes

Synthesis of gold complex **1** $[AubpyCl_2]Cl$[S3]

Dipyridine (312mg, 2 mmol) in water (20mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398mg, 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 (320mg, 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).

Synthesis of gold complex **2** $[AuPy_2Cl_2]Cl$[S4]

Pyridine (316mg, 4 mmol) in water (20mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398mg, 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

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(S1) J. A. Hodges and R.T. Raines, *Org. Lett*., 2006, **8**, 4695.

(S2) Z. P. Li, S. D. Bohle and C. J. Li, *Pro. Natl. Acad. Sci. USA*, 2006, **103**, 8928.

(S3) R. Hayoun, D. K. Zhong, A. L. Rheingold and L. H. Doerrer, *Inorg. Chem*., 2006, **45**, 6120.

desired gold(III) complex **2** as a yellow powder (369mg, 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).

Synthesis of gold complex **3** $PicAuCl_2$[S5]

2-picolinic acid (246mg, 2 mmol) in water (20mL) was added slowly to a stirred solution of sodium tetrachloroaurate (III) hydrate (398mg, 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 (268mg, 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).

General procedure for Au-catalyzed cyanation of tertiart amines*:*

A 25 mL round-bottom flask equipped with magnetic stirrer, was charged with amine (0.5 mmol), MeOH (1 mL) and gold complex **1** (10 mol%), 1.2 eq. TBHP(5-6 M in decane). After the addition of TMSCN (1.0 mmol), the resulting mixture was continuously stirred at room temperature. At the end of the reaction as monitored by TLC, the mixture was added into aqueous $NaHCO_3$ and 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.

(S4) P. Bourosh, O. Bologa, Y. Simonov, N. Gerbeleu, J. Lipkowski and M. Gdaniec, *Inorg. Chim. Acta*, 2007, **360**, 3250.

(S5) A. Dar, K. Moss, S. M. Cottrill, R. V. Parish, C. A. McAuliffe, R. G. Pritchard, B. Beagley and J. Sandbank, *J. Chem. Soc. Dalton Trans*., 1992, 1907.

2-(methyl(phenyl)amino)acetonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33-7.27 (m, 2H, ArH), 6.94-6.88 (m, 3H, ArH), 4.19 (s, 2H, CH_2), 3.03 (s, 3H, CH_3).

2-((4-bromophenyl)(methyl)amino)acetonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (d, J = 9.0 Hz, 2H, ArH), 6.74 (d, J = 9.0 Hz, 2H, ArH), 4.16 (s, 2H, CH_2), 2.98 (s, 3H, CH_3).

2-(methyl(*p*-tolyl)amino)acetonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.12 (d, J = 8.7 Hz, 2H, ArH), 6.81 (d, J = 8.7 Hz, 2H, ArH), 4.14 (s, 2H, CH_2), 2.97 (s, 3H, CH_3), 2.29 (s, 3H, CH_3).

2-(methyl(*m*-tolyl)amino)acetonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.19-7.16 (m, 1H, ArH), 6.75-6.67 (m, 3H, ArH), 4.15 (s, 2H, CH_2), 2.98 (s, 3H, CH_3), 2.33 (s, 3H, CH_3).

2-(methyl(o-tolyl)amino)acetonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.26-7.22 (m, 3H, ArH), 7.11-7.09 (m, 1H, ArH), 3.89 (s, 2H, CH_2), 2.88 (s, 3H, CH_3), 2.32 (s, 3H, CH_3).

2-phenylcyclopentanecarbonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.29-7.27 (m, 3H, ArH), 6.83-6.82 (m, 1H,

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(S6) S. Singhal, S. L. Jain and B. Sain, *Chem. Commun*., 2009, 2371.

ArH), 6.71-6.08 (m, 1H, ArH), 4.45-4.44 (m, 1H, CH), 3.50-3.36 (m, 2H, CH_2), 2.41-2.27 (m, 4H, $2CH_2$).

2-phenylcyclohexanecarbonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32-7.23 (m, 3H, ArH), 7.01-6.94 (m, 2H, ArH), 3.47-3.39 (m, 1H, CH), 3.08-2.95 (m, 2H, CH_2), 1.99-1.26 (m, 6H, $3CH_2$).

2-(ethyl(phenyl)amino)propanenitrile[S7]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33-7.30 (m, 2H, ArH), 7.17-7.14 (m, 1H, ArH), 7.00-6.98 (m, 1H, ArH), 6.69-6.59 (m, 1H, ArH), 4.49-4.08 (m, 1H, CH), 3.37-3.12 (m, 2H, CH_2), 1.28-1.16 (m, 6H, $2CH_3$).

2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile[S6]

Known compound; the NMR spectroscopic data agree with those given in literature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39-7.34 (m, 3H, ArH), 7.30-7.27 (m, 3H, ArH), 7.25-7.23 (m, 2H, ArH), 7.11-7.02 (m, 1H, ArH), 5.53 (s, 1H, CH), 3.83-3.49 (m, 2H, CH_2), 3.17-2.89 (m, 2H, CH_2).

(S7) W. McMeeking and T. S. Stevens, *J. Chem. Soc*., 1933, 347.