Supporting Information
for
Highly Efficient Au(I)-Catalyzed Intramolecular Addition of
 β -Ketoamide to Unactivated Alkenes

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General Experimental Section. Reagents were obtained commercially and used without further purification unless indicated otherwise. The $\text{Au}(\text{PPh}_3)\text{Cl}^{1,2}$ and $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}^{S1,2}$ catalysts and β -ketoamide^{S3} starting materials were prepared following literature procedures. Toluene was freshly distilled from sodium/benzophenone under a nitrogen atmosphere. 1,2-Dichloroethane was freshly distilled from calcium hydride under a nitrogen atmosphere. Anhydrous acetonitrile and 1,4-dioxane were used directly from Aldrich. Solvent was removed under reduced pressure and the residue obtained was chromatographed on a silica gel column (230-400 mesh) using a gradient solvent system (EtOAc / *n*-hexane as eluant unless specified otherwise). ^1H and ^{13}C NMR spectra were measured on either a Bruker DPX-500, DPX-400 or DPX-300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Mass spectra were determined on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on a Bio-RAD PTS-165 spectrometer.

Table S1. The Effect of Catalyst and Solvent on the Reaction of β -Ketoamide **1a**^a.

entry	catalyst	solvent	yield (%)
1	5 mol% Au(PPh ₃)Cl/5 mol% AgOTf	toluene	87
2	5 mol% Au(PPh ₃)Cl	toluene	0
3	5 mol% AgOTf	toluene	Trace
4	5 mol% AuCl ₃ /5 mol% AgOTf	toluene	Trace
5	5 mol% AuCl ₃	toluene	0
6	5 mol% CF ₃ SO ₃ H	toluene	0
7	5 mol% Au(PPh ₃)Cl/5 mol% AgOTf	CH ₃ CN	35
8	5 mol% Au(PPh ₃)Cl/5 mol% AgOTf	dioxane	83
9	5 mol% Au(PPh ₃)Cl/5 mol% AgOTf	ClCH ₂ CH ₂ Cl	38
10	5 mol% Au[P(<i>t</i> -butyl) ₂ (<i>o</i> -biphenyl)]Cl / 5 mol% AgOTf	toluene	97

^a Yield determined by ¹H NMR of crude reaction mixture.

General Procedure for Gold(I)-Catalyzed Cyclization of N-Alkenyl β -Ketoamide to Lactams

To a toluene solution (3 mL) containing Au[P(*t*-butyl)₂(*o*-biphenyl)]Cl (0.02 mmol) and AgOTf (0.02 mmol) was added β -ketoamide (0.4 mmol), and the resultant mixture was stirred at 50 °C for 5 h. The solvent was removed and the crude residue was purified by silica gel column chromatography to give the lactam product.

3-Acetyl-4-methyl-1-benzyl-2-pyrrolidinone **2a**

Colorless oil, ketone:enol > 40:1; ¹H NMR (500 MHz, CDCl₃) δ 7.20-7.35 (m, 5H), 4.45 (d, 1H, *J* = 14.7 Hz), 4.40 (d, 1H, *J* = 14.7 Hz), 3.39 (dd, 1H, *J* = 9.3, 7.7 Hz), 3.23 (d, 1H, *J* = 7.1 Hz), 2.83 (m, 1H), 2.77 (dd, 1H, *J* = 9.3, 6.4 Hz), 2.45 (s, 3H),

1.05 (d, 3H, $J = 6.7$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 203.6, 169.6, 135.9, 128.8, 128.1, 127.7, 63.7, 52.1, 46.9, 30.4, 28.3, 18.8; IR (neat, cm^{-1}) 2964, 2928, 1714, 1682, 1495, 1455, 1357, 1259, 1164, 701; MS (EI) m/z 231 [M^+]; HRMS (EI) calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ 231.1259, found 231.1262.

3-Acetyl-4-methyl-1-methyl-2-pyrrolidinone 2b

Colorless oil, ketone:enol > 40:1; ^1H NMR (300 MHz, CDCl_3) δ 3.47-3.55 (m, 1H), 3.16 (d, 1H, $J = 6.7$ Hz), 2.84-2.95 (m, 2H), 2.83 (s, 3H), 2.41 (s, 3H), 1.11 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 203.6, 169.5, 63.5, 54.9, 30.2, 29.8, 28.0, 18.9; IR (neat, cm^{-1}) 2973, 2930, 1715, 1678, 1498, 1437, 1354, 1260, 1169; MS (EI) m/z 155 [M^+]; HRMS (EI) calcd. for $\text{C}_8\text{H}_{13}\text{NO}_2$ 155.0946, found 155.0992.

3-Benzoyl-4-methyl-1-benzyl-2-pyrrolidinone 2c

Colorless oil, ketone:enol = 15:1; ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, 2H, $J = 7.1$ Hz), 7.46-7.61 (m, 3H), 7.23-7.36 (m, 5H), 4.49 (d, 1H, $J = 14.5$ Hz), 4.43 (d, 1H, $J = 14.5$ Hz), 4.14 (d, 1H, $J = 5.8$ Hz), 3.57 (dd, 1H, $J = 9.2, 7.4$ Hz), 2.84-2.99 (m, 2H), 1.11 (d, 3H, $J = 6.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 195.9, 169.9, 136.5, 135.9, 133.4, 129.3, 128.6, 128.4, 128.0, 127.5, 58.9, 52.4, 46.8, 30.3, 19.1; IR (neat, cm^{-1}) 2973, 2924, 1703, 1664, 1493, 1443, 1338, 1257, 1221, 696; MS (EI) m/z 293 [M^+]; HRMS (EI) calcd. for $\text{C}_{19}\text{H}_{19}\text{NO}_2$ 293.1416, found 293.1421.

2-Benzyl-4-methyl-2-azaspiro[4,4]nonane-1,6-dione 2d

Colorless oil, inseparable mixture of two diastereomers in ratio of 3:1; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.36 (m, 5H+5H $\times$ 3), 4.40-4.57 (m, 2H+2H $\times$ 3), 3.60 (dd, 1H, $J = 9.3, 7.2$ Hz), 3.23 (t, 1H $\times$ 3, $J = 9.5$ Hz), 3.12 (t, 1H $\times$ 3, $J = 9.1$ Hz), 2.73 (dd, 1H, $J = 9.3, 4.4$ Hz), 2.64 (m, 1H $\times$ 3), 2.18-2.56 (m, 5H+4H $\times$ 3), 1.86-2.04 (m, 2H+2H $\times$ 3),

1.03 (d, 3H $\times$ 3, J = 7.0 Hz), 0.94 (d, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 217.3, 216.8, 173.6, 172.9, 136.2, 128.7, 128.6, 127.9, 127.6, 127.5, 62.8, 61.9, 51.9, 51.1, 46.9, 46.8, 39.8, 38.5, 37.8, 33.1, 32.6, 28.2, 20.4, 19.6, 15.6, 12.5; IR (neat, cm^{-1}) 2973, 2924, 1734, 1690, 1672, 1493, 1425, 1265, 1134, 735, 696; MS (EI) m/z 257 [M^+]; HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ 257.1415, found 257.1414.

2-Benzyl-4-methyl-2-azaspiro[4,5]decane-1,6-dione 2e

Two diastereomers could be separated on a silica gel column.

Minor diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.19-7.34 (m, 5H), 4.47 (d, 1H, J = 14.7 Hz), 4.38 (d, 1H, J = 14.7 Hz), 3.25 (dd, 1H, J = 9.5, 7.5 Hz), 3.08 (m, 1H), 2.99 (m, 1H), 2.71 (dd, 1H, J = 9.5, 7.3 Hz), 2.47 (dt, 1H, J = 14.7, 3.7 Hz), 2.27 (m, 1H), 2.10 (m, 1H), 2.00 (m, 1H), 1.65-1.76 (m, 3H), 0.92 (d, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 208.5, 172.8, 136.3, 128.7, 127.9, 127.6, 61.5, 50.4, 46.8, 40.4, 31.7, 30.2, 26.9, 20.7, 13.4; IR (neat, cm^{-1}) 2936, 2863, 1695, 1672, 1493, 1431, 1319, 1257, 1221, 1122, 746, 696; MS (EI) m/z 271 [M^+]; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ 271.1572, found 271.1574.

Major diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.23-7.34 (m, 5H), 4.49 (d, 1H, J = 14.8 Hz), 4.44 (d, 1H, J = 14.8 Hz), 3.14 (dd, 1H, J = 9.2, 7.8 Hz), 3.02 (t, 1H, J = 9.1 Hz), 2.60 (m, 1H), 2.15-2.34 (m, 4H), 1.79-1.97 (m, 3H), 1.73 (m, 1H), 1.09 (d, 3H, J = 7.0 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 208.9, 174.1, 136.2, 128.6, 127.9, 127.5, 61.8, 51.3, 46.8, 41.8, 39.6, 34.6, 24.6, 21.2, 14.1; IR (neat, cm^{-1}) 2947, 2868, 1703, 1672, 1487, 1437, 1319, 1257, 1128, 740, 690; MS (EI) m/z 271 [M^+]; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ 271.1572, found 271.1576.

3-Acetyl-4,5-dimethyl-1-benzyl-2-pyrrolidinone 2f

Two diastereomers could be separated on a silica gel column.

Minor diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.21-7.34 (m, 5H), 4.92 (d, 1H, $J = 15.0$ Hz), 4.00 (d, 1H, $J = 15.0$ Hz), 3.21 (d, 1H, $J = 8.9$ Hz), 2.99 (m, 1H), 2.48 (s, 3H), 2.38 (m, 1H), 1.20 (d, 3H, $J = 6.2$ Hz), 1.03 (d, 3H, $J = 6.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 203.6, 169.8, 136.3, 128.7, 127.9, 127.5, 63.1, 58.0, 44.3, 36.4, 30.5, 18.0, 17.2; IR (neat, cm^{-1}) 2970, 2923, 1736, 1624, 1493, 1441, 1342, 1265, 1140, 735, 690; MS (EI) m/z 245 [M^+]; HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.1415, found 245.1413.

Major diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.18-7.33 (m, 5H), 4.96 (d, 1H, $J = 15.1$ Hz), 3.96 (d, 1H, $J = 15.1$ Hz), 3.53 (m, 1H), 3.29 (d, 1H, $J = 9.3$ Hz), 2.84 (m, 1H), 2.45 (s, 3H), 1.03 (d, 3H, $J = 6.6$ Hz), 0.98 (d, 3H, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 203.8, 169.5, 136.2, 128.6, 127.8, 127.5, 61.3, 54.1, 44.3, 32.8, 30.6, 13.9, 13.5; IR (neat, cm^{-1}) 2986, 2924, 1720, 1672, 1425, 1358, 1257, 1165, 696; MS (EI) m/z 245 [M^+]; HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.1415, found 245.1414.

3-Acetyl-4-methyl-5-phenyl-1-benzyl-2-pyrrolidinone 2g

Two diastereomers could be separated on a silica gel column.

Major diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.39 (m, 6H), 7.03-7.09 (m, 4H), 5.13 (d, 1H, $J = 14.7$ Hz), 4.41 (d, 1H, $J = 8.5$ Hz), 3.54 (d, 1H, $J = 14.7$ Hz), 3.41 (d, 1H, $J = 10.7$ Hz), 3.11 (m, 1H), 2.51 (s, 3H), 0.59 (d, 3H, $J = 6.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 203.6, 170.3, 136.3, 135.7, 128.8, 128.6, 128.2, 128.1, 127.8, 127.6, 63.2,

60.7, 45.0, 33.6, 30.8, 15.2; IR (neat, cm^{-1}) 2973, 2926, 1717, 1676, 1493, 1416, 1350, 1227, 1161, 735, 700; MS (EI) m/z 307 [M^+]; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ 307.1572, found 307.1576.

Minor diastereomer: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.00-7.41 (m, 10H), 4.99 (d, 1H, $J = 14.5$ Hz), 3.79 (d, 1H, $J = 8.2$ Hz), 3.48 (d, 1H, $J = 14.5$ Hz), 3.29 (d, 1H, $J = 9.9$ Hz), 2.73 (m, 1H), 2.53 (s, 3H), 0.99 (d, 3H, $J = 6.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 203.3, 170.2, 138.2, 135.9, 128.9, 128.7, 128.6, 128.5, 127.8, 127.6, 66.9, 62.8, 44.8, 38.7, 30.7, 16.5; IR (neat, cm^{-1}) 2973, 2920, 1722, 1676, 1493, 1416, 1350, 1238, 1161, 729, 690; MS (EI) m/z 307 [M^+]; HRMS (EI) calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ 307.1572, found 307.1579.

3-Acetyl-4,4-dimethyl-1-benzyl-2-pyrrolidinone 2h

Colorless oil, ketone:enol = 10:1; ^1H NMR (300 MHz, CDCl_3) δ 7.24-7.37 (m, 5H), 4.51 (d, 1H, $J = 14.7$ Hz), 4.42 (d, 1H, $J = 14.7$ Hz), 3.24 (s, 1H), 3.17 (d, 1H, $J = 9.4$ Hz), 2.83 (d, 1H, $J = 9.4$ Hz), 2.28 (s, 3H), 1.15 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.3, 170.9, 135.9, 128.6, 128.1, 127.6, 66.4, 58.6, 46.7, 37.0, 32.5, 28.9, 22.3; IR (neat, cm^{-1}) 2967, 2924, 1703, 1672, 1493, 1437, 1358, 1302, 1203, 1153, 696; MS (EI) m/z 245 [M^+]; HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.1415, found 245.1419.

3-Acetyl-4-methyl-1-benzyl-2-piperidone 2i

Colorless oil, ketone:enol = 1.1:1; ^1H NMR (300 MHz, CDCl_3) δ 15.13 (s, 1H), 7.23-7.35 (m, 5H+5H $\times$ 1.1), 4.40-4.80 (m, 2H+2H $\times$ 1.1), 3.42 (td, 1H $\times$ 1.1, $J = 12.8$, 3.9

Hz), 3.08-3.32 (m, 2H+3H×1.1), 2.82 (m, 1H), 2.36 (s, 3H×1.1), 2.27-2.35 (m, 1H), 2.00 (s, 3H), 1.82-1.94 (m, 1H), 1.61 (m, 1H×1.1), 1.47 (m, 1H×1.1), 1.05 (d, 3H, $J = 7.0$ Hz), 0.97 (d, 3H×1.1, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 205.8, 169.9, 169.4, 166.5, 137.1, 136.6, 128.6, 128.5, 127.9, 127.5, 127.4, 127.3, 101.0, 63.1, 50.1, 49.7, 45.7, 42.5, 31.1, 30.2, 29.2, 28.2, 27.6, 19.8, 19.6, 17.9; IR (neat, cm^{-1}) 2967, 2924, 1720, 1628, 1499, 1443, 1350, 1265, 727, 696; MS (EI) m/z 245 [M^+]; HRMS (EI) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.1415, found 245.1413.

7-benzyl-10-methyl-7-azaspiro[4,5]decane-1,6-dione 2j

Colorless oil, inseparable mixture of two diastereomers in ratio of 1.3:1; ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.33 (m, 5H+5H×1.3), 4.80 (d, 1H, $J = 14.8$ Hz), 4.65 (d, 1H×1.3, $J = 14.7$ Hz), 4.41 (d, 1H×1.3, $J = 14.7$ Hz), 4.36 (d, 1H, $J = 14.8$ Hz), 3.16-3.29 (m, 2H+2H×1.3), 2.73 (m, 1H), 2.63 (m, 1H×1.3), 2.49 (m, 1H), 2.12-2.39 (m, 5H×1.3+4H), 1.81-2.05 (m, 2H+2H×1.3), 1.52-1.61 (m, 1H+1H×1.3), 1.00 (d, 3H, $J = 6.8$ Hz), 0.87 (d, 3H×1.3, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 218.2, 217.9, 171.3, 170.4, 136.84, 136.82, 128.5, 127.7, 127.5, 127.2, 127.1, 59.8, 59.0, 50.4, 49.8, 46.1, 45.7, 40.4, 39.6, 36.8, 35.2, 32.4, 30.5, 26.7, 20.8, 19.9, 16.6, 16.0; IR (neat, cm^{-1}) 2965, 2924, 1736, 1624, 1493, 1441, 1342, 1265, 1140, 735, 690; MS (EI) m/z 271 [M^+]; HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_2$ 271.1572, found 271.1577.

3-Acetyl-4-ethyl-5-methyl-1-benzyl-2-pyrrolidinone 2k

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 7.20-7.33 (m, 5H), 4.91 (d, 1H, $J = 15.0$ Hz), 3.98 (d, 1H, $J = 15.0$ Hz), 3.33 (d, 1H, $J = 7.2$ Hz), 3.08 (m, 1H), 2.48 (s, 3H), 2.37 (m, 1H), 1.49 (m, 1H), 1.30 (m, 1H), 1.21 (d, 3H, $J = 6.3$ Hz), 0.82 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 203.8, 169.5, 136.3, 128.7, 128.0, 127.6,

61.8, 56.9, 44.3, 42.3, 30.5, 26.5, 19.2, 11.6; IR (neat, cm^{-1}) 2973, 2924, 1720, 1672, 1493, 1418, 1358, 1240, 1165, 740, 696; MS (EI) m/z 259 [M^+]; HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ 259.1572, found 259.1567.

3-Benzoyl-4-ethyl-5-methyl-1-benzyl-2-pyrrolidinone 2l

Colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 8.14 (m, 2H), 7.46-7.61 (m, 3H), 7.21-7.35 (m, 5H), 4.91 (d, 1H, $J = 15.0$ Hz), 4.24 (d, 1H, $J = 7.1$ Hz), 4.04 (d, 1H, $J = 15.0$ Hz), 3.20 (m, 1H), 2.55 (m, 1H), 1.57 (m, 1H), 1.38 (m, 1H), 1.30 (d, 3H, $J = 6.3$ Hz), 0.80 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 169.8, 136.8, 136.4, 133.3, 129.4, 128.6, 128.4, 127.9, 127.4, 57.2, 56.8, 44.5, 44.4, 26.6, 19.1, 11.8; IR (neat, cm^{-1}) 2965, 2924, 1720, 1625, 1497, 1443, 1350, 1263, 727, 695; MS (EI) m/z 321 [M^+]; HRMS (EI) calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_2$ 321.1729, found 321.1727.

About the Stereochemistry of Products 2. The 3,4-*trans* stereochemistry for **2a–2c**, **2f**, **2g**, **2k**, and **2l** was proposed by comparison with the related compounds previously reported in the literature, which all have a 3,4-*trans* stereochemistry.^{S4} The chemical shift of 3-H ($\delta = 3.16\text{--}4.24$ ppm) and the coupling constant between 3-H and 4-H ($J = 5.8\text{--}10.7$ Hz) for **2a–2c**, **2f**, **2g**, **2k**, and **2l** are comparable to the corresponding values previously reported for the related compounds ($\delta = 3.1\text{--}4.2$ ppm for 3-H and $J = 6\text{--}11$ Hz between 3-H and 4-H).^{S4} In the cases of **2f**, **2g**, and **2k**, the 3,5-*trans* or 3,5-*cis* configuration was assigned on the basis of the presence or absence, respectively, of cross-peak between 3-H and 5-Me or 5-Ph in the H-H NOESY spectra. The 3,5-*cis* stereochemistry for **2l** was proposed on the basis of that observed for its congener **2k**.

^1H NMR Measurements of a Mixture of 1a and $\text{Au}[\text{P}(t\text{-Bu})_2(o\text{-biphenyl})]\text{Cl}/\text{AgOTf}$ in CDCl_3 under Various Conditions. The ^1H NMR spectrum

of a 5:1:1 mixture of **1a** (0.2 mmol), Au[P(*t*-butyl)₂(*o*-biphenyl)]Cl (0.04 mmol) and AgOTf (0.04 mmol) in CDCl₃ (1 mL) was measured after the mixture was stirred at 50 °C for 1 h (see Figure S1; the spectra for **1a** and Au[P(*t*-butyl)₂(*o*-biphenyl)]Cl are shown in Figure S2), which shows a new signal at a lower field than the -CH=CH₂ signal of **1a** (Figure S1b). We assign this new signal to the -CH=CH₂ signal of the alkene complex of Au(I) with **1a**. A downfield shift of the -CH=CH₂ signal upon coordination of the alkene group to Au(I) was reported previously.^{S5}

The NMR spectra of a 1:1:1 mixture of **1a** (0.1 mmol), Au[P(*t*-butyl)₂(*o*-biphenyl)]Cl (0.1 mmol) and AgOTf (0.1 mmol) in CDCl₃ (1 mL) under various conditions were also examined, which are depicted in Figures S3–S7. The ¹H-¹H COSY spectrum shown in Figure S4 is consistent with the assignment of the above new signal to the -CH=CH₂ proton. A comparison of the spectrum at -20 °C (Figure S3) with that at 20 °C (Figure S5) showed that the splitting between the -CH=CH₂ signals of the coordinated and uncoordinated **1a** increased upon lowering temperature, suggesting the presence of an equilibrium between **1a** and the Au(I)-alkene complex in solution. The ¹H NMR spectra measured after the mixture was stirred at 20 °C for 0.5, 1, 2, 5, and 10 h (Figures S5–S7) revealed that the proposed Au(I)-alkene complex still existed in solution after 5 h, but almost completely disappeared after 10 h.

Minor diastereomer CN1C(=O)C2CCCC2C1=O **2e**

Major diastereomer

H-H NOESY of minor diastereomer

Major diastereomer

2f

Minor diastereomer

H-H NOESY of minor diastereomer

Figure S1. (a) ^1H NMR (400 MHz) spectrum of a 5:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at 50 °C after 1 h. (b) Comparison of the olefinic signals in (a) (upper) with those of **1a** (lower) under the same conditions.

Figure S2. ^1H NMR (400 MHz) spectra of (a) **1a** and (b) $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ in CDCl_3 at 20 $^\circ\text{C}$.

Figure S3. ^1H NMR (500 MHz) spectrum of a 1:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at $-20\text{ }^\circ\text{C}$ after 15 min.

Figure S4. ^1H - ^1H COSY (500 MHz) spectrum of a 1:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at $-20\text{ }^\circ\text{C}$ after 15 min.

Figure S5. ^1H NMR (400 MHz) spectra of a 1:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at 20°C after (a) 0.5 h and (b) 1 h.

Figure S6. ^1H NMR (400 MHz) spectra of a 1:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at 20°C after (a) 2 h and (b) 5 h.

Figure S7. ^1H NMR (400 MHz) spectrum of a 1:1:1 mixture of **1a**, $\text{Au}[\text{P}(t\text{-butyl})_2(o\text{-biphenyl})]\text{Cl}$ and AgOTf in CDCl_3 at 20°C after 10 h.

Figure S8. MALDI-TOF MS spectrum of a solution of **1p**, Au[P(*t*-butyl)₂(*o*-biphenyl)]Cl (20 mol%) and AgOTf (20 mol%) in toluene (spectrum **a**) showing a cluster peak at *m/z* 756.287 which can be attributed to the adduct formed between Au⁺[P(*t*-butyl)₂(*o*-biphenyl)] and **1p**. The observed isotopic distribution well matches the calculated one (spectrum **b**).

Spectrum a

Applied Biosystems Voyager System 4146

Voyager Spec #1=>MC[BP = 713.3, 6382]

Mode of operation: Reflector
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual
3197.3
Accelerating voltage: 20000 V
Grid voltage: 75%
Mirror voltage ratio: 1.12
Guide wire 0: 0.001%
Extraction delay time: 200 nsec
Acquisition mass range: 600 – 900 Da
Number of laser shots: 50/spectrum
Laser intensity: 2816
Laser Rep Rate: 3.0 Hz
Calibration type: External – D:\Ricky Hol3year\2006\26Oct06\calmix1_0001.ca
Calibration matrix: a-Cyano-4-hydroxycinnamic acid
Low mass gate: 600 Da
Timed ion selector: Off
Digitizer start time: 35.873
Bin size: 0.5 nsec
Number of data points: 16067
Vertical scale 0: 500 mV
Vertical offset: 0%
Input bandwidth 0: 500 MHz
Sample well: G5_a
Plate ID: IC1
Serial number: 4146
Instrument name: Voyager-DE STR
Plate type filename: C:\VOYAGER\96 well X2 plate.plt
Lab name: PE Biosystems
Absolute x-position: 20854.4
Absolute y-position: 15519.9
Relative x-position: -37.1246
Relative y-position: -367.786
Shots in spectrum: 200
Source pressure: 1.304e-007
Mirror pressure: 5.962e-009
TC2 pressure: 0.00872
TIS gate width: 8
TIS flight length: 1131

Spectrum b

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