Supporting Information for Manuscript

Efficient Cycloisomerization of Propargyl Amides by Electrophilic Gold(I) Complexes of KITPHOS Monophosphines: A Comparative Study

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Experimental Section.

General Procedure for the Gold-Catalyzed Cycloisomerizations using Precursors 4a-d. A flame-dried Schlenk flask charged with **4a-d** (0.01 mmol), AgOTf (0.0026 g, 0.01 mmol) and dichloromethane (1.0 mL) was stirred for 30 min, after which propargyl amide (0.5 mmol) was added and the resulting mixture stirred for the allocated time. The reaction mixture was diluted with diethyl ether, 1,3-dinitrobenzene added (0.084 g, 0.5 mmol) and the resulting mixture passed through a short silica plug. The solvent was removed and the residue analyzed by ^{1}H NMR spectroscopy to determine conversions before being purified by column chromatography, eluting with hexane:ethyl acetate. Known products were characterised by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry and high resolution mass spectrometry.

General Procedure for the Gold-Catalyzed Cycloisomerizations using 5 and 6. A flame-dried Schlenk flask charged with **5** or **6** (0.01 mmol), propargyl amide (0.5 mmol) and dichloromethane (1.0 mL) and the resulting mixture stirred for the allocated time. The reaction mixture was diluted with diethyl ether, 1,3-dinitrobenzene added (0.084 g, 0.5 mmol) and the resulting mixture passed through a short silica plug. The solvent was removed and the residue analyzed by ^{1}H NMR spectroscopy to determine conversions before being purified by column chromatography, eluting with hexane:ethyl acetate. Known products were characterised by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry and high resolution mass spectrometry (HRMS).

2-tert-Butyl-5-methylene-4,5-dihydrooxazole (Table 1, Entries 1–6). ^{1}H NMR (500.16 MHz, $CDCl_3$, δ): 4.63 (dt, J = 2.75 Hz, 1H, CH_aH$_b$), 4.39 (dd, J = 2.75 Hz, 2H, CH_2), 4.21 (dt, J = 2.75 Hz, 1H, CH$_a$$H_b$), 1.22 (s, 9H, C(C$H_3$)$_3$); ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, δ): 173.8 (C=N), 159.6 (C=CH$_2$), 82.7 (C=CH$_2$), 57.8 (CH$_2$), 33.4 (C(CH$_3$)$_3$), 27.4 (C(CH$_3$)$_3$); MS (EI$^+$) *m/z* 140 [M+H]$^+$.

2-(Cyclohexyl)-5-methylene-4,5-dihydro-1,3-oxazole (Table 1, Entries 7–12). ^{1}H NMR (500.16 MHz, $CDCl_3$, δ): 4.62 (dt, J = 2.16 Hz, 1H, CH_aH$_b$), 4.39 (dd, J = 2.16 Hz, 2H, CH_2), 4.21 (dt, J = 2.16 Hz, 1H,

CH_aH_b), 2.34 (tm, J = 11.4 Hz, 1H, Cy-*H*), 1.94 (dm, J = 10.5 Hz, 2H, Cy-*H*), 1.77 (m, 2H, Cy-*H*), 1.64 (m, 1H, Cy-*H*), 1.44 (qd, J = 11.9, 2.8 Hz, Cy-H), 1.26 (m, 4H, Cy-*H*); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 170.6 (*C*=N), 159.0 (*C*=CH_2), 82.7 (C=*C*H_2), 57.0 (*C*H_2), 37.3 (Cy), 29.4 (Cy), 25.8 (Cy), 25.5 (Cy); MS (EI^+) *m/z* 165 $[M+H]^+$.

5-Methylene-2-phenyl-4,5-dihydrooxazole (Table 1, Entries 13–18). ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.96 (d, J = 6.9 Hz, 2H, C_6H_5), 7.29 (t, J = 7.40 Hz, 1H, C_6H_5), 7.40 (t, J = 7.60 Hz, 2H, C_6H_5), 4.80 (dt, J = 3.2 Hz, 1H, C*H*$_a$H$_b$), 4.63 (dd, J = 3.2 Hz, 2H, C*H*$_2$), 4.35 (dt, J = 3.2 Hz, 1H, CH_aH_b); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 163.6 (*C*=N), 158.7 (*C*=CH_2), 131.7 (C_6H_5), 128.4 (C_6H_5), 127.9 (C_6H_5), 126.7 (C_6H_5), 83.7 (C=*C*H_2), 57.7 (*C*H_2); MS (EI^+) *m/z* 160 $[M+H]^+$.

5-Methylene-2-(thiophen-2-yl)-4,5-dihydrooxazole (Table 1, Entries 19–24). ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.64 (dd, J = 3.7, 0.9 Hz, 1H, thieny-*H*), 7.48 (dd, J = 4.9, 0.9 Hz, 1H, thienyl-*H*), 7.09 (dd, J = 4.5, 3.7 Hz, 1H, thienyl-*H*), 4.78 (dt, J = 2.8 Hz, 1H, C*H*$_a$H$_b$), 4.60 (dd, J = 2.8 Hz, 2H, C*H*$_2$), 4.34 (dt, J = 2.8 Hz, 1H, CH_aH_b); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 158.6 (*C*=N), 158.2 (*C*=CH_2), 130.8 (C_4H_3S), 130.3 (C_4H_3S), 129.4 (C_4H_3S), 128.0 (C_4H_3S), 84.1 (C=*C*H_2), 57.6 (*C*H_2); MS (EI^+) *m/z* = 165 $[M]^+$.

2-(2-Furyl)-5-methylene-4,5-dihydro-1,3-oxazole (Table 1, Entries 25–30). ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.54 (d, J = 1.8 Hz, 1H, furyl-*H*), 6.98 (d, J = 3.6 Hz, 1H, furyl-*H*), 6.47 (dd, J = 3.6, 1.8 Hz, 1H, furyl-*H*), 4.78 (dt, J = 3.2, 3.2 Hz, 1H, C*H*$_a$H$_b$), 4.60 (dd, J = 3.2, 3.2 Hz, 2H, C*H*$_2$), 4.34 (dt, J = 3.2, 3.2 Hz, 1H, CH_aH_b); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 158.1 (*C*=N), 155.9 (*C*=CH_2), 145.6 (C_4H_3O), 141.9 (C_4H_3O), 114.9 (C_4H_3O), 111.6 (C_4H_3O), 84.2 (C=*C*H_2), 57.3 (*C*H_2); MS (EI^+) *m/z* = 150 $[M+H]^+$; HRMS (ESI^+): exact mass calcd for $C_8H_8NO_2$ $[M+H]^+$ requires m/z 150.0555, found *m/z* 150.0601.

***E*-5-Methylene-2-styryl-4,5-dihydrooxazole (Table 1, Entries 31–36).** ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.48 (dd, J = 7.7, 1.7 Hz, 2H, C_6H_5), 7.24 (d, J = 16.0 Hz, 1H, C_6H_5HC=CH), 7.36–7.33 (m, 4H,

C_6H_5), 6.60 (d, J = 16.0 Hz, 1H, C_6H_5HC=CH), 4.48 (dt, J = 3.2, 3.2 Hz, 1H, CH_aH_b), 4.60 (dd, J = 3.2, 3.2 Hz, 2H, CH_2), 4.34 (dt, J = 3.2, 3.2 Hz, 1H, CH_aH_b); $^{13}C\{^1H\}$ NMR (100.52 MHz, $CDCl_3$, δ): 163.5 (C=N), 158.4 (C=CH_2), 140.7 (C_6H_5HC=CH), 134.8 (C_6H_5), 129.7 (C_6H_5), 128.8 (C_6H_5), 127.5 (C_6H_5), 114.0 (C_6H_5HC=CH), 83.3 (C=$C$$H_2$), 57.6 ($C$$H_2$); MS (EI$^+$) *m/z* = 185 $[M]^+$; HRMS (ESI$^+$): exact mass calcd for $C_{12}H_{12}NO$ $[M+H]^+$ requires m/z 186.0919, found *m*/*z* 186.0927.