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Supplementary information

Synthesis and catalytic applications of 1,2,3-triazolylidene gold(I) complexes in silver-free oxazoline syntheses and C–H bond activation

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Contents:

1 Synthesis of triazoles and triazolium precursors

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl acetate (pre-1b)

4-Dimethylaminopyridine (60 mg, 0.49 mmol), NEt_3 (4.1 mL, 30 mmol) and acetic anhydride (1.4 mL, 2.0 mmol) were added to a solution of 2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (1.35g, 7.4 mmol) in dry CH_2Cl_2 (20 mL,) and stirred for 3 days. The reaction mixture was partitioned between CH_2Cl_2 (50 mL) and H_2O (150 mL). The aqueous phase was further extracted with CH_2Cl_2 (3 x 100 mL). The combined organic phases were washed with brine (2 x 150 mL), dried with $MgSO_4$, filtered, and all volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and an excess of Et_2O added, resulting in a white precipitate. This suspension was gravity filtered, the mother liquor was retained and the volatiles removed under reduced pressure. Finally, the product was purified by column chromatography (SiO_2; pentane/EtOAc 3:2). The product was obtained as a clear oil which solidified by flash cooling (1.55 g, 6.1 mmol, 93 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, $^3J_{HH}$ = 7.4Hz, 3H, CH_2CH_3), 1.31-1.41 (m, 2H, CH_2CH_3), 1.84 (s, 6H, $C(CH_3)_2$), 1.85-1.93 (m, 2H, NCH_2CH_2), 1.98 (s, 3H, C=OCH_3), 4.31 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 7.49 (s, 1H, $C_{trz}H$) $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 13.6 (CH_2CH_3), 19.9(CH_2CH_3), 22.4 (C=OCH_3), 27.5 ($C(CH_3)_2$), 32.4 (NCH_3CH_2), 50.2(NCH_2), 77.0 ($C(CH_3)_2$), 121.2 ($C_{trz}H$), 151.3 ($C_{trz}C$), 170.2 (*C*=O) HRMS (ESI+): *m/z* 248.1375 $[M + Na]^+$ (Calcd. for $C_{11}H_{19}N_3O_2Na$, 248.1379)

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (pre-f)

To a solution of NaN_3 (2.09 g, 32. mmol) in $H_2O/^tBuOH$ (14 mL, 1:1 v/v) was added 1-Iodobutane (1.10 mL, 11. mmol) and the mixture was stirred for 2 days. 2-methyl-3-butyne (1.10 mL, 11. mmol), sodium ascorbate (420 mg, 2.1 mmol) and $CuSO_4 \cdot 5H_2O$ (60 mg, 0.24 mmol) were added, and the reaction was irradiated with microwaves for 6 h at 100°C. The reaction mixture was diluted with H_2O (100 mL) and extracted with EtOAc (3 x 100 mL). Any emulsion formed was broken by Büchner filtration. The organic layers were combined, washed with water (100 mL), brine (100 mL), dried over $MgSO_4$, gravity filtered and the volatiles removed under reduced pressure yielding a green to brown oil. Remaining salts were removed by dissolving the oil in Et_2O (100 mL), drying with $MgSO_4$ followed by gravity filtration and removal of volatiles under reduced pressure. The oil was then purified using column chromatography (SiO_2; pentane/EtOAc 1:3). The product was obtained as a yellow oil (0.881 g, 4.8 mmol, 46 % yield).^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, $^3J_{HH}$ = 7.4Hz, 3H, CH_2CH_3), 1.29-1.37 (m, 2H, C*H*$_2$CH$_3$), 1.62 (s, 6H, C(CH$_3$)$_2$), 1.82-1.90 (m, 2H, NCH$_2$C*H*$_2$), 4.30 (t, $^3J_{HH}$ = 7.3Hz, 2H, NCH$_2$), 7.42 (s, 1H, C$_{Trz}$H) ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 13.6 (CH$_2$*C*H$_3$), 19.9(*C*H$_2$CH$_3$), 30.6 (C(*C*H$_3$)$_2$), 32.4 (NCH$_2$*C*H$_2$), 50.1(NCH$_2$), 68.6 (*C*(CH$_3$)$_2$), 119.0 (C$_{trz}$H), 155.7 (*C*$_{trz}$C) HRMS (ESI+): *m/z* 184.1443 [M+H]$^+$ (cald. for $C_9H_{18}N_3O$ 184.1450)

Triazolium 1b

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl acetate (0.433 g, 1.9 mmol) was dissolved in Et$_2$O (5mL) and cooled to 0 °C. Addition of MeOTf (0.240 mL, 2.1 mmol) caused a clear oil to settle out almost immediately. The reaction was stirred for 1h, while the ice bath was maintained. An excess of cold Et$_2$O was added to allow maximum amount of product to settle out. The solvent was decanted and the oil rinsed with cold Et$_2$O and then cold pentane. The product was dried *in vacuo* yielding a viscous oil (0.85 g, 2.2 mmol, 90 % yield) This triazolium salt was stored in the freezer until further use. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.98 (t, 7.3Hz, 3H, CH$_2$C*H*$_3$), 1.36-1.46 (m, 2H, C*H*$_2$CH$_3$), 1.91 (s, 6H, C(CH$_3$)$_2$), 1.98-2.05 (m, 2H, NCH$_2$C*H*$_2$), 2.11 (s, 3H, C=OCH$_3$), 4.26 (s, 3H, NCH$_3$), 4.60 (t, 7.5Hz, 2H, NCH$_2$), 8.72 (s, 1H, C$_{trz}$H) ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 13.4 (CH$_2$*C*H$_3$), 19.5(*C*H$_2$CH$_3$), 21.4 (C=O*C*H$_3$), 26.5 (C(*C*H$_3$)$_2$), 31.1 (NCH$_2$*C*H$_2$), 39.5 (NCH$_3$), 54.3 (NCH$_2$), 74.3 (*C*(CH$_3$)$_2$), 129.0 (C$_{trz}$H), 146.6 (*C*$_{trz}$C), 169.9 (C=O) HRMS (ESI+): *m/z* 240.1711 [M – OTf]$^+$ (calcd. for $C_{12}H_{22}N_3O_2$, 240.1712)

Triazolium 1c

A solution of 4-butyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-1,2,3-triazole (0.38g, 0.81mmol) and $CF_3(CF_2)_5(CH_2)_2I$ in MeCN (20 mL) was irradiated for 10 h at 150 °C. Volatiles were removed under reduced pressure. The residue was dissolved in minimal CH$_2$Cl$_2$ and an excess of Et$_2$O (100 mL) added causing a gelatinous suspension to form. Centrifugation separated a pale yellow precipitate from a yellow supernatant. The precipitate was washed, followed by centrifugation with Et$_2$O (2 x 100 mL), and pentane (100 mL) and dried under vacuum. The supernatants were combined, volatiles removed, and the residue redissolved in MeCN (20 mL), irradiated with microwaves for 11 h at 160 °C, and the reaction mixture purified as before The precipitates were combined yielding the product as a white solid (0.252 g, 0.27 mmol, 33% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.00 (t, $^3J_{HH}$ = 7.3Hz, 3H, CH$_3$), 1.45-1.55 (m, 2H, C*H*$_2$CH$_3$), 1.79-1.86 (m, 2H, C$_{trz}$CH$_2$C*H*$_2$), 2.89 – 2.93 (m, 2H, C$_{trz}$C*H*$_2$), 2.97 – 3.13 (m, 4H, 2 x CH$_2$CF$_2$), 4.91 (t, $^3J_{HH}$ = 6.5Hz, 2H, N3C*H*$_2$), 5.25 (t, $^3J_{HH}$ = 6.5Hz, 2H, N1C*H*$_2$), 9.33 (1H, s, C$_{Trz}$H) ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 14.0 (CH$_3$), 22.3

(*C*H_2CH_3), 23.8 (C_{trz}*C*H_2CH_2), 29.1 ($C_{trz}CH_2$*C*H_2), 30.1 (t, $^2J_{CF}$ = 21.4Hz, N3CH_2*C*H_2), 31.0 (t, $^2J_{CF}$ = 21.9 Hz, N1CH_2*C*H_2), 44.3 (b, N3*C*H_2), 47.4 (b, N1*C*H_2), 130.3 (C_{trz}H), 145.7 ($C_{trz}C_{nBu}$) $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -126.37-(-126.23) (m, 4F), -123.43 (bs, 2F), -123.22 (bs, 2F), -122.99 (bs, 4F), -122.01-(-121.94) (m, 4F), -114.09-(-113.97) (m, 2F), -113.97-(-113.81) (m, 2F), -80.89-(-80.99) (m, 6F) HRMS (ESI+): *m/z* 818.1086 $[M – I]^+$ (calcd. for $C_{22}H_{18}N_3F_{26}$, 818.1090) Anal. Calcd. for $C_{22}H_{18}F_{26}IN_3$: C, 27.95; H, 1.92; N, 4.45%. Found: C, 27.50; H, 1.57; N, 4.20%.

Triazolium 1f (tetrafluoroborate salt)

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (2.20 g, 12. mmol) and Me_3OBF_4 (2.05g, 14 mmol) were suspended in dry CH_2Cl_2 (100 mL) and stirred under N_2 atmosphere for 18 h, after which MeOH (5 mL) was added to quench the reaction. After 30 min of stirring, the volatiles were removed under reduced pressure. The resulting clear oil was washed with an excess of Et_2O. The oil was then suspended in CH_2Cl_2, filtered through Celite, and filtrate evaporated to dryness. The residue was redissolved in a minimum amount of CH_2Cl_2 and slowly added to cold Et_2O with vigorous stirring, which gave a white precipitate. The Et_2O was decanted and the solid washed with pentane. The residue was thoroughly dried affording the product as a hydroscopic white solid (2.7 g, 9.5 mmol, 79 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, $^3J_{HH}$ = 7.4Hz, 3H, CH_2*C*H_3), 1.32-1.45 (m, 2H, C*H*$_2$$CH_3$),1.66 (s, 6H, $C(CH_3)_2$), 1.92-2.00 (m, 2H, NCH_2C*H*$_2$), 4.38 (s, 3H, NCH_3), 8.26 (C_{Trz}H) $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 13.4 (CH_2*C*H_3), 19.5 (*C*H_2CH_3), 29.0 (C(*C*H_3)$_2$), 31.0 (NCH_2*C*H_2), 40.0 (NCH_3) ,53.8 (NCH_2), 67.5 (*C*$(CH_3)_2$), 127.4 (C_{trz}H), 149.2 (C_{trz}C) HRMS (ESI+): *m/z* 198.1603 $[M – BF_4]^+$ (calcd. for $C_{10}H_{20}N_3O$, 198.1606) Anal. Calcd for $C_{10}H_{20}N_3OBF_4$: C, 42.13; H, 7.07; N, 14.74%. Found: C, 41.86; H, 6.95; N, 14.81%.

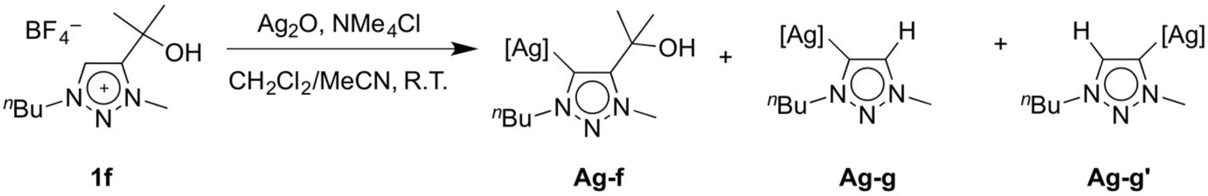
Triazolium 1f (triflate salt)

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (0.473 g, 2.6 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C and MeOTf (0.850 mL, 7.5 mmol) was added. The reaction was stirred for 16 h, then excess Et_2O was added. The formed oil was collected by decantation and dissolved in a minimal amount of CH_2Cl_2. This solution was added dropwise to cold Et_2O. The formed white precipitate was collected by filtration and dried, thus yielding the title product as a hydroscopic white solid (0.629 g, 0.91 mmol, yield 69 %). ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, $^3J_{HH}$ = 7.4Hz, 3H, CH_2*C*H_3), 1.38-1.48 (m, 2H, C*H*$_2$$CH_3$),1.70 (s, 6H, $C(CH_3)_2$), 1.96-2.03

(m, 2H, $NCH_2\mathit{CH}_2$), 4.43 (s, 3H, NCH_3), 8.36 ($C_{trz}H$) $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 13.4 ($CH_2\mathit{CH}_3$), 19.6 (CH_2CH_3), 29.2 ($C(\mathit{CH}_3)_2$), 31.1 ($NCH_2\mathit{CH}_2$), 40.2 (NCH_3) ,53.9 (NCH_2), 67.2 ($\mathit{C}(CH_3)_2$), 127.4 ($C_{trz}H$), 149.9 ($\mathit{C}_{trz}C$) Anal. Calcd for $C_{11}H_{20}F_3N_3O_4S$: C, 38.04; H, 5.80; N, 12.10%. Found: C, 37.94; H, 5.59; N, 11.93%.

2 Reactivity of 1f with Ag_2O

Table S1. Product distribution from the reaction of Ag_2O and 1f using varying amounts of Ag_2O

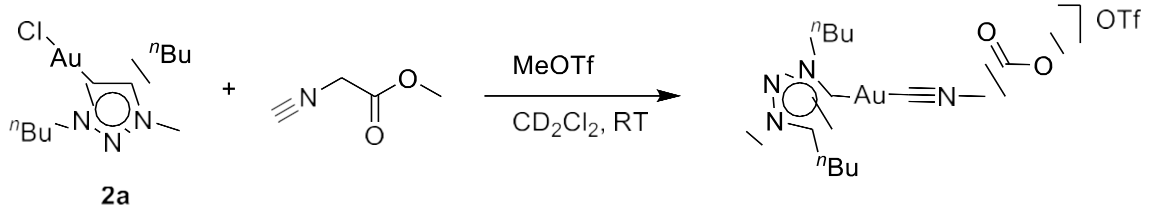


Entry	Ag_2O Eqv.	**1f** (%)	**Ag-f**	**Ag-g/g'**	Ratio Ag decomposition
1	0.5	21	32	48	55/45
2	1	19	71	10	60/40
3	2	0	81	19	58/42

[Ag] is either AgCl or $[Ag(trz)]BF_4$

3. Reactivity of complexes 2 with MeOTf

Preparation of [Au(trz)(isonitrile)]OTf



Methyl isocyanoacetate (7.8 µL, 0.086 mmol), and then MeOTf (18.3 µL, 0.16 mmol) was added to a solution of **2a** (35 mg, 0.081 mmol) in CD_2Cl_2 (2 mL). The reaction mixture was stirred protected from light for 20 h. The volatiles were removed yielding the product as an yellow oil (48.2 mg, 0.075 mmol, 92 %). ^{1}H (400 MHz, CD_2Cl_2): δ 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3), 1.32–1.40 (m, 2H, $N(CH_2)_2CH_2$), 1.40-1.48 (m, 2H, $C_{trz}(CH_2)_2CH_2$), 1.69–1.77 (m, 2H, $C_{trz}CH_2CH_2$), 1.97–2.04 (m, 2H, NCH_2CH_2), 2.80-2.76 (m, 2H,$C_{trz}CH_2$), 3.88 (s, 3H, OCH_3), 4.06 (s, 3H, NCH_3), 4.44 (t, $^3J_{HH}$ = 7.2 Hz, 2H, NCH_2), 4.75 (s, 2H, $CNCH_2$) ^{13}C{^{1}H}(101 MHz, CD_2Cl_2): δ 13.7, 14.0 (2 x CH_2CH_3), 20.1 ($N(CH_2)_2CH_2$), 22.8 ($C_{trz}(CH_2)_2CH_2$, 25.1 ($C_{trz}CH_2$), 31.9 ($C_{trz}CH_2CH_2$), 33.0 (NCH_2CH_2), 37.2 (NCH_3), 46.4 ($CNCH_2$), 54.6 (OCH_3), 56.2 (NCH_2), 150.5 ($C_{trz}C$), 152 (Au–CN), 163.1, 163.3 (C_{trz}-Au and COO) NC-Au not resolved, and CH_3O overlaps with CD_2Cl_2 ^{19}F{^{1}H} (282 MHz, CD_2Cl_2): δ –78.96 (s).

Coordination of isonitrile was inferred from the upfield shift of the isonitrile carbon from 160 (in the free ligand) to 151.9 ppm in the complex. Moreover, the methylene group bound to the isonitrile functionality was shifted downfield both in ^{13}C and ^{1}H NMR spectra (δ_C from 43.2 to 46.6, and δ_H from 4.25 to 4.75) upon ligation to the Au(trz) synthon. Of note, no such shifts were observed when the reaction was performed in the absence of MeOTf, suggesting that formation of the chloride-free [Au(trz)]$^+$ intermediate is promoted by MeOTf.

Spectra of the product from reaction of 2c with MeOTf

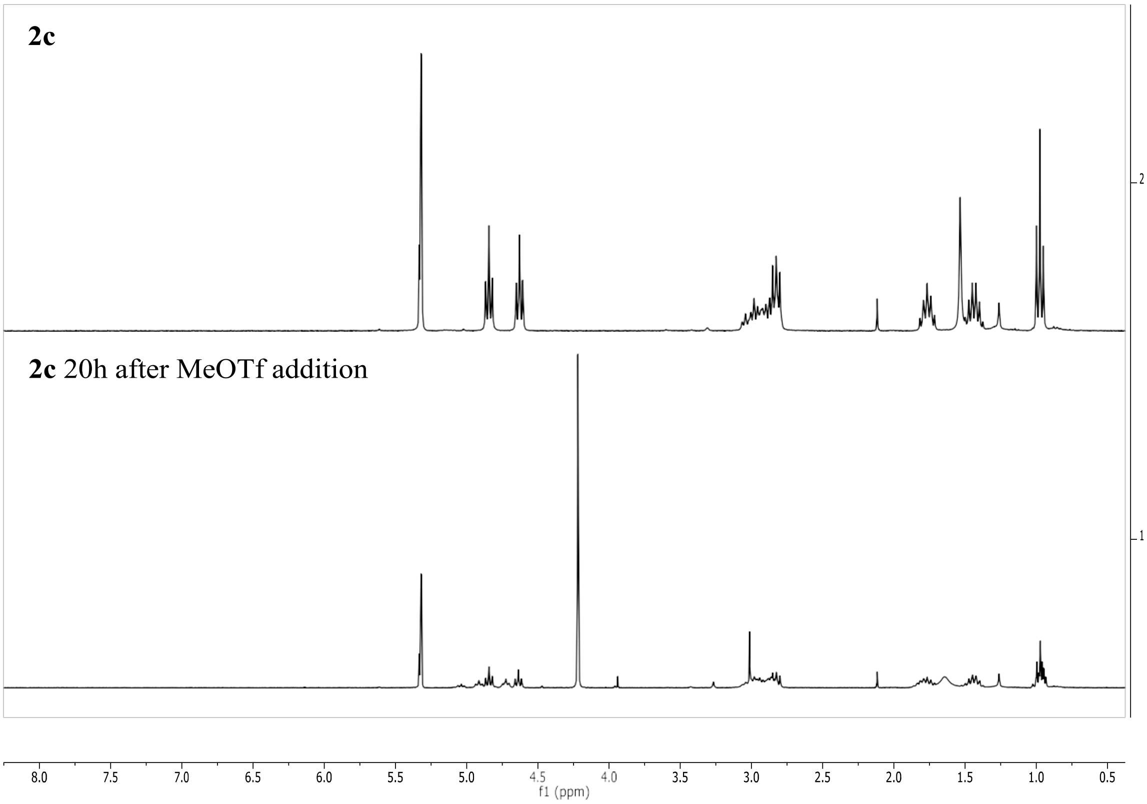


Figure S1. ^{1}H NMR traces for the reaction of **2c** with MeOTf

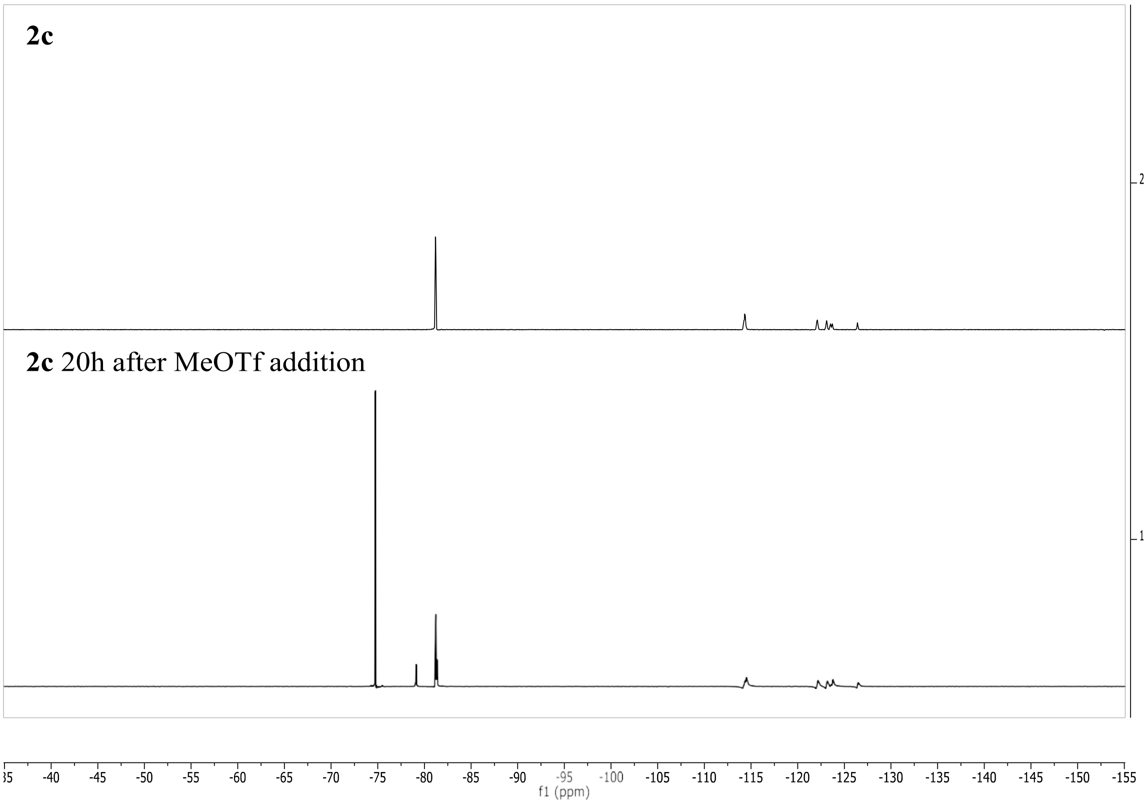
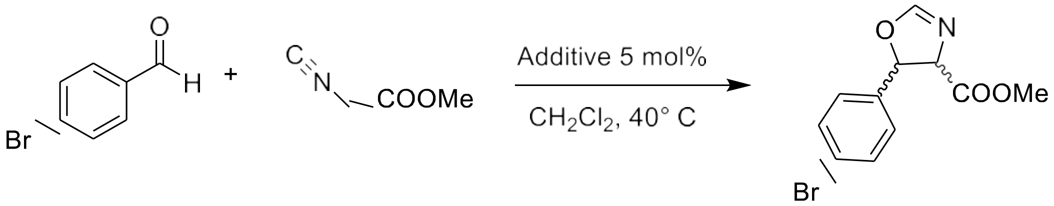


Figure S2. ^{19}F NMR traces for the reaction of **2c** with MeOTf

4 Details pertaining to catalytic oxazoline syntheses

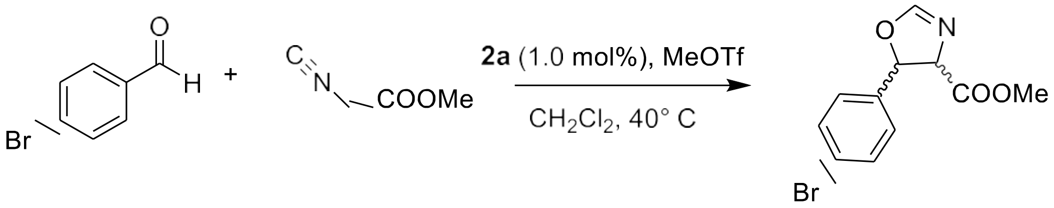
Table S2. Conversions (%) for blank reactions for catalytic oxazoline synthesis



Time (h)	-	MeOTF	KOTf	KBF_4	KPF_6	KPF_6[a]
4	-	-	6	11	15	14
8	6	16	21	21	19	25
24	36	30	32	42	37	39
cis/*trans*		14/86	12/88	12/88	12/88	-

General conditions: 4-bromobenzyaldehyde (1.57 mmol), methyl isocyanoacetate (1.43 mmol), NEt*i*Pr_2 (0.14 mmol), Additive (0.05 mmol), trimethoxybenezene (0.36 mmol), CH_2Cl_2 (4 mL), 40° C, 8h; Conversions and *cis*/*trans* ratio determined by ^1H NMR spectroscopy, averaged over 2 runs. [a] Additive (0.02mmol)

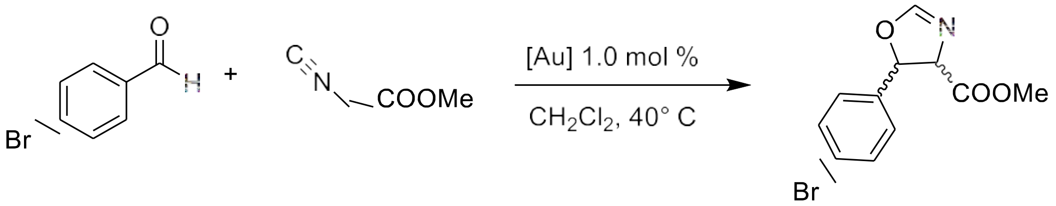
Table S3. Conversion (%) for varying MeOTf mol% activation of 2a for oxazoline formation[a]



Time (h)	1.1 mol%[b]	2 mol%[b]	5 mol%[c]
0	0.0	0.0	0.0
2	13.0	17.5	45.0
4	21.0	37.8	70.0
8	39.0	62.0	92.0
24	81.0	94.8	100.0
cis/*trans*	26/74	27/73	27/73

[a] General conditions: 4-bromobenzyaldehyde (1.57 mmol), methyl isocyanoacetate (1.43 mmol), NEt*i*Pr_2 (0.14 mmol), TrzAuCl (0.014 mmol), Additive (0.028 mmol), trimethoxybenezene (0.36 mmol), CH_2Cl_2 (4 mL), 40° C, 8h; Conversions and *cis*/*trans* ratio determined by ^1H NMR spectroscopy; [b] Average of 4 runs, (0.265 M MeOTF in CH_2Cl_2); [c] Average of 2 runs

Table S4. Conversion (%) for [Au]/Activator systems for catalytic oxazoline formation[a]



Time (h)	2a/-	2a/KOTf	2a/KBF_4	2a/KPF_6	2b/KPF_6	2c/KPF_6	2e/KPF_6
2	-	26	10	42	34	25	35
4	16	38	17	69[b]	64	43	60
8	24	61	21	93[b]	88	75	87
24	47	96	38	100[b]	100	100	100
cis/trans	23/77	28/72	18/82	26/74[b]	27/73	29/71	29/71

[a] General conditions: 4-bromobenzyaldehyde (1.57 mmol), methyl isocyanoacetate (1.43 mmol), NEt*i*Pr_2 (0.14 mmol), TrzAuCl (0.014 mmol), Additive (0.028 mmol), trimethoxybenezene (0.36 mmol), CH_2Cl_2 (4 mL), 40° C, 8h; Conversions and *cis*/*trans* ratio determined by ^1H NMR spectroscopy, averaged over 2 runs; [b] Average over 5 runs

5 Crystallographic details

Table S5. Crystal data and structure refinement for 2b

CCDC No	1481152	
Empirical formula	$C_{12}H_{21}AuClN_3O_2$	
Formula weight	471.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.0817(2) Å	α = 90°.
	b = 9.70652(12) Å	β = 100.1394(13)°.
	c = 12.2839(2) Å	γ = 90°.
Volume	1535.42(4) $Å^3$	
Z	4	
Density (calculated)	2.041 Mg/m^3	
Absorption coefficient	9.757 mm^{-1}	
F(000)	904	
Crystal size	0.2456 x 0.1841 x 0.1412 mm^3	
Theta range for data collection	2.97 to 32.74°.	
Index ranges	-19<=h<=19, -14<=k<=14, -15<=l<=17	
Reflections collected	21706	
Independent reflections	5327 [R(int) = 0.0396]	
Completeness to theta = 31.00°	99.7 %	
Absorption correction	Analytical	
Max. and min. transmission	0.353 and 0.250	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5327 / 0 / 177	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0446	
R indices (all data)	R1 = 0.0262, wR2 = 0.0466	
Largest diff. peak and hole	1.848 and -2.385 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for 2f

CCDC No	1481154	
Empirical formula	$C_{10}H_{19}AuClN_3O$	
Formula weight	429.7	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.4494(2) Å	α = 90°.
	b = 11.8071(3) Å	β = 90.017(3)°.
	c = 15.6623(3) Å	γ = 90°.
Volume	1377.59(6) Å3	
Z	4	
Density (calculated)	2.072 Mg/m3	
Absorption coefficient	10.858 mm-1	
F(000)	816	
Crystal size	0.215 x 0.156 x 0.046 mm3	
Theta range for data collection	1.725 to 28.282°.	
Index ranges	-9<=h<=9, -15<=k<=15, -20<=l<=20	
Reflections collected	17191	
Independent reflections	3401 [R(int) = 0.0301]	
Completeness to theta = 25.242°	100 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.626 and 0.196	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3401 / 0 / 151	
Goodness-of-fit on F2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0783	
R indices (all data)	R1 = 0.0346, wR2 = 0.08	
Largest diff. peak and hole	3.928 and -1.464 e.Å-3	

Table S7. Crystal data and structure refinement for 2g

CCDC No	1481151	
Empirical formula	$C_7H_{13}AuClN_3$	
Formula weight	371.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.66636(6) Å	α = 82.2181(9)°.
	b = 13.6052(2) Å	β = 78.8756(9)°.
	c = 13.6584(2) Å	γ = 87.9581(8)°.
Volume	1023.61(2) $Å^3$	
Z	4	
Density (calculated)	2.411 Mg/m^3	
Absorption coefficient	14.586 mm^{-1}	
F(000)	688	
Crystal size	0.3838 x 0.1745 x 0.0991 mm^3	
Theta range for data collection	3.02 to 32.98°.	
Index ranges	-8<=h<=8, -20<=k<=20, -20<=l<=20	
Reflections collected	65960	
Independent reflections	7351 [R(int) = 0.0627]	
Completeness to theta = 32.00°	99.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.335 and 0.094	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7351 / 0 / 221	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0201, wR2 = 0.0440	
R indices (all data)	R1 = 0.0237, wR2 = 0.0460	
Largest diff. peak and hole	1.140 and -1.877 e.$Å^{-3}$	

Table S8. Crystal data and structure refinement for 3a.

CCDC No	1481153	
Empirical formula	$C_{30}H_{36}AuF_3N_3O_3PS$	
Formula weight	803.61	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.0044(2) Å	α = 89.133(2)°.
	b = 11.9604(3) Å	β = 81.768(2)°.
	c = 15.0383(3) Å	γ = 86.780(2)°.
Volume	1600.31(6) Å^3	
Z	2	
Density (calculated)	1.668 Mg/m^3	
Absorption coefficient	4.764 mm^{-1}	
F(000)	796	
Crystal size	0.1619 x 0.1374 x 0.1310 mm^3	
Theta range for data collection	2.78 to 29.66°.	
Index ranges	-12<=h<=11, -15<=k<=15, -20<=l<=20	
Reflections collected	30102	
Independent reflections	7972 [R(int) = 0.0458]	
Completeness to theta = 27.00°	99.2 %	
Absorption correction	Analytical	
Max. and min. transmission	0.620 and 0.544	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7972 / 0 / 382	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0687	
R indices (all data)	R1 = 0.0339, wR2 = 0.0717	
Largest diff. peak and hole	3.102 and -1.672 e.Å^{-3}	