



Supporting Information

for

Ligand effects, solvent cooperation, and large kinetic solvent deuterium isotope effects in gold(I)-catalyzed intramolecular alkene hydroamination

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Experimental procedures, kinetic data, and relevant spectra for kinetics reactions and intermediates

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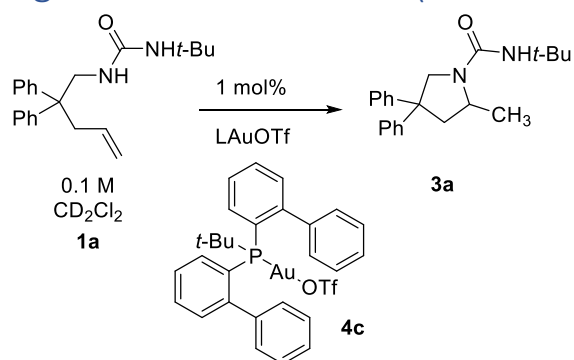
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General Experimental

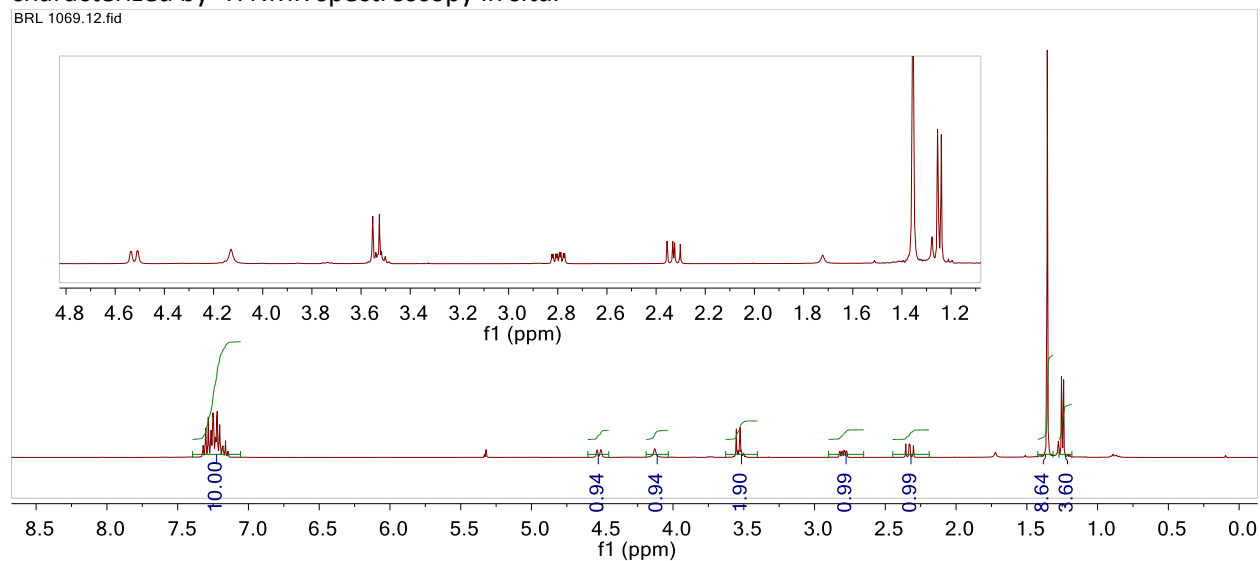
Unless otherwise noted commercial materials were used without further purification. Complexes were prepared in an oxygen-free, moisture-free glovebox or under Argon using Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Unless otherwise stated, the deuterated solvents for kinetics experiments were used as received. All other solvents were purchased anhydrous. NMR spectra were obtained on Bruker spectrometers operating at a proton frequency of either 300, 400 or 500 MHz. Unless otherwise noted, spectra were collected at 25 °C. For kinetic plots, the total concentrations of alkene starting material and cyclized product were normalized, assuming that the sum of the signals for each were constant.

Observed rates and corresponding errors for individual experiments were calculated using the LINEST function in EXCEL. Where multiple trials were conducted, standard deviation on the average was calculated.

Ligand Effect with Urea (Table 1 in Paper)



The urea starting material was prepared according to literature procedure¹ and the cyclized product was characterized by ¹H NMR spectroscopy in situ.



¹H NMR Spectrum of 3a: (CD₂Cl₂, 400.17 MHz): 7.33–7.11 (m, 10H), 4.52 (dd, J=10.8, 2.1 Hz, 1H), 4.13 (s, 1H), 3.54 (d, J=10.8 Hz, 1H), 3.51 (m, 1H), 2.80 (ddd, J=12.3, 6.4, 2.2 Hz, 1H), 2.33 (dd, J=12.3, 9.2 Hz, 1H), 1.36 (s, 9H), 1.25 (d, J=6.1 Hz, 3H).

A stock solution of catalyst (0.0524 M) was prepared by dissolving **4c** (740.53 g/mol, 77.6 mg, 0.10 mmol) in 1.94 mL of CD₂Cl₂. Urea alkene **1a** (336.48 g/mol, 24 mg, 0.071 mmol) was dissolved 0.687 mL of CD₂Cl₂ and transferred to an NMR tube. Catalyst solution (13 μL, 0.0007 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.1 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least ~85% conversion.

	CD ₂ Cl ₂	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × K _{obs} /s ⁻¹	
BRL 1065	0.687 mL	0.013 mL	0.0007 mmol	1 mol %	28 ± 1	average: 58 ± 27
BRL 1067	0.687 mL	0.013 mL	0.0007 mmol	1 mol %	79 ± 6	
BRL 1069	0.687 mL	0.013 mL	0.0007 mmol	1 mol %	67 ± 7	

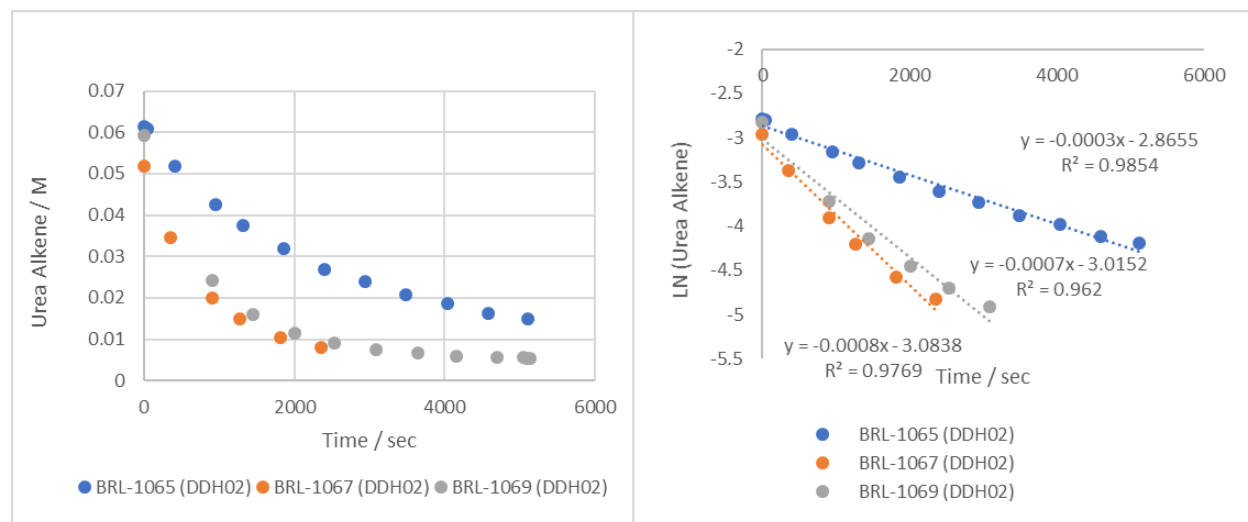
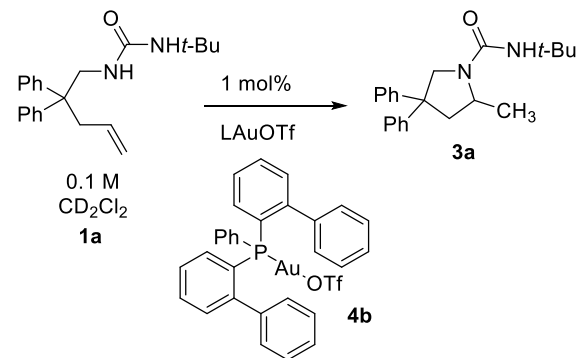


Figure S1. Raw plots of urea alkene decay (0.1 M) in 0.7 mL of CD₂Cl₂ with 0.0007 mmol **4c** (1 mol %) and corresponding first order plots.



A stock solution of catalyst (0.054 M) was prepared by dissolving **4b** (760.53 g/mol, 120.6 mg, 0.159 mmol) in 2.94 mL of CD₂Cl₂. Urea alkene **1a** (336.48 g/mol, 24 mg, 0.071 mmol) was dissolved 0.687 mL of CD₂Cl₂ and transferred to an NMR tube. Catalyst solution (13 μL, 0.0007 mmol) was injected to initiate the

reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.1 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least $\approx 94\%$ conversion.

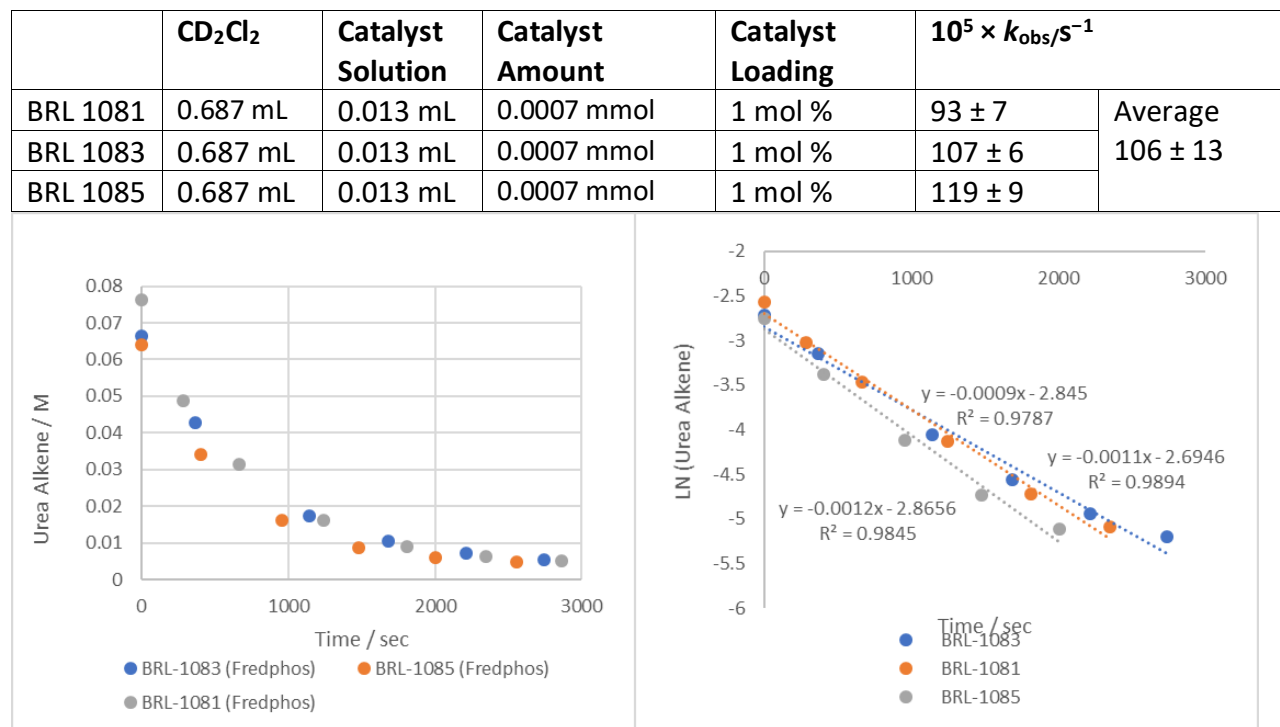
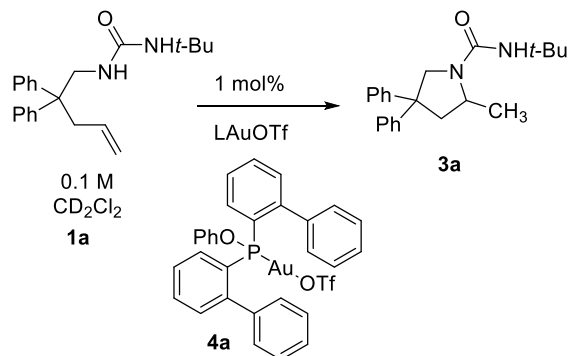


Figure S2. Raw plots of urea alkene **1a** decay (0.1 M) in 0.7 mL of CD_2Cl_2 with 0.0007 mmol of **4b** (1 mol %) and corresponding first order plots.



A stock solution of catalyst (0.028M) was prepared by dissolving **4a** (776.52 g/mol, 85.3 mg, 0.11 mmol) in 3.95 mL of CD_2Cl_2 . Urea alkene **1a** (336.48 g/mol, 25 mg, 0.074 mmol) was dissolved 0.675 mL of CD_2Cl_2 and transferred to an NMR tube. Catalyst solution (25 μL , 0.0007 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.1 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least $\approx 92\%$ conversion.

	CD_2Cl_2	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$	
BRL 1031	0.675 mL	0.025 mL	0.0007 mmol	1 mol %	192 ± 10	

BRL 1035	0.675 mL	0.025 mL	0.0007 mmol	1 mol %	178 ± 18	average: 206 ± 37
BRL 1037	0.675 mL	0.025 mL	0.0007 mmol	1 mol %	247 ± 12	

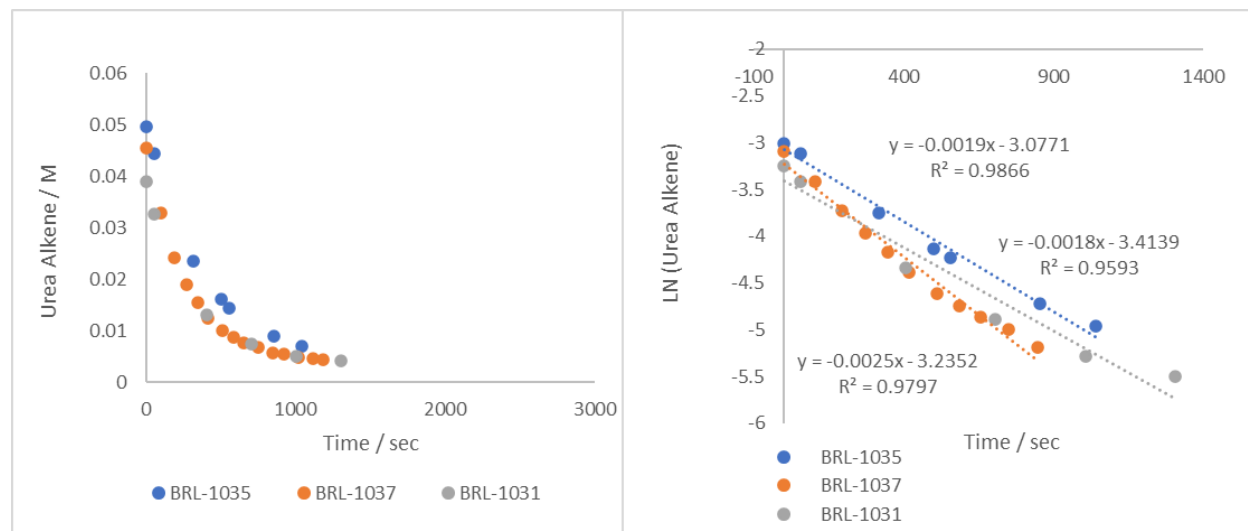
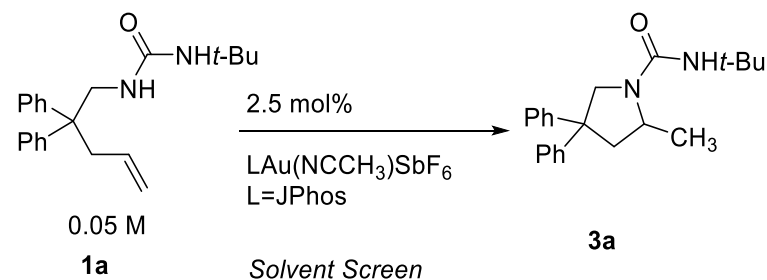


Figure S3. Raw plots of urea alkene decay **1a** (0.1 M) in 0.7 mL of CD_2Cl_2 with 0.0007 mmol of **4c** (1 mol %) and corresponding first order plots.



Solvent Effect (Table 2 in Paper)

A representative procedure is as follows. A stock solution of catalyst (0.036 M) was prepared by dissolving $\text{JPhosAu}(\text{NCCH}_3)\text{SbF}_6$ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CH_2Cl_2 . Urea alkene **1a** (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in 0.675 mL of CH_2Cl_2 and transferred to an NMR tube. The catalyst solution (25 μL , 0.000892 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M). The sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. Similar procedures were followed with variation of the reaction solvent.

MeOH-d₄

	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRR-2039	3.68 ± 0.02
BRL-4031	4.42 ± 0.03
BRL-4033	4.24 ± 0.02

BRL-4035	4.42 ± 0.06
Average	4.2 ± 0.3

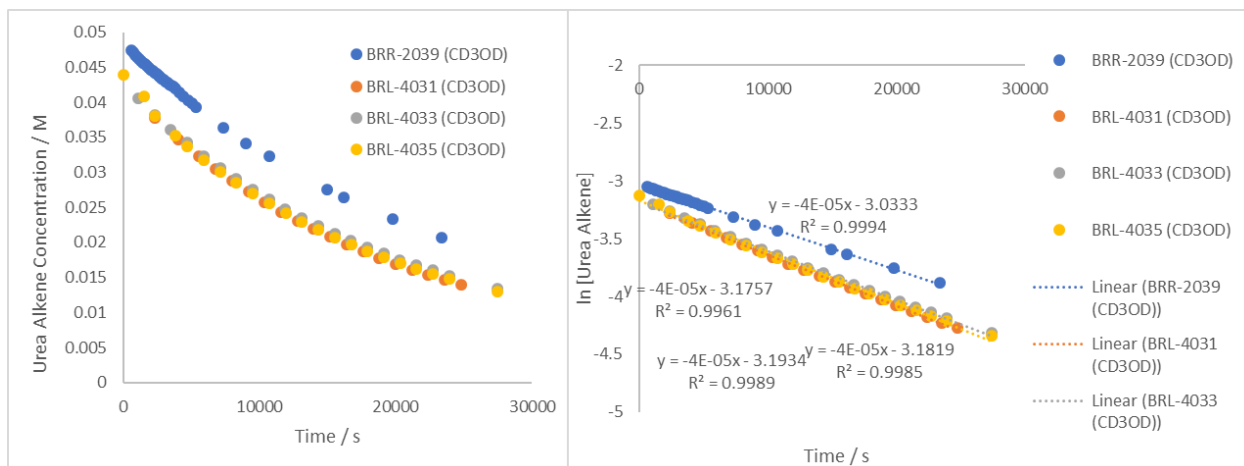


Figure S4. Raw plots of urea alkene decay (0.05 M) in 0.7 mL of solvent with JPhosAu(NCCH₃)SbF₆ (2.5 mol %) and corresponding first order plots.

Acetonitrile

	$10^5 \times k_{obs}/s^{-1}$
BRR-2033	1.75 ± 0.01

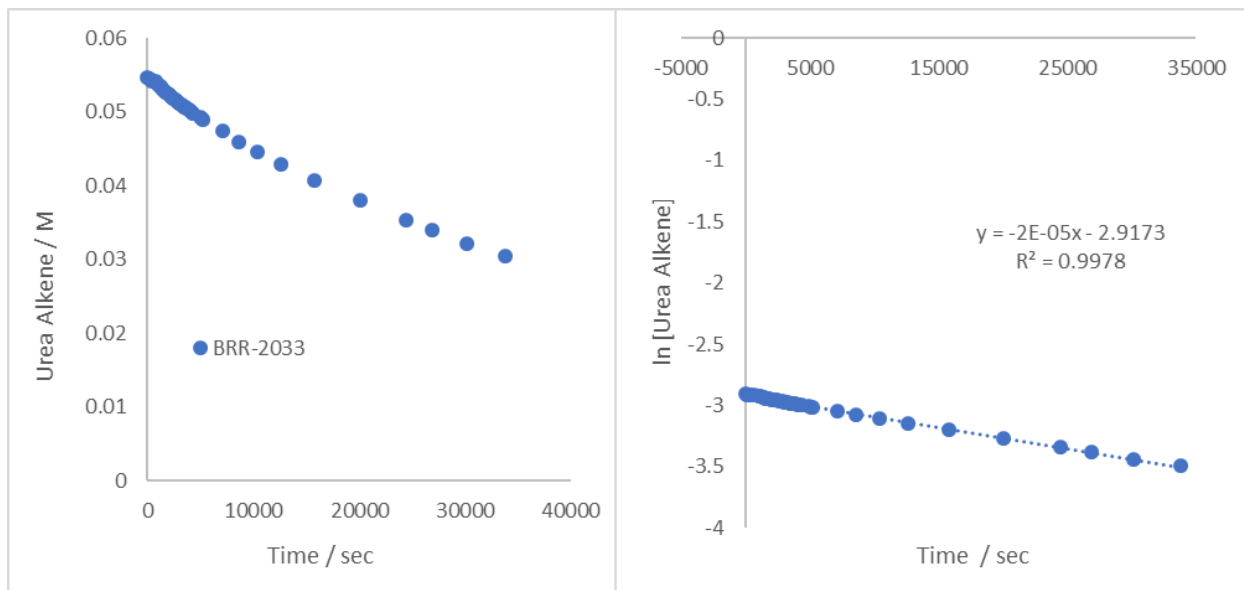


Figure S5. Raw plots of urea alkene decay (0.05 M) in 0.7 mL of solvent with JPhosAu(NCCH₃)SbF₆ (2.5 mol %) and corresponding first order plots.

THF-D8

	$10^5 \times k_{obs}/s^{-1}$
BRL-6021	90 ± 3

BRL-6023	41.9 ± 0.9
BRL-6025	105 ± 4
BRL-6033	95 ± 4
BRL-6035	105 ± 5
Average	87 ± 26

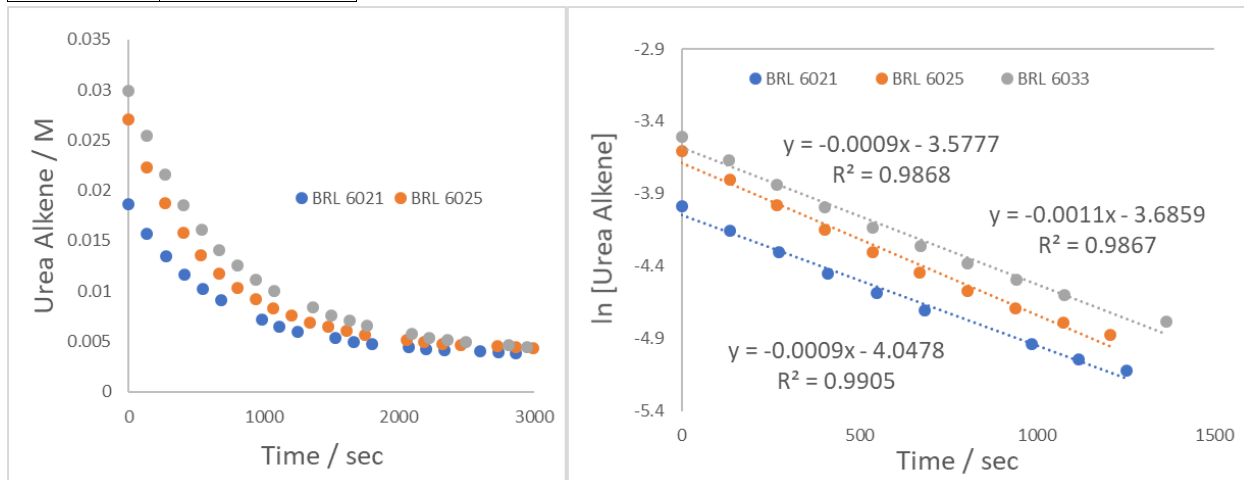


Figure S6. Raw plots of urea alkene decay (0.05 M) in 0.7 mL of THF-d₈ with JPhosAu(NCCH₃)SbF₆ (2.5 mol %) and corresponding first order plots.

DCM-d₂ with 10% CD₃OD (v/v)

	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRR-6117	166 ± 13
BRR-6119	133 ± 2
Average	150 ± 23

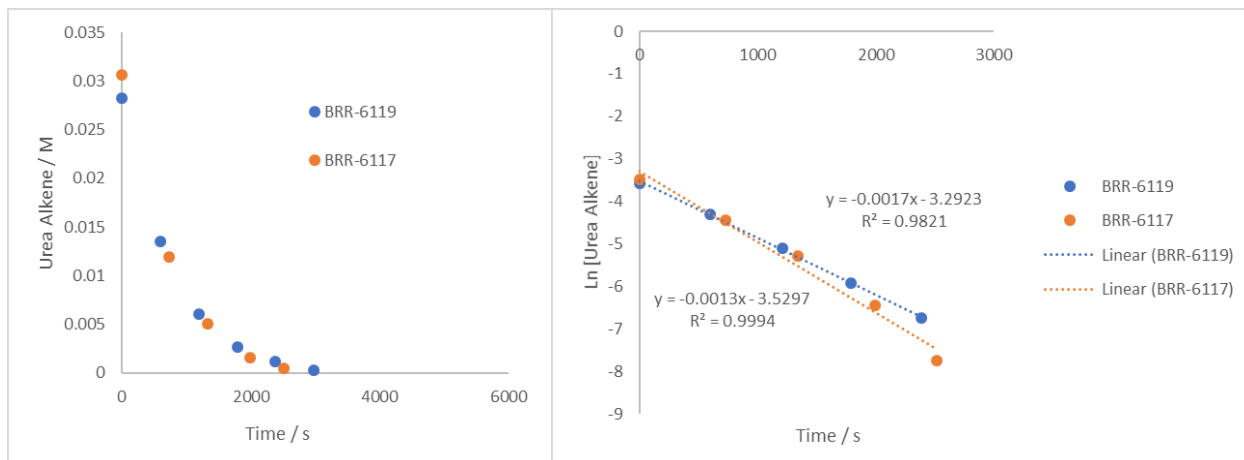


Figure S7. Raw plots of urea alkene decay (0.05 M) in 0.7 mL solvent (540 μL CD_2Cl_2 with 60 μL CD_3OD) with JPhosAu(NCCH₃)SbF₆ (2.5 mol %) and corresponding first order plots.

DCM-d2 with 10% CH₃OH (v/v)

This procedure utilized 60 μL CH_3OH with 540 μL CD_2Cl_2 . A rate constant of 0.008 s^{-1} was estimated based on the observed 90% conversion by the collection of the 1st NMR spectrum obtained (time ca 300 seconds).

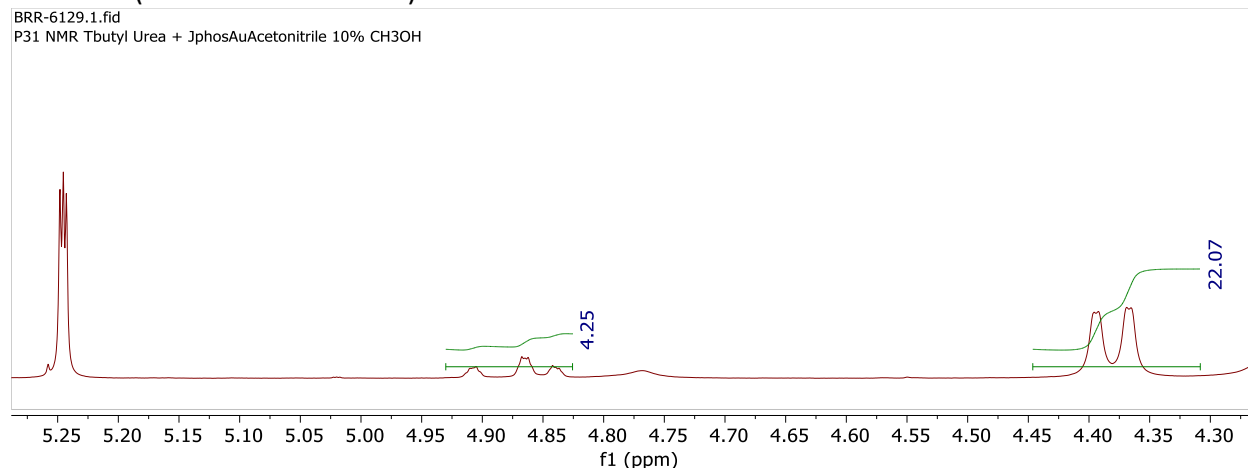


Figure S8. ¹H NMR spectrum collected within 5 minutes of catalyst addition, for reaction of **1a** with [JPhosAu(NCCH₃)]SbF₆ in CD_2Cl_2 with 10% CH_3OH (v/v).

CH_2Cl_2

First order plots were linear up to $\approx 66\%$ conversion.

	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL-2033	51 ± 2
BRL-2035	52 ± 2
BRL-2037	50 ± 2
Average	51 ± 1

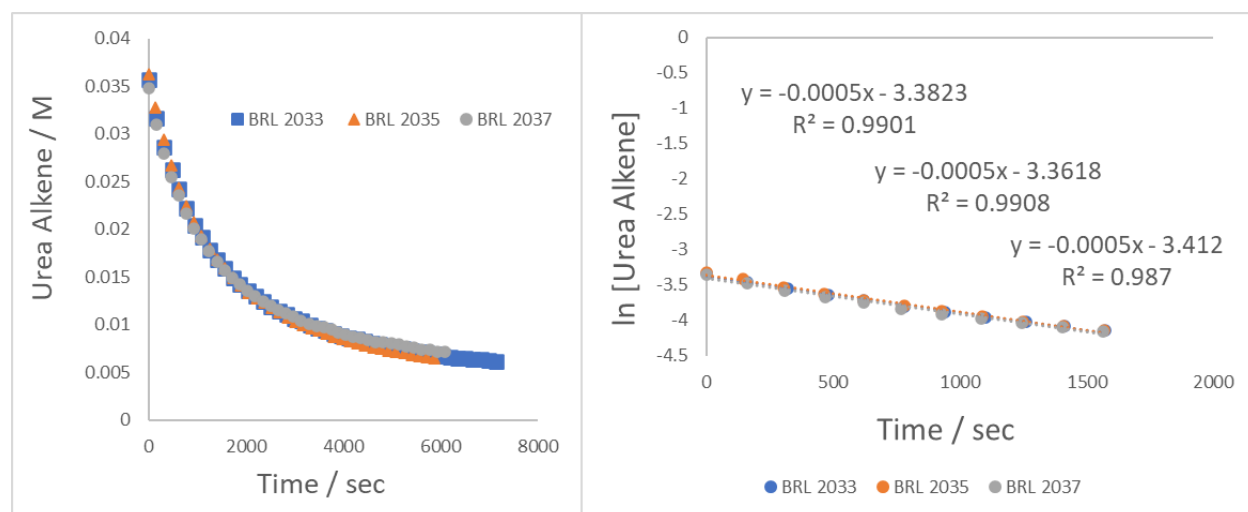


Figure S9. Raw plots of urea alkene decay (0.05 M) in 0.7 mL of CH_2Cl_2 with 0.0009 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (2.5 mol %) and corresponding first order plots.

CD_2Cl_2

First order plots were linear up to 70% conversion.

	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL-4139	35.9 ± 0.8
BRL-4141	35.8 ± 0.9
BRL-4143	38 ± 1
Average	37 ± 1

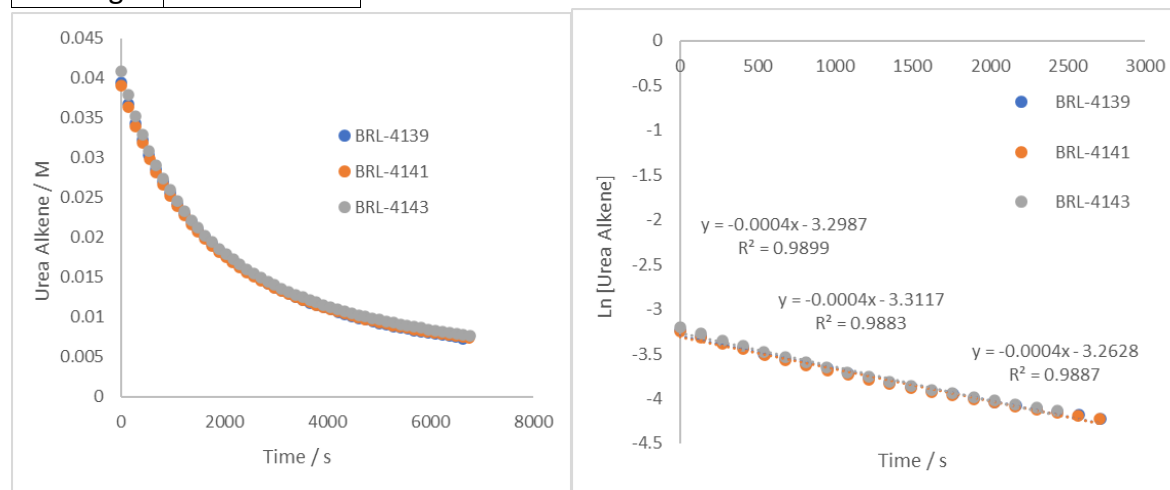


Figure S10. Raw and first order plots of urea alkene decay (0.05 M) in 0.7 mL of CD_2Cl_2 with $[\text{JPhosAu}(\text{CNCH}_3)]\text{SbF}_6$ (2.5 mol %).

CH₃OH

Negligible differences in rate were seen when using JPhosAuOTf versus [JPhosAu(NCCH₃)]SbF₆. Plots were linear up to ≥80% conversion.

	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{obs}/S^{-1}$	
BRL-2039*	50 μ L	0.00089 mmol	2.5 mol %	50 ± 1	Average 50 ± 7
BRL-1127	25 μ L	0.00089 mmol	2.5 mol %	46 ± 1	
BRL-1129	25 μ L	0.00089 mmol	2.5 mol %	61.5 ± 0.7	
BRL-1131	25 μ L	0.00089 mmol	2.5 mol %	45 ± 1	

*With [JPhosAu(NCCH₃)]SbF₆.

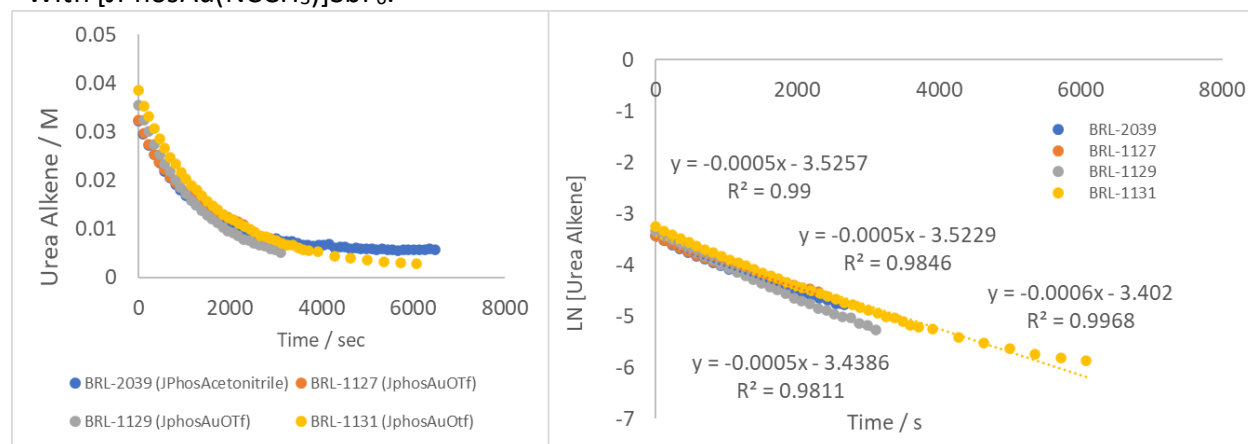
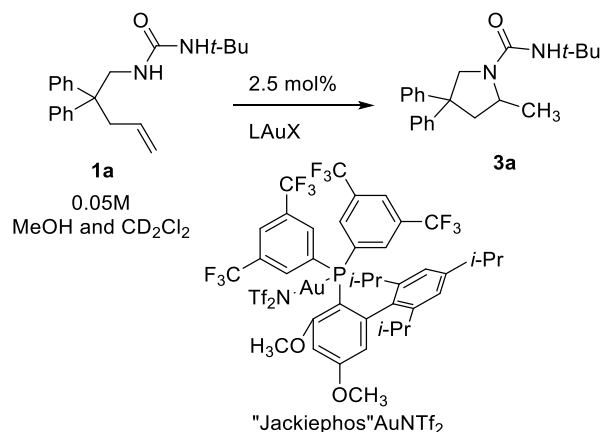


Figure S11. Raw plots of urea alkene decay (0.05 M) in 0.7 mL of CH₃OH with 0.00089 mmol of [JPhosAu(CNCH₃)]SbF₆ (2.5 mol %) or JPhosAuOTf and corresponding first order plots

JackiephosAuNTf₂ in MeOH versus CD₂Cl₂

When JackiephosAuNTf₂ was used, rates were not the same in DCM and MeOH. Also reactions of **1a** with JackiephosAuNTf₂ are slightly slower than with JphosAuOTf when in pure MeOH.



CD₂Cl₂

A stock solution of catalyst (0.016 M) was prepared by dissolving Jackiephos-Au-(NTf)₂ (1273.78 g/mol, 28.4 mg, 0.022 mmol) in 1.38 mL of CD₂Cl₂. Urea alkene (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in 0.645 mL (645 μL) of CD₂Cl₂ and transferred to an NMR tube. Catalyst solution (55 μL, 0.00089 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. However, these two reactions afforded the product in full conversion too fast for the NMR spectrometer to detect any changes. If we assume 95% conversion at 5 minutes this corresponds to a $k_{\text{obs}} = 0.01 \text{ s}^{-1}$.

CH₃OH

A stock solution of catalyst (0.0178 M) was prepared by dissolving JackiephosAu(NTf₂) (1273.78 g/mol, 114 mg, 0.089 mmol) in 5 mL of CH₃OH. Urea alkene (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in 0.650 mL (650 μL) of CH₃OH and transferred to an NMR tube. Catalyst solution (50 μL, 0.00089 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 66% conversion.

	CH ₃ OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × $k_{\text{obs}}/\text{s}^{-1}$	
BRL 4057	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	26.2 ± 0.6	Average 23 ± 5
BRL 4059	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	16.7 ± 0.2	
BRL 4061	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	25.9 ± 0.6	

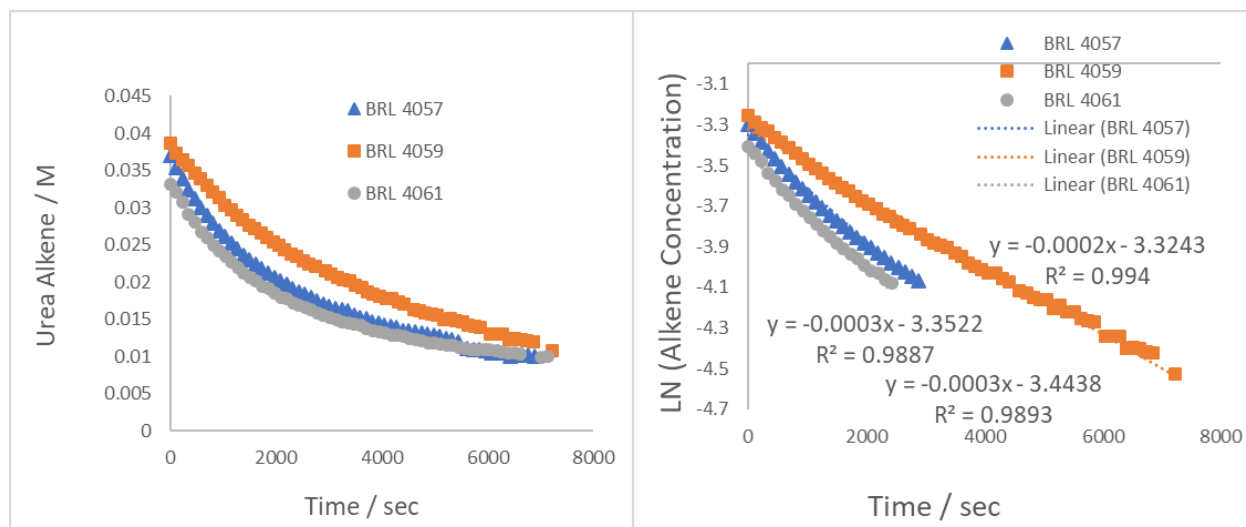
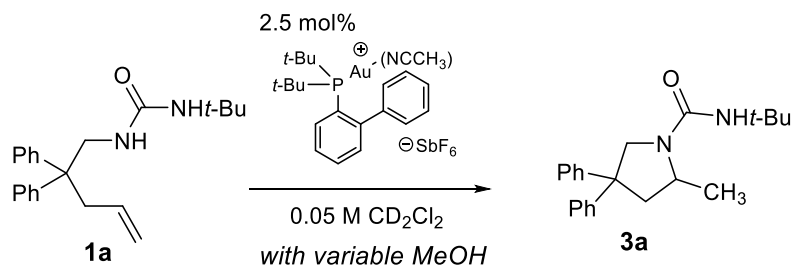


Figure S12. Raw and first order plots of urea alkene (0.05 M) decay in 0.7 mL of CH_3OH with 0.00089 mmol of JackiephosAuNTf₂ (2.5 mol %).

Rate with Mixed DCM/Methanol and [JPhosAu(NCCH₃)]SbF₆ (Figure 2 in Paper)



Procedure in CD_2Cl_2 with variable amounts of MeOH. A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CD_2Cl_2 . Urea Alkene (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in 0.67 mL, 0.65 mL or 0.62 mL of CD_2Cl_2 with variable amount of methanol and then the solution was transferred to an NMR tube. Catalyst solution (25 μL , 0.000892 mmol) was injected to initiate the reaction after bringing the total volume to 0.7 mL (substrate was at a concentration of 0.05 M). The sample was immediately transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 84%.

	Methanol	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 2019	5 μL	0.025 mL	0.0009 mmol	2.5 mol %	97 ± 3
BRL 2021	25 μL	0.025 mL	0.0009 mmol	2.5 mol %	381 ± 6
BRL 2023	55 μL	0.025 mL	0.0009 mmol	2.5 mol %	539 ± 30

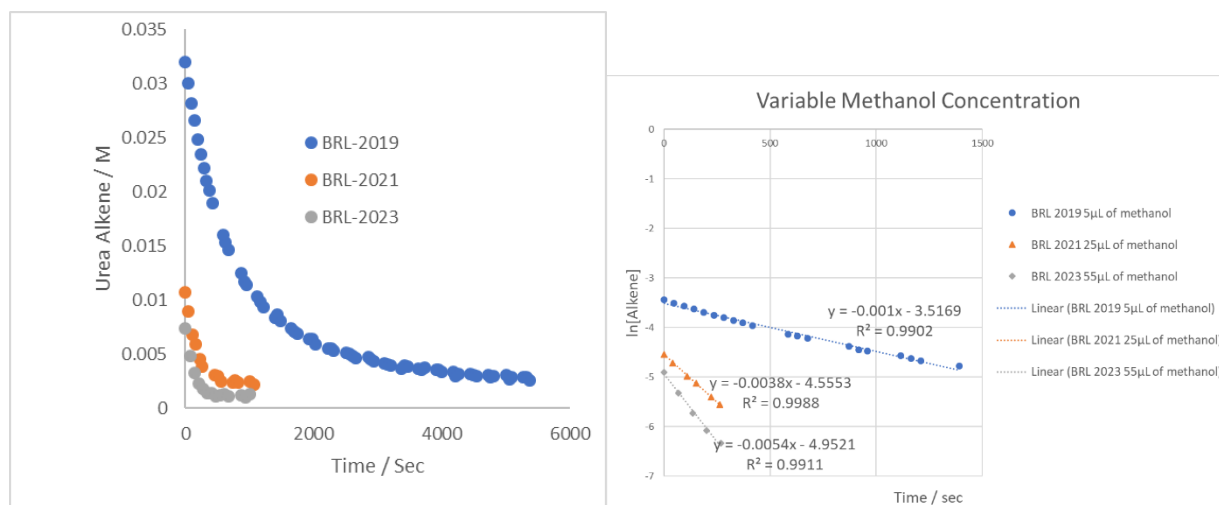
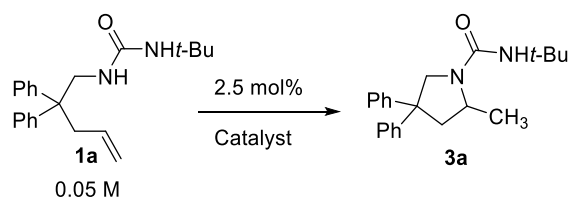


Figure S13. Raw plots of urea alkene decay (0.05 M) in variable amount of CD_2Cl_2 and CH_3OH (total volume 0.7 mL) with 0.00089 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (2.5 mol %), and the corresponding first order plots.

Variable Impact of Additive Depending on Catalyst and Solvent (Table 3/ Figure 3 In paper)



$[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (**5**) in DCM-d_2 , Rate boosted than plateaus with water additive.

$[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ in CD_2Cl_2 Rate boosted than plateaus with Water

A stock solution of catalyst (0.0356 M) was prepared by dissolving $[\text{JohnphosAu}(\text{acetonitrile})]\text{SbF}_6$ (772.17 g/mol, 68.9 mg, 0.089 mmol) in 2.50 mL of CD_2Cl_2 . Urea alkene (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in variable amount of CD_2Cl_2 and variable amount of H_2O , and then transferred to an NMR tube. Catalyst solution (25 μL , 0.00089 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 76% conversion.

	CD_2Cl_2	H_2O	Catalyst Solution	Catalyst Amount	Catalyst Load	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 2013	0.675 mL	5 μL	0.025 mL	0.00089 mmol	2.5 mol %	95 ± 3
BRL 2015	0.650 mL	25 μL	0.025 mL	0.00089 mmol	2.5 mol %	110 ± 3
BRL 2017	0.620 mL	55 μL	0.025 mL	0.00089 mmol	2.5 mol %	104 ± 3

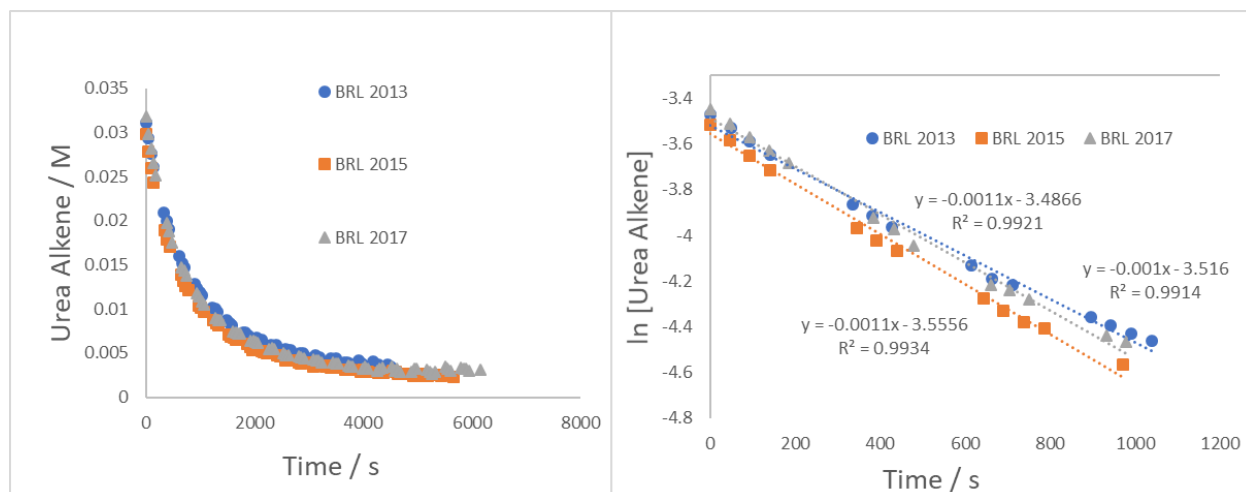
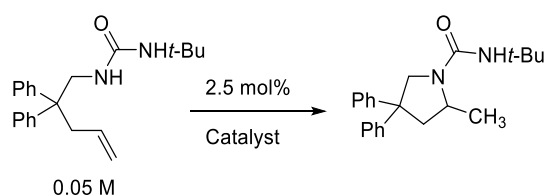


Figure S14. Raw and first order plots of urea alkene decay (0.05 M) in variable amount of CD_2Cl_2 and H_2O (total volume 0.7 mL) with 0.00089 mmol of $[\text{JPhosAu}(\text{acetonitrile})]\text{SbF}_6$ catalyst (2.5 mol %).



JPhosAuOTf (**4d**) in DCM, *Enhanced by Water*

JPhosAuOTf in CD_2Cl_2 Enhanced by Water

A stock solution of catalyst (0.0356 M) was prepared by dissolving JPhosAuOTf (664.44 g/mol, 36.2 mg, 0.054 mmol) in 1.53 mL of CD_2Cl_2 or by 73.2 mg (0.11 mmol) in 3.09 mL. Urea alkene (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in variable amount of CD_2Cl_2 and variable amount of H_2O , and then transferred to an NMR tube. Some reactions utilized CD_2Cl_2 that was pre-treated with molecular sieves. Catalyst solution (25 μL , 0.00089 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 80% conversion.

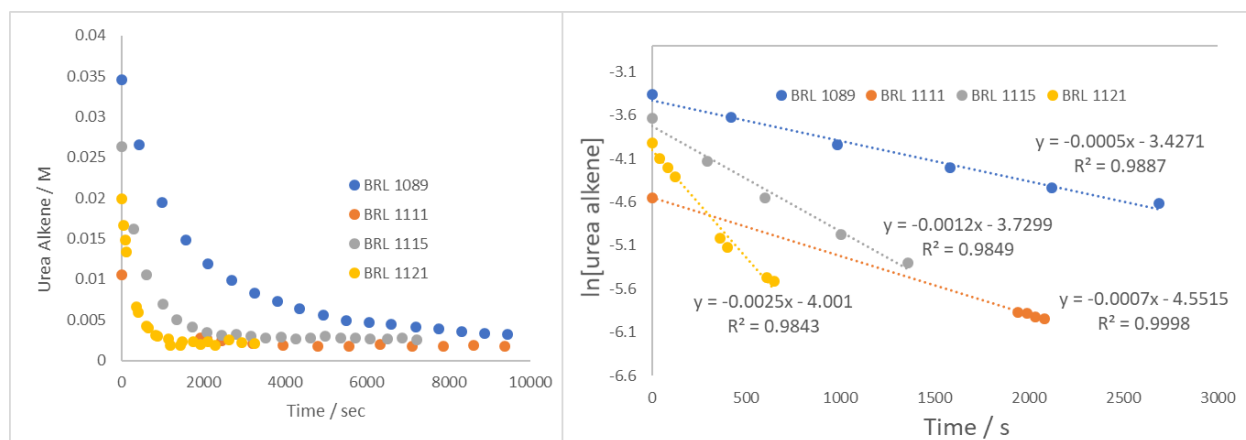
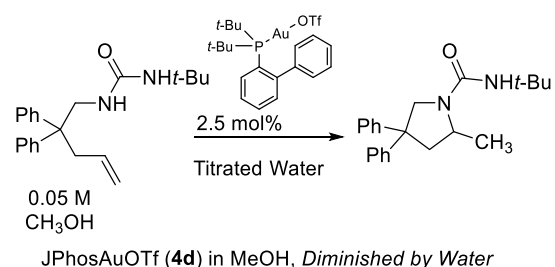


Figure S15. Raw and first order plots of urea alkene decay (0.05 M) in variable amount of $\text{CD}_2\text{Cl}_2/\text{H}_2\text{O}$ (total volume 0.7 mL) with 0.00089 mmol of JPhosAuOTf catalyst (2.5 mol %).

	CD_2Cl_2	H_2O	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 1089	0.675 mL	none	0.025 mL	0.00089 mmol	2.5 mol %	47 ± 3
BRL 1111	0.675 mL*	2 μL	0.025 mL	0.00089 mmol	2.5 mol %	67.4 ± 0.6
BRL 1115	0.665 mL*	10 μL	0.025 mL	0.00089 mmol	2.5 mol %	121 ± 9
BRL 1121	0.635 mL*	40 μL	0.025 mL	0.00089 mmol	2.5 mol %	249 ± 13

*Solvent pre-treated with molecular sieves.

JPhosAuOTf in MeOH Diminished by Water



A similar procedure was followed as in the previous section.

	MeOH	Water	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 1143	0.675 mL	0 μL	0.025 mL	0.00089 mmol	2.5 mol %	48.2 ± 0.8
BRL 1141	0.65 mL	25 μL	0.025 mL	0.00089 mmol	2.5 mol %	19.5 ± 0.2
BRL 1145	0.635 mL	40 μL	0.025 mL	0.00089 mmol	2.5 mol %	11.1 ± 0.4

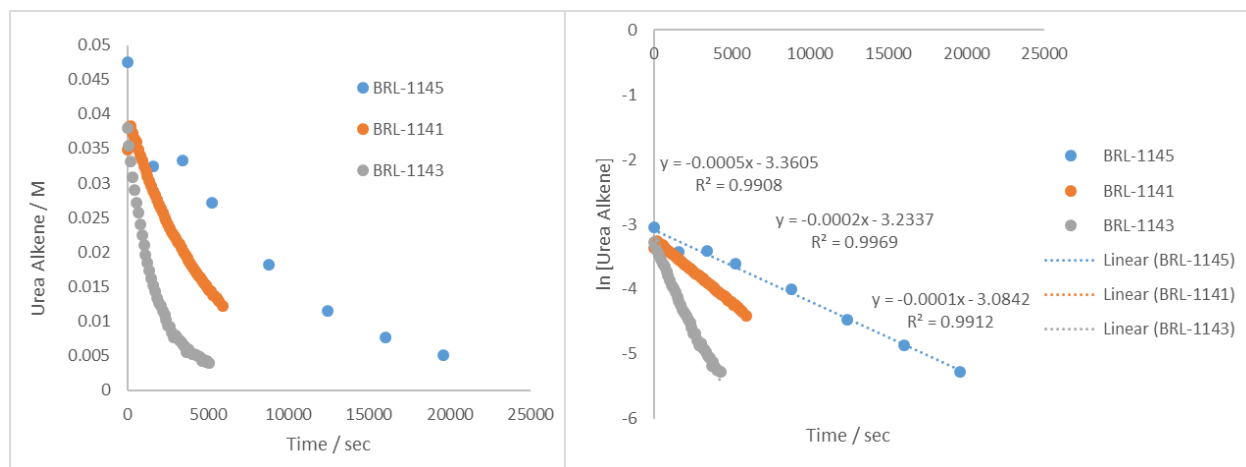
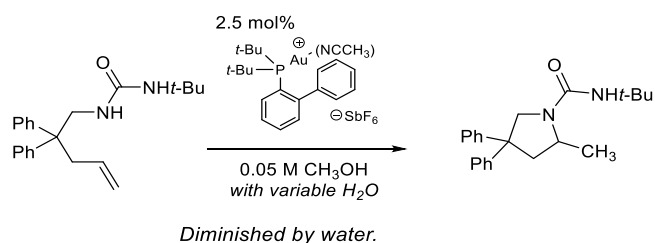


Figure S16. Raw and first order plots of urea alkene decay (0.05 M) in variable amount of CH₃OH/H₂O (total volume 0.7 mL) with 0.00089 mmol of JPhosAuOTf catalyst (2.5 mol %).

JPhosAu(NCCH₃)SbF₆ in MeOH Diminished by Water



A similar procedure was followed. At 75 μ L water, precipitates began to form, and the sample was turbid.

	MeOH	Water	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 2039	0.65 mL	0 μ L	0.05 mL	0.00089 mmol	2.5 mol %	50 ± 1
BRL 2041	0.625 mL	25 μ L	0.05 mL	0.00089 mmol	2.5 mol %	11.5 ± 0.3
BRL 2043	0.575 mL	75 μ L	0.05 mL	0.00089 mmol	2.5 mol %	6.5 ± 0.4

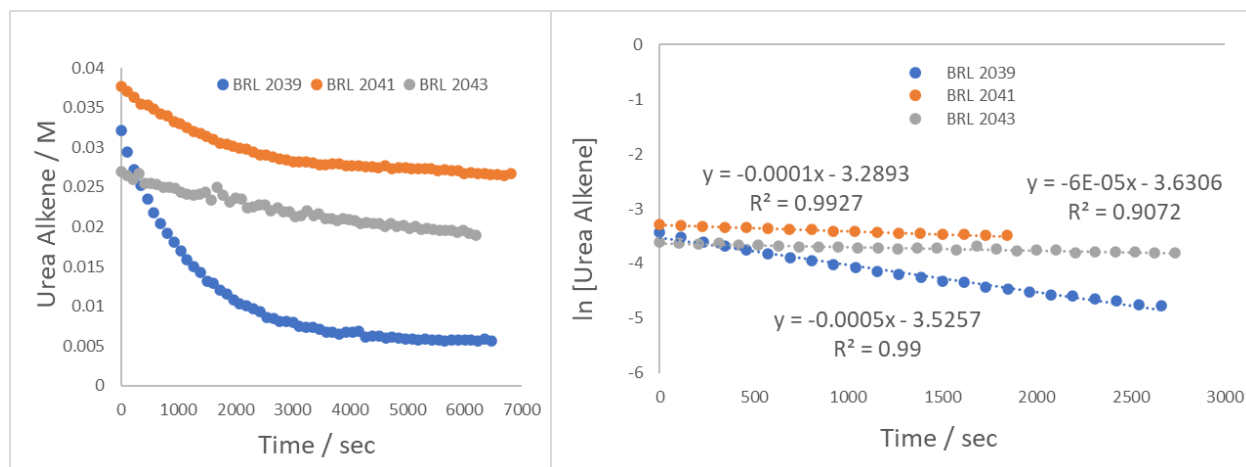
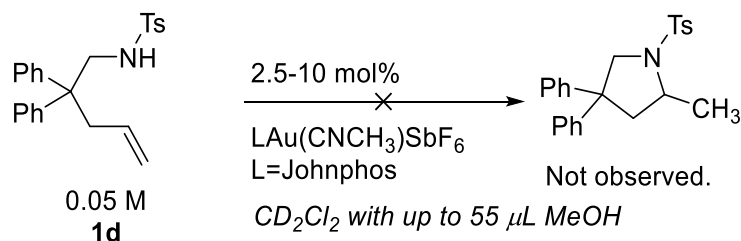


Figure S17. Raw and first order plots of urea alkene decay (0.05 M) in variable amount of CH₃OH/H₂O (total volume 0.7 mL) with 0.00089 mmol of JPhosAu(NCCH₃)SbF₆ catalyst (2.5 mol %).

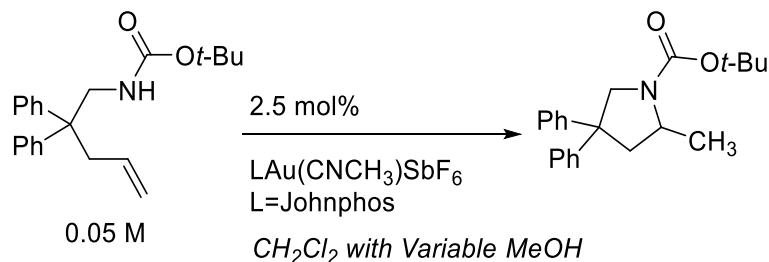
Reactions with Various Substrates (Table 4 in Paper)



Reaction with Sulfonamide (**1d**) and [JphosAu(NCCH₃)]SbF₆

Sulfonamide **1d** (0.05 M, 0.7 mL CD₂Cl₂) did not react on measurable timescales at room temperature. No product was observed with up to 10 mol % JPhosAu(NCCH₃)SbF₆ after 48 hours with and without added CH₃OH (up to 55 μL). The expected product was characterized previously.^[S2]

Reaction with Carbamate (**1b**) and [JphosAu(NCCH₃)]SbF₆



The carbamate starting material was prepared according to literature procedure^[S3] and the cyclized carbamate product was characterized previously.^[S2]

A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CH₂Cl₂. Carbamate alkene **1b** (337.46 g/mol, 12 mg, 0.036 mmol) was dissolved in variable amounts of CH₂Cl₂ with variable amounts of CH₃OH and transferred to an NMR tube. Catalyst solution (25 μL, 0.000892 mmol) was injected to initiate the reaction and to bring the total volume

to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least $\approx 26\%$ conversion, the reactions were not followed to completion. The cyclized product was characterized previously.

	CH_2Cl_2	CH_3OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 2061	0.67 mL	5 μL	0.025 mL	0.0009 mmol	2.5 mol %	0.97 ± 0.02
BRL 2063	0.65 mL	25 μL	0.025 mL	0.0009 mmol	2.5 mol %	6.11 ± 0.09
BRL 2065	0.62 mL	55 μL	0.025 mL	0.0009 mmol	2.5 mol %	6.9 ± 0.2

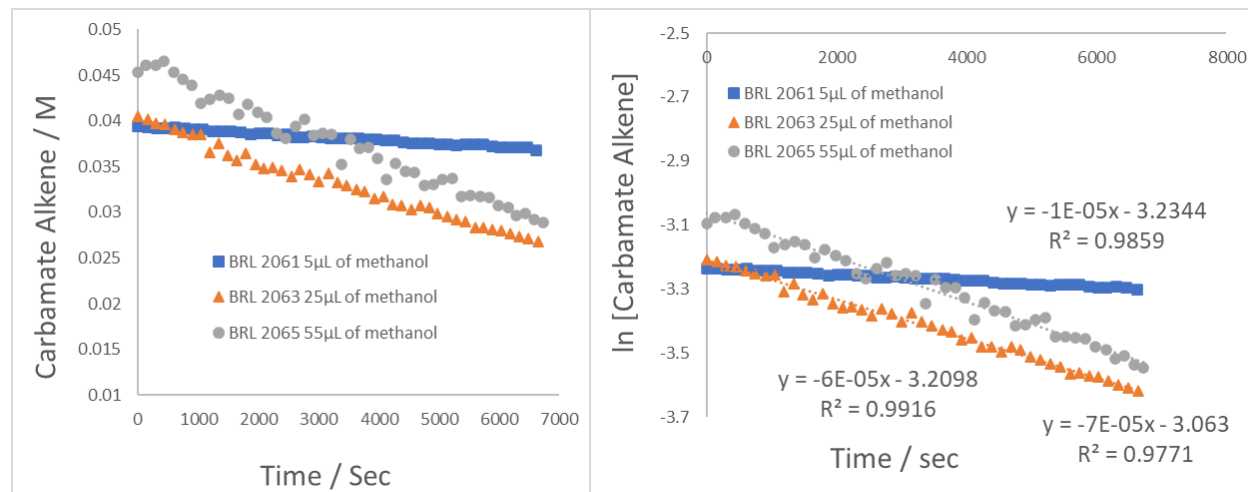
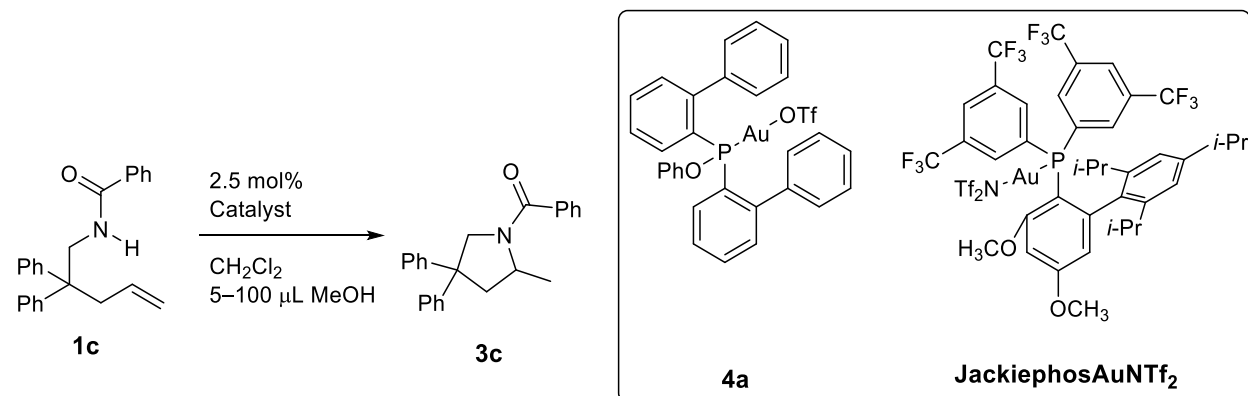


Figure S18. Raw plots of alkene carbamate decay (0.05 M) in variable amounts of CH_2Cl_2 and variable amounts of CH_3OH (total volume 0.7 mL) and with 0.0009 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (2.5 mol %) and corresponding first order plots.

Reactions with Benzamide (**1c**)(Table 5 in Paper)



The benzamide starting material (**1c**) was prepared according to literature procedure, and the product (**3c**) was characterized previously.^[S4]

Representative Procedure. Stock solutions of catalyst (0.035 M) were prepared in CH₂Cl₂. Alkene benzamide **1c** (341.45 g/mol, 12 mg, 0.0351 mmol) was dissolved in variable amounts of CH₂Cl₂ and variable amounts of CH₃OH, and then transferred to an NMR tube. Catalyst solution (25 μL, 0.00088 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to the end of acquisition of data (40-70% for **4a**). Pseudo first order plots were linear up to at least 52% conversion for JackiephosAuNTf₂.

	CH ₂ Cl ₂	CH ₃ OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × K _{obs} /s ⁻¹
BRL-2113 (Catalyst 5)	0.595 mL	55 μL	0.050 mL	0.00088 mmol	2.5 mol %	Plot not shown. 14% Conversion at 24 hours
BRL 3033 (Catalyst 4a)	0.670 mL	5 μL	0.025 mL	0.00088 mmol	2.5 mol %	0.158 ± 0.001
BRL 3035 (Catalyst 4a)	0.650 mL	25 μL	0.025 mL	0.00088 mmol	2.5 mol %	0.36 ± 0.02
BRL 3041 (Catalyst 4a)	0.620 mL	55 μL	0.025 mL	0.00088 mmol	2.5 mol %	0.37 ± 0.02
BRL 3055 (JackiephosAuNTf ₂)	0.620 mL	55 μL	0.025 mL	0.00088 mmol	2.5 mol %	1.02 ± 0.09
BRL3059 (JackiephosAuNTf ₂)	0.575 mL	100 μL	0.025 mL	0.00088 mmol	2.5 mol %	0.82 ± 0.07 (Plot not shown)

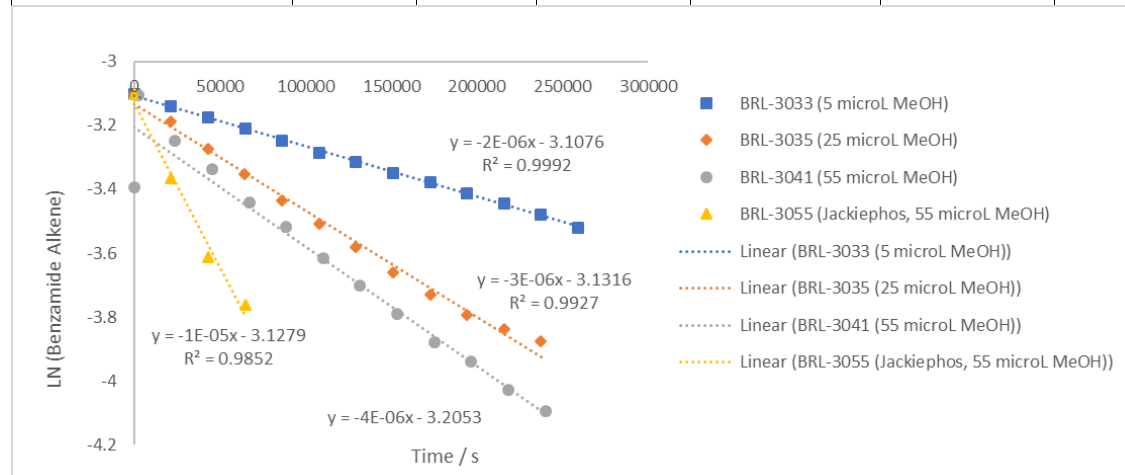
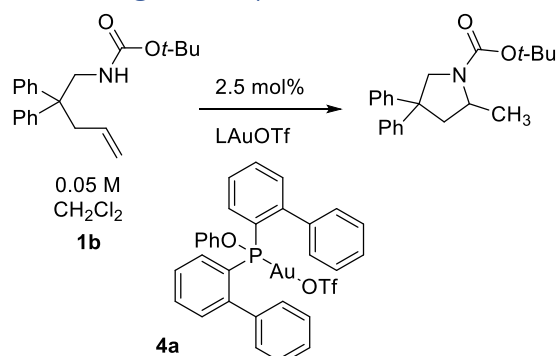


Figure S19. First order plots of alkene carbamate decay (0.05 M) in variable amounts of CH₂Cl₂ and CH₃OH (total volume 0.7 mL) and with 0.0009 mmol (2.5 mol %) of catalysts JackiephosAuNTf₂ and **4a**.

Examining Decomposition in Reaction with carbamate (**1b**) and Catalysts **4c** and **4a**



A stock solution of catalyst (0.036 M) was prepared by dissolving catalyst **4a** (776.52 g/mol, 99.7 mg, 0.128 mmol) in 3.67 mL of CH₂Cl₂. Carbamate alkene **1b** (337.46 g/mol, 12 mg, 0.036 mmol) was dissolved in variable amounts of CH₂Cl₂ and variable amounts of CH₃OH and transferred to an NMR tube. Catalyst solution (25 μ L, 0.000889 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 34% conversion (no methanol) and 80% conversion (with methanol).

	CH ₂ Cl ₂	CH ₃ OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × k _{obs} /s ⁻¹
BRL 2071	0.675 mL	no	0.025 mL	0.0009 mmol	2.5 mol %	1.981 ± 0.007
BRL 2073	0.670 mL	5 μ L	0.025 mL	0.0009 mmol	2.5 mol %	17.01 ± 0.08
BRL 2075	0.650 mL	25 μ L	0.025 mL	0.0009 mmol	2.5 mol %	21.7 ± 0.1

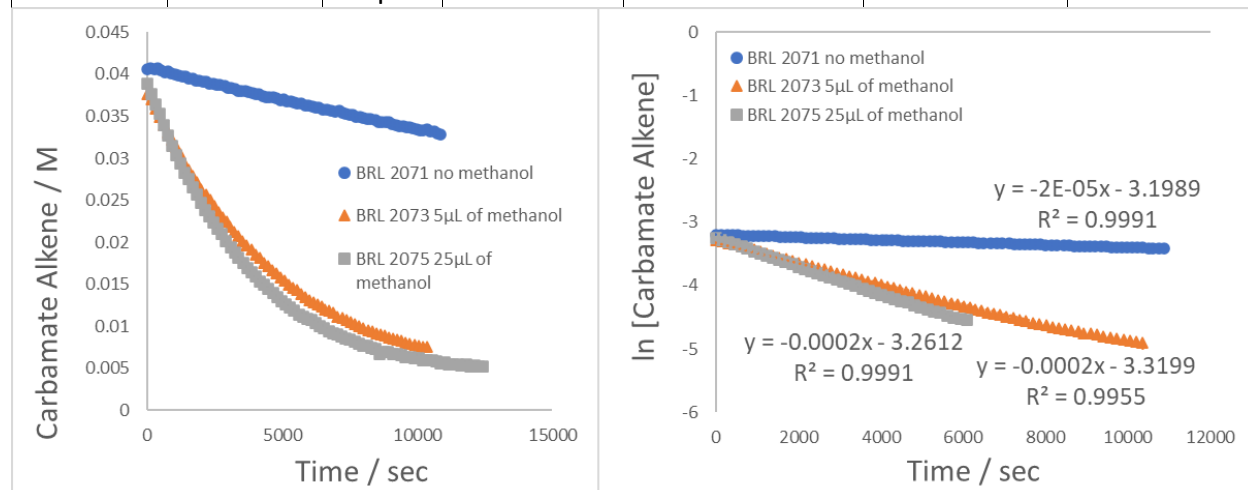


Figure S20. Raw plots of alkene carbamate decay (0.05 M) in variable amounts of CH₂Cl₂ and CH₃OH (total volume 0.7 mL) with 0.0009 mmol of **4a** (2.5 mol %) and the corresponding first order plots.

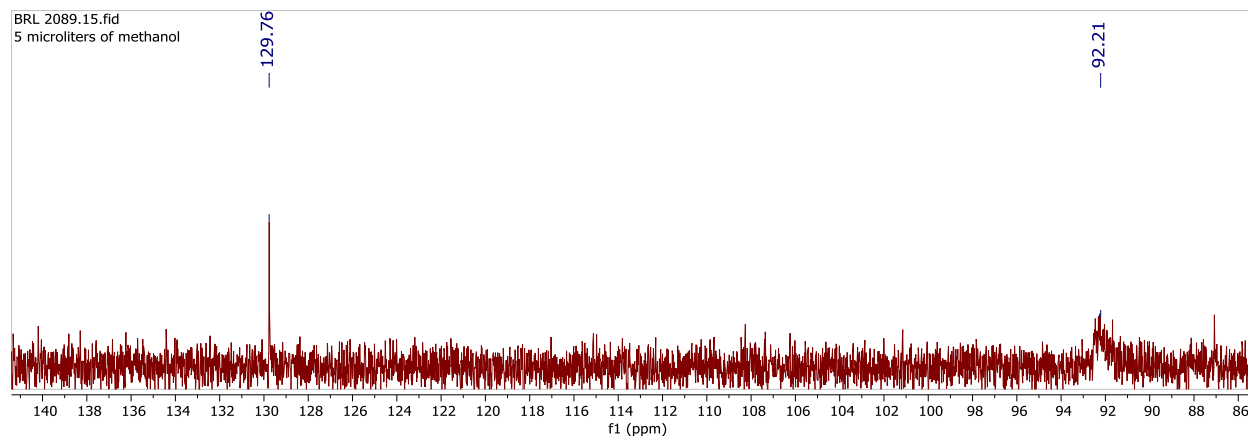
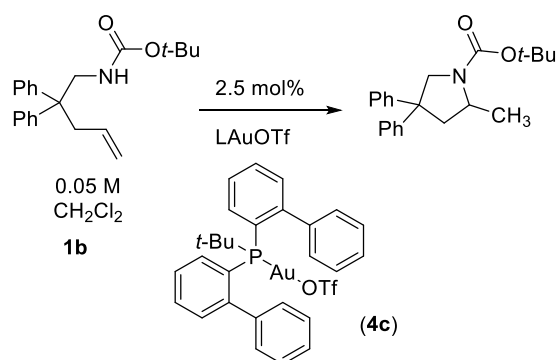


Figure S21. ^{31}P NMR Spectrum (161.98 MHz, CH_2Cl_2) at approximately 50% conversion during reaction of alkene carbamate (0.05 M) in CH_2Cl_2 with 5 μL CH_3OH (total volume 0.7 mL) and **4a** (2.5 mol %).



A stock solution of catalyst (0.036 M) was prepared by dissolving **4c** (740.53 g/mol, 133.8 mg, 0.181 mmol) in 5.08 mL of CH_2Cl_2 . Carbamate alkene **1b** (337.46 g/mol, 12 mg, 0.036 mmol) was dissolved in variable amounts of CH_2Cl_2 and variable amounts of CH_3OH and transferred to an NMR tube. Catalyst solution (25 μL , 0.000892 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to 20% conversion (no methanol) and $\approx 80\%$ conversion (with methanol).

	CH_2Cl_2	CH_3OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 2081	0.675 mL	0	0.025 mL	0.0009 mmol	2.5 mol %	0.205 ± 0.009
BRL 2083	0.670 mL	5 μL	0.025 mL	0.0009 mmol	2.5 mol %	8.58 ± 0.01
BRL 2085	0.650 mL	25 μL	0.025 mL	0.0009 mmol	2.5 mol %	12.68 ± 0.07

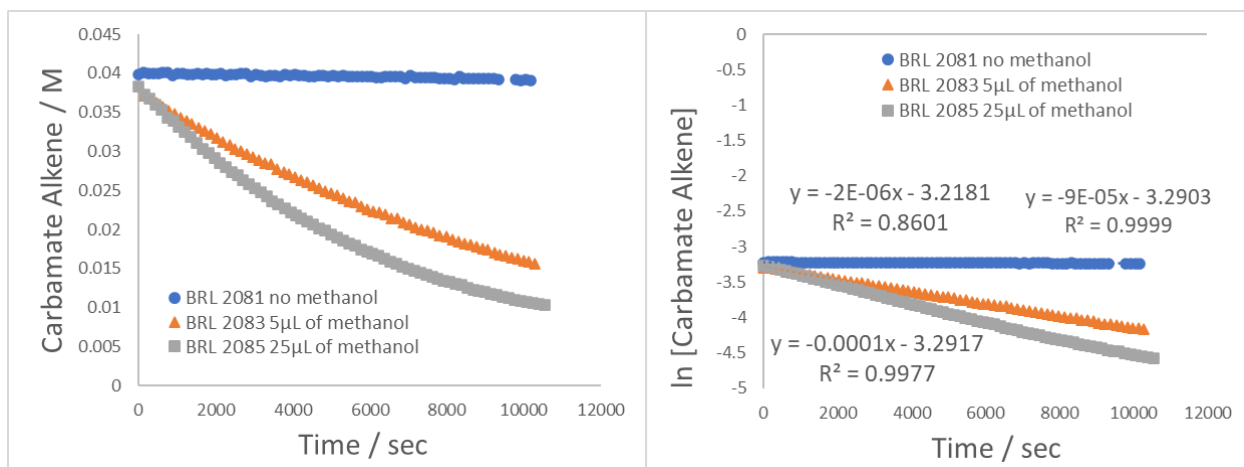
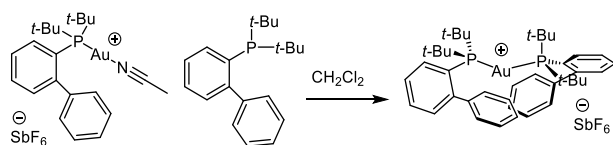


Figure S22. Raw and first order plots of carbamate alkene **1b** decay (0.05 M) in variable amounts of CH_2Cl_2 and CH_3OH (total volume 0.7mL) and with 0.0009 mmol of catalyst **4c** (2.5mol %).

Bisphos Syntheses, ^{31}P Chemical Shifts for Decomposition Byproducts



JPhos Gold Bisphos. Gold acetonitrile (0.3 g, 0.39 mmol) was weighed into a vial and ligand (0.156 g, 0.52 mmol) was weighed into a separate flask. DCM (6 mL) was added to the gold acetonitrile and the solution transferred to the ligand. Additional DCM was used to rinse the vial to complete the transfer of gold acetonitrile to the flask. The solution was stirred for 30 minutes. The solvent was removed in vacuo and NMR spectra collected. The solid was recrystallized with 2:1 Hexanes/DCM at -20 degrees C (yield not determined).

See manuscript for ^{31}P NMR spectrum (Figure 4).

Jackiephos Bisphos. The ^{31}P chemical shift for the decomposition product of Jackiephos gold was confirmed by treating L-AuNTf₂ I with 1 equivalent of free ligand in CD_2Cl_2 .

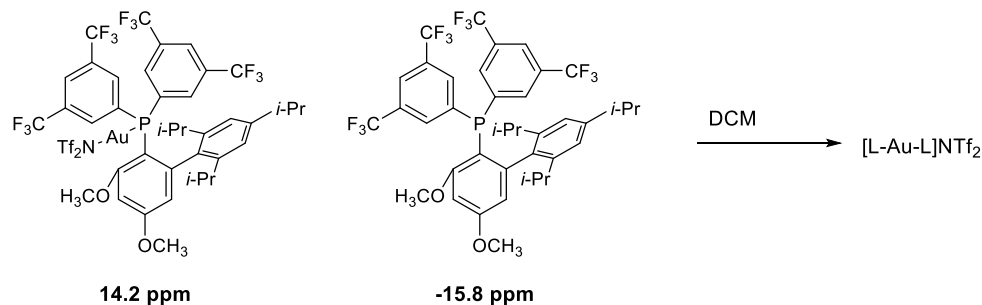
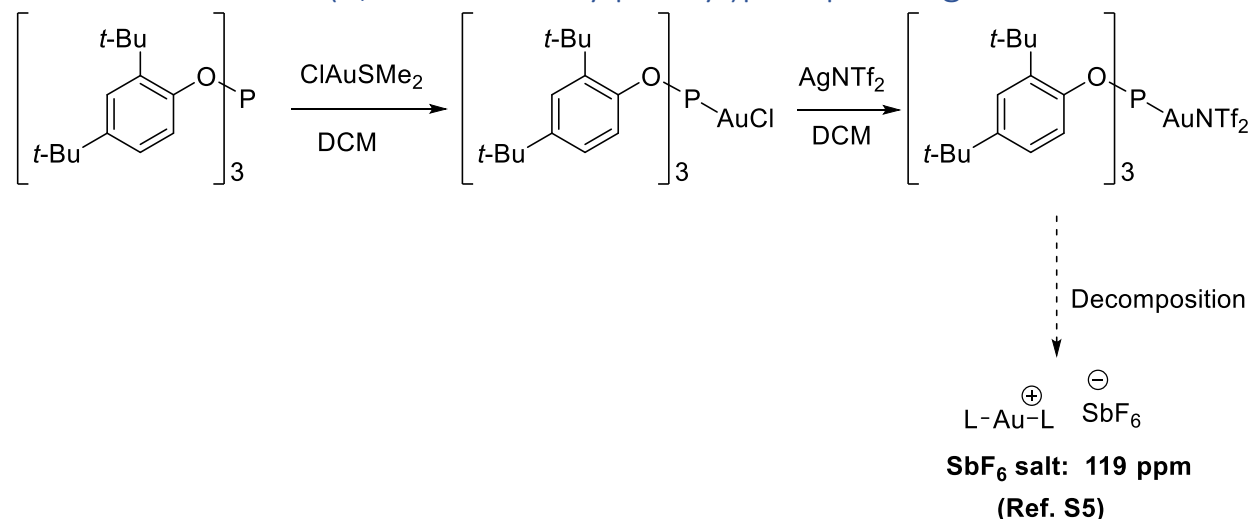
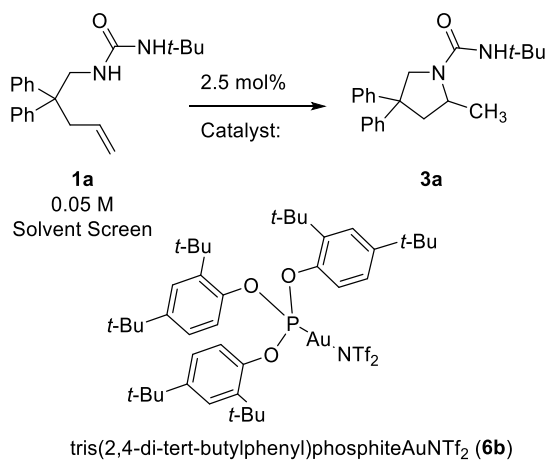


Figure S24. ^{31}P NMR Spectrum (121.51 MHz, CD_2Cl_2) after combining LAuCl , free ligand, and AgSbF_6 .

Reactions with tris(2,4-di-tert-butylphenyl)phosphite ligand.



The decomposition product $[(\text{R}_3\text{P-Au-PR}_3)]\text{SbF}_6$ was reported previously.^[S5] The L-Au-NTf_2 catalyst was reported previously.^[S6] The L-Au-Cl pre-catalyst was reported previously.^[S7]



When tris(2,4-di-tert-butylphenyl)phosphiteAuNTf₂ (**6b**) was tested as a catalyst it showed moderate activity, but near complete formation of decomposed product $[(\text{R}_3\text{P-Au-PR}_3)]\text{NTf}_2$ as indicated by the near identical ^{31}P chemical shift to the SbF_6 variant reported previously.

A stock solution of catalyst (**6b**) was prepared by dissolving **6b** (90.2 mg, 1124.03 g/mol, 0.080 mmol) in 2.28 mL of CH_2Cl_2 . Urea Alkene **1a** (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in variable amounts of CH_2Cl_2 and variable amounts of CH_3OH and transferred to an NMR tube. Catalyst solution (25 μL , 0.00088 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to $\approx 84\%$ conversion.

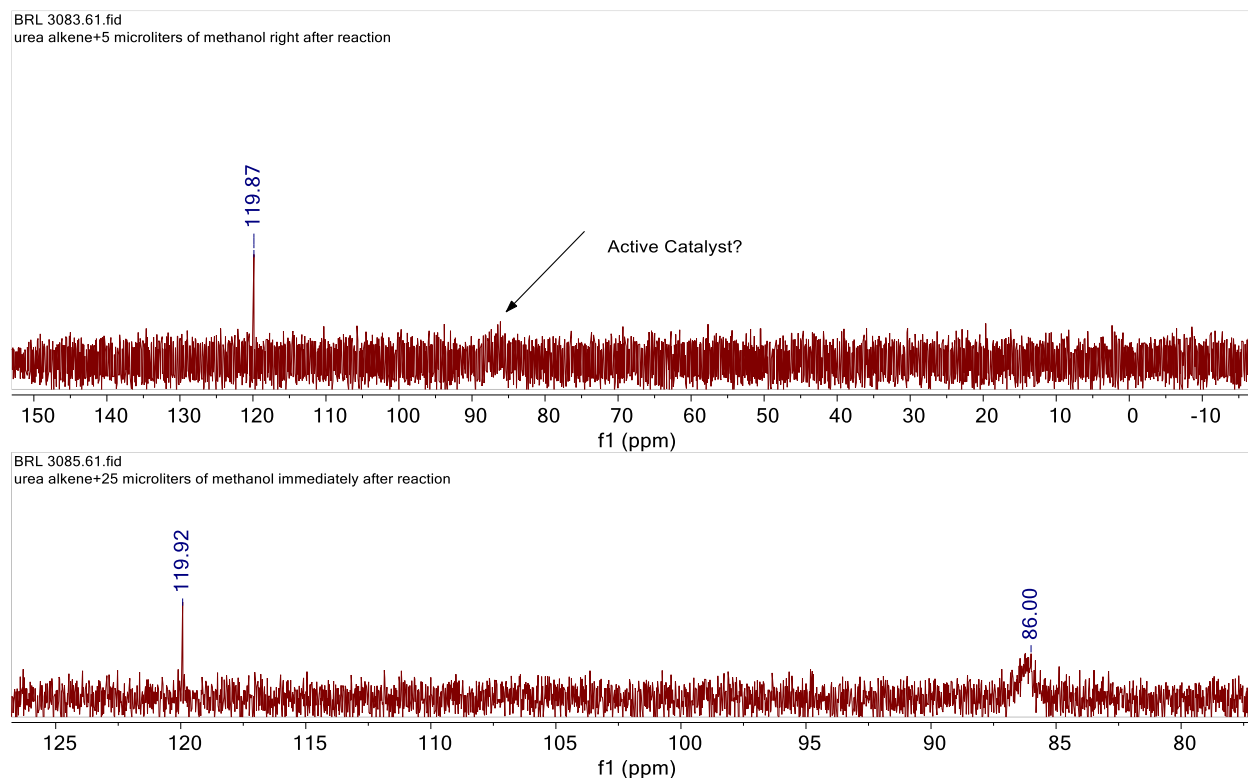


Figure S25. NMR spectra (^{31}P , 161.98 MHz) that show the decomposition of the catalyst **6b** ($\delta=119.9$ ppm, 2.5 mol %) during the reaction of urea alkene (**1a**) (0.05 M, CH_2Cl_2) with 5 and 25 μL MeOH.

	CH_2Cl_2	CH_3OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 3083	0.670 mL	5 μL	0.025 mL	0.00088 mmol	2.5 mol %	65 ± 1
BRL 3085	0.650 mL	25 μL	0.025 mL	0.00088 mmol	2.5 mol %	69 ± 1

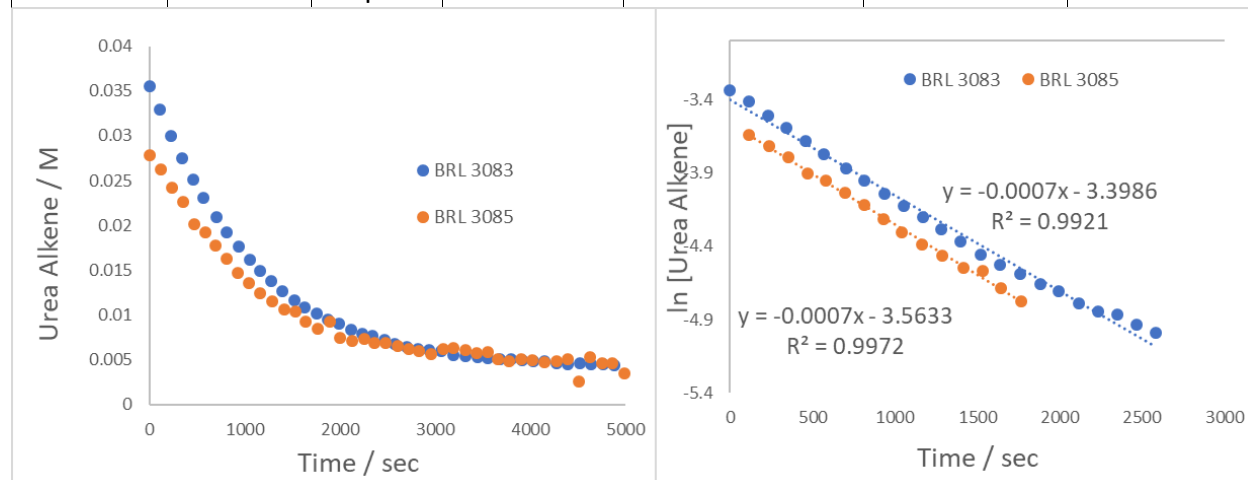
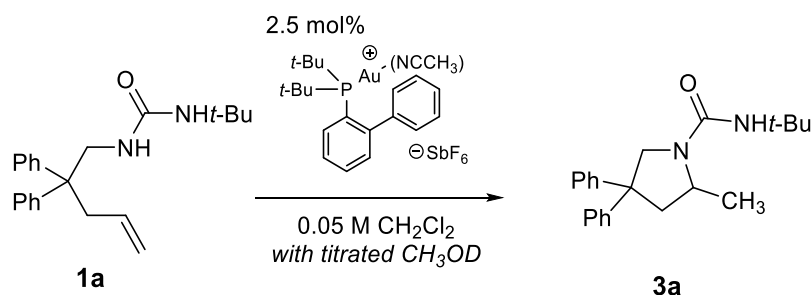


Figure S26. Raw plots of urea alkene **1a** decay (0.05 M) in 0.7 mL of CH_2Cl_2 with 0.00088 mmol of **6b** (2.5 mol %) and the corresponding first order plots.

Kinetic Isotope Effect Measurements (Table 7 and 8 In paper)

Urea with Titrated CH₃OD (Compare to Figure S13 for KIE)



A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CH₂Cl₂. Urea alkene **1a** (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in variable amount of CH₂Cl₂ with variable amount of CH₃OD and transferred to an NMR tube. Catalyst solution (25 μ L, 0.000892 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 52% conversion.

	CH ₂ Cl ₂	CH ₃ OD	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × k _{obs} /s ⁻¹
BRL 2047	0.67 mL	5 μ L	0.025 mL	0.0009 mmol	2.5 mol %	70 ± 2
BRL 2049	0.65 mL	25 μ L	0.025 mL	0.0009 mmol	2.5 mol %	130 ± 10
BRL 2051	0.62 mL	55 μ L	0.025 mL	0.0009 mmol	2.5 mol %	81 ± 1

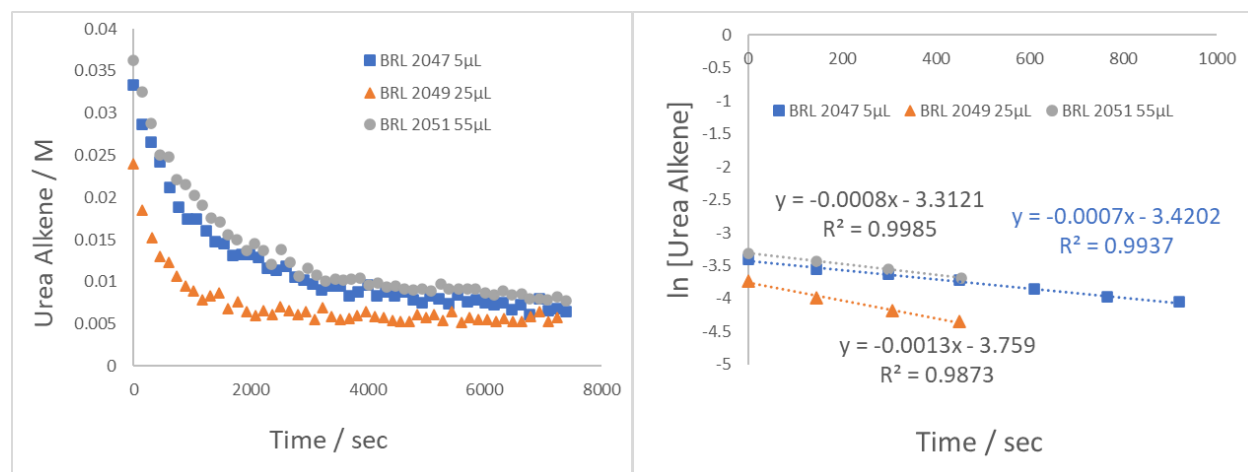
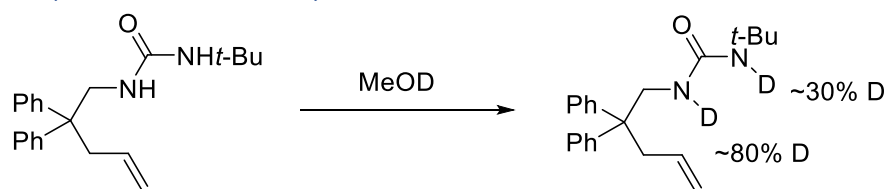


Figure S27. Raw plots of urea alkene decay (0.05 M) in variable amounts of CH₂Cl₂ and variable amounts of CH₃OD (total volume 0.7 mL) and with 0.0009 mmol of [JPhosAu(NCCH₃)]SbF₆ (2.5 mol %) and first order plots of alkene decay.

Preparation of Partially Deuterated Urea and Rate



Partially deuterated urea alkene was prepared according to the following procedure. 75 mg of urea alkene (0.075 g, 336.48 g/mol, 0.22 mmol) was dissolved in 2.5 mL of CH₃OD and stirred for 24 hours before the solvent, CH₃OD, was removed via high vacuum. This was repeated 3 times. Partially deuterated **1a** was isolated (0.065 g, ≈86%). The N-H adjacent to the *t*-butyl group incorporated less deuterium than the N-H adjacent to the methylene as determined by ¹H NMR integration.

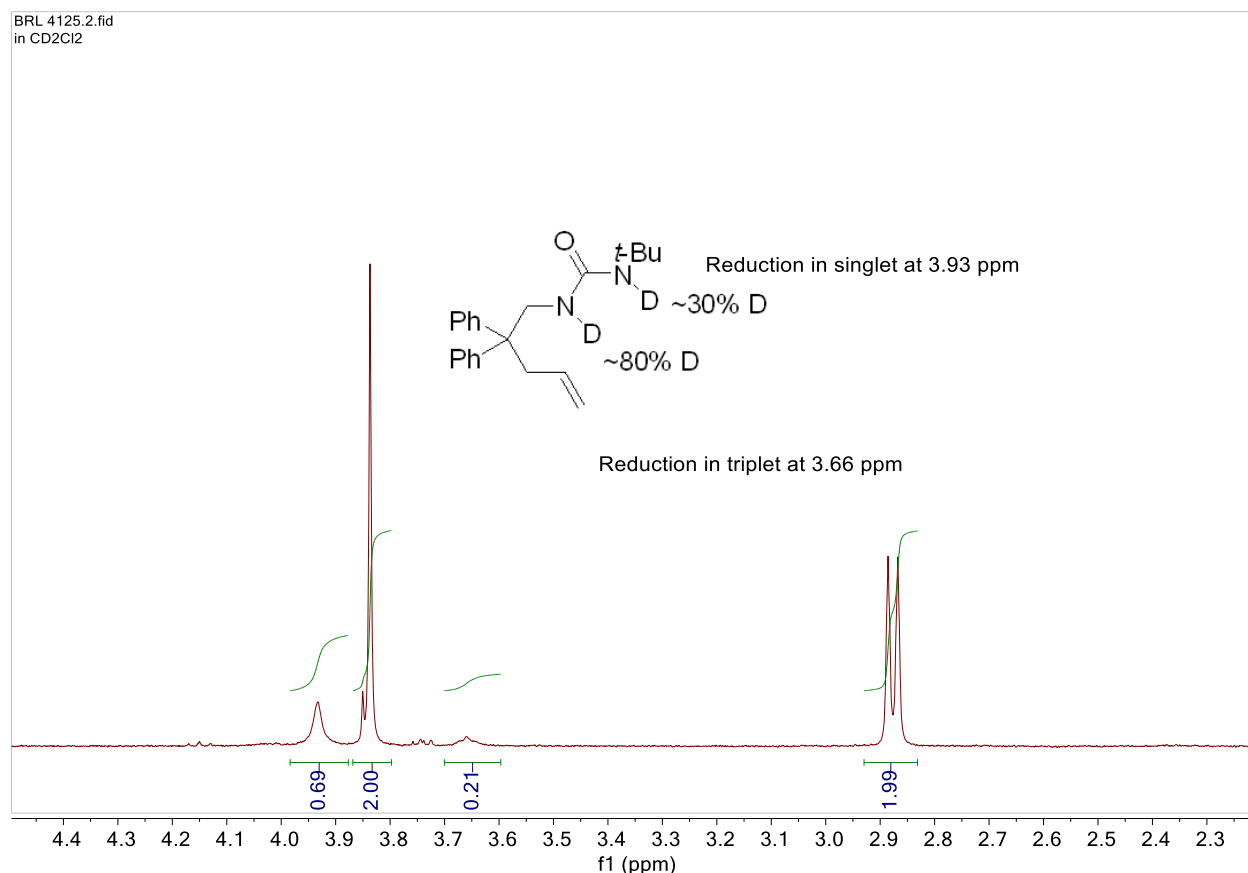


Figure S28. Expansion showing partial N-H deuterium incorporation (500 MHz, CD₂Cl₂).

Reaction of Partially Deuterated Urea with [JphosAu(NCCH₃)]SbF₆

A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CD₂Cl₂. Deuterated urea Alkene (≈337.48g/mol, 12 mg, 0.036 mmol) was dissolved in 675 μL of CD₂Cl₂ and transferred to an NMR tube. Catalyst solution (25 μL, 0.000892 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra

collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 60% conversion. In all cases, 30-60% deuterium incorporation was observed in the product methyl (δ 20.96 ppm, 1:1:1 triplet) and the incorporation amount estimated by ^{13}C NMR integration.

	CD_2Cl_2	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$	k_{obs} average
BRL 4127	0.675 mL	0.025 mL	0.000892 mmol	2.5 mol %	41 ± 1	48 ± 8
BRL 4129	0.675 mL	0.025 mL	0.000892 mmol	2.5 mol %	45 ± 1	
BRL 4131	0.675 mL	0.025 mL	0.000892 mmol	2.5 mol %	57 ± 2	

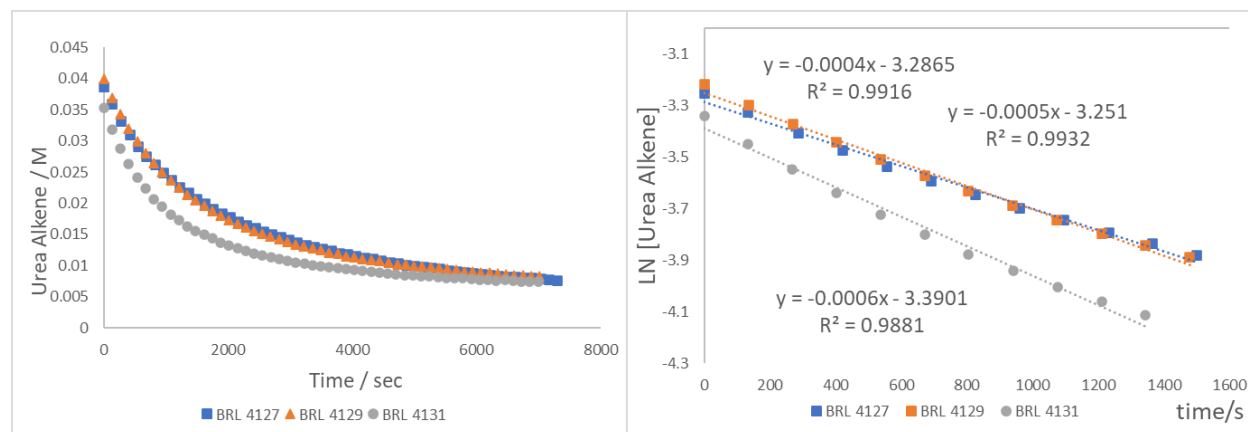


Figure S29. Raw and first order plots of monodeuterated urea alkene decay (0.05 M) in 0.7mL of CH_2Cl_2 and with 0.00089 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (2.5 mol %).

Carbamate with Titrated CD_3OD (Compare to Figure S18 for KIE)

The same procedure applied to the kinetic experiments adopting CD_3OD as the additive. Pseudo first order plots were linear up to at least $\approx 20\%$ conversion, but the reactions were not followed to completion.

	CH_2Cl_2	CD_3OD	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
BRL 5075	0.67 mL	5 μL	0.025 mL	0.0009 mmol	2.5 mol %	0.54 ± 0.02
BRL 5077	0.65 mL	25 μL	0.025 mL	0.0009 mmol	2.5 mol %	2.15 ± 0.01
BRL 5079	0.62 mL	55 μL	0.025 mL	0.0009 mmol	2.5 mol %	1.76 ± 0.02

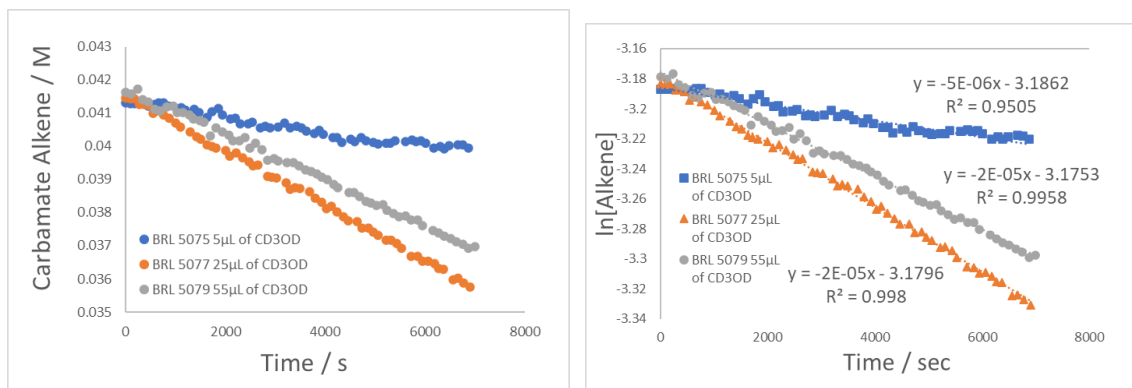
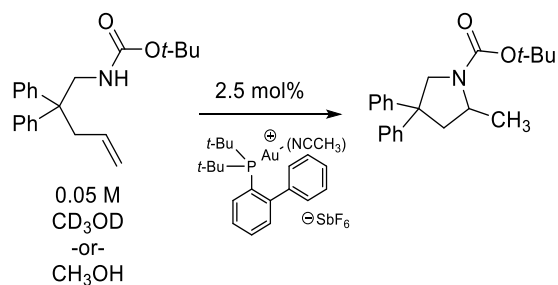


Figure S30. Raw plots of alkene decay (0.05 M) in variable amounts of CH_2Cl_2 and variable amounts of CD_3OD (total volume 0.7 mL) and with 0.0009 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (2.5 mol %) and the corresponding first order plots.

Solvent Deuterium Isotope Effects (Carbamate/Johnphos)



Solvent $k(\text{H/D}) = 6.3$

Pure CD₃OD Solvent

	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$	
BRL 4039	0.025 mL	0.0009 mmol	2.5 mol %	0.130 ± 0.002	Average 0.127 ± 0.003
BRL 4041	0.025 mL	0.0009 mmol	2.5 mol %	0.126 ± 0.002	
BRL 4043	0.025 mL	0.0009 mmol	2.5 mol %	0.125 ± 0.002	

Pure CH₃OH Solvent

	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$	
BRL 4045	0.025 mL	0.0009 mmol	2.5 mol %	0.9 ± 0.1	Average 0.8 ± 0.1
BRL 4047	0.025 mL	0.0009 mmol	2.5 mol %	0.7 ± 0.1	
BRL 4049	0.025 mL	0.0009 mmol	2.5 mol %	NA/peak overlap	

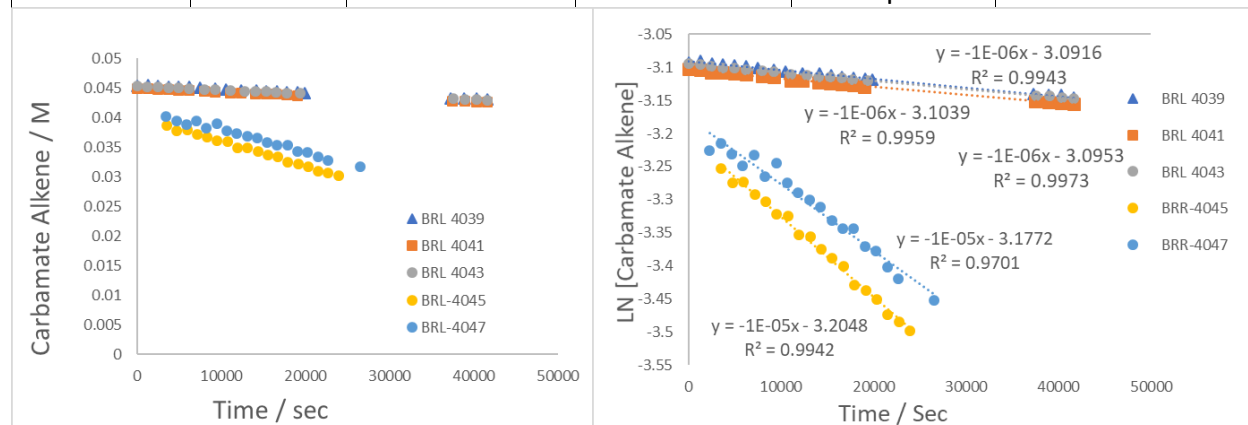
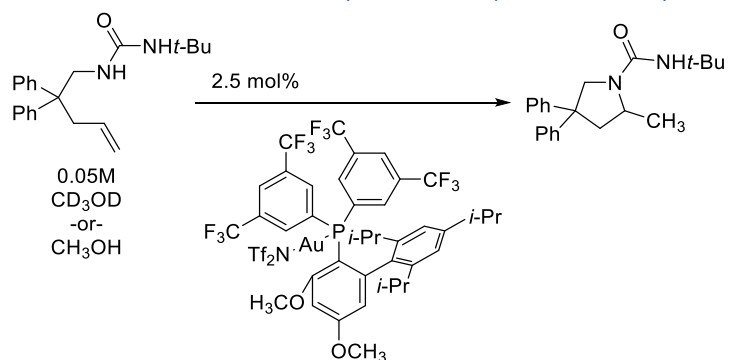


Figure S31. Raw and first order plots of carbamate alkene decay (0.05 M) in 0.7 mL of CH₃OH or CD₃OD and with 0.0009 mmol of [JPhosAu(NCCH₃)]SbF₆ (2.5 mol %).

Solvent Deuterium Isotope Effects (Urea/Jackiephos)



$$\text{Solvent } k(\text{H/D}) = 7.4$$

Pure CH₃OH Solvent

	CH ₃ OH	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × <i>k</i> _{obs} /s ⁻¹	
BRL 4057	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	26.2 ± 0.6	Average 23 ± 5
BRL 4059	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	16.7 ± 0.2	
BRL 4061	0.65 mL	0.05 mL	0.00089 mmol	2.5 mol %	25.9 ± 0.6	

See earlier Figure S12. for plots.

Pure CD₃OD Solvent

	CD ₃ OD	Catalyst Solution	Catalyst Amount	Catalyst Loading	10 ⁵ × <i>k</i> _{obs} /s ⁻¹	
BRL 4065	0.65 mL	0.050 mL	0.0009 mmol	2.5 mol %	2.05 ± 0.02	Average 3.1 ± 0.9
BRL 4067	0.65 mL	0.050 mL	0.0009 mmol	2.5 mol %	3.57 ± 0.01	
BRL 4069	0.65 mL	0.050 mL	0.0009 mmol	2.5 mol %	3.686 ± 0.007	

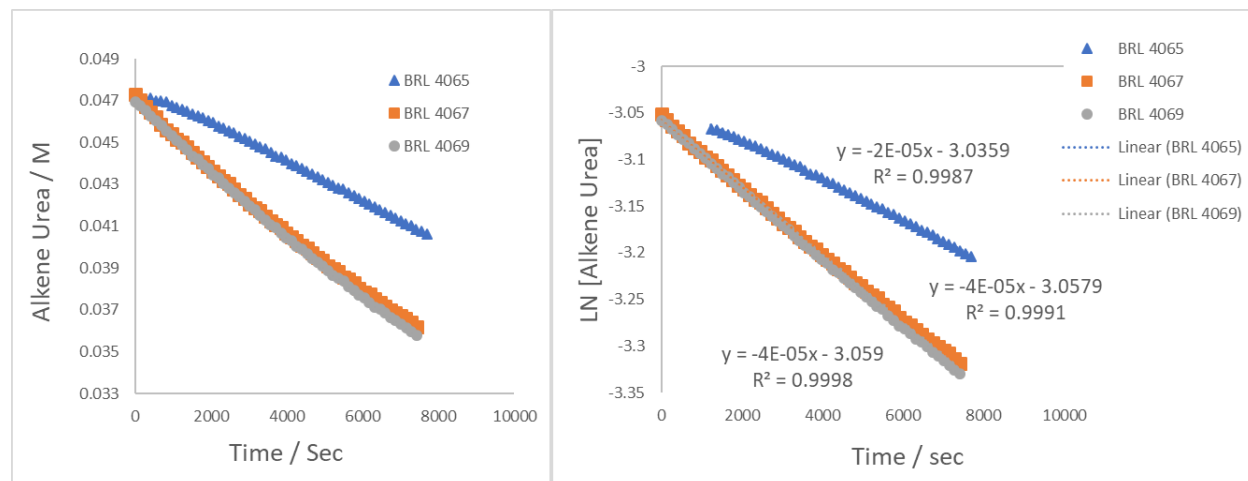
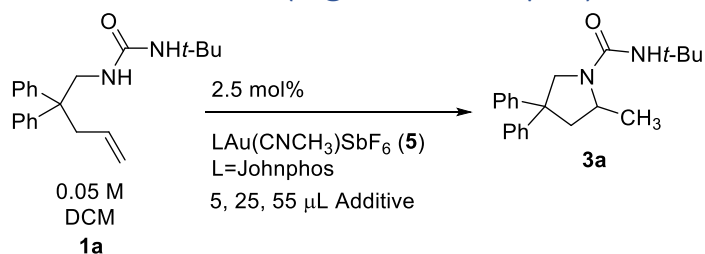


Figure S32. Raw and first order plots of urea alkene decay (0.05 M) in 0.7 mL of CD₃OD and with 0.0009 mmol of Jackiephos-Au-NTf₂ (2.5 mol %).

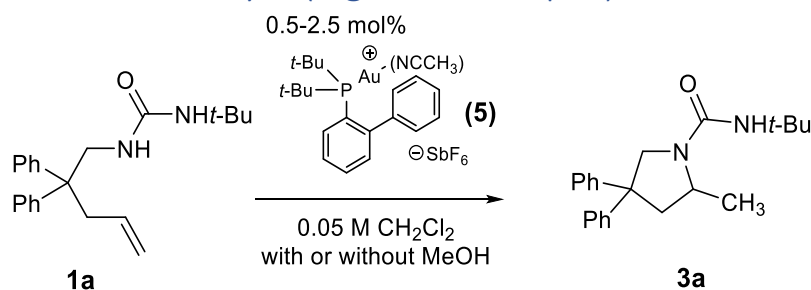
Other Additives (Figure 6 in Paper)



A stock solution of catalyst (0.036 M) was prepared by dissolving [JPhosAu(NCCH₃)]SbF₆ (772.17 g/mol, 138 mg, 0.179 mmol) in 5 mL of CH₂Cl₂. Urea alkene (336.48 g/mol, 12 mg, 0.0356 mmol) was dissolved in variable amounts of CH₂Cl₂ and variable amounts of additives, including but not limited to ethanol, n-propanol, isopropanol, hexafluoroisopropanol (HFIP), etc., and then transferred to an NMR tube. Catalyst solution (25 μL , 0.00089 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes.

Notebook	Solvent	Additive	Amount	Conc./M	$k_{\text{obs}} \times 10^5$
3087	CH ₂ Cl ₂	1-PrOH	5 μL	0.095	58.2 ± 1.2
3089			25 μL	0.48	112.3 ± 4.6
3091			55 μL	1.05	184 ± 33
3093	CH ₂ Cl ₂	2-PrOH (i-PrOH)	5 μL	0.094	57.9 ± 1.9
3095			25 μL	0.47	133.1 ± 5.8
3097			55 μL	1.03	270.5 ± 9.7
3099	CH ₂ Cl ₂	CH ₃ CH ₂ OH (ethanol)	5 μL	0.12	63.5 ± 2.0
3101			25 μL	0.61	166.4 ± 9.2
3103			55 μL	1.4	353.0 ± 12.6
3107	CH ₂ Cl ₂	1,1,1,3,3,3-hexafluoro- isopropanol (HFIP)	5 μL	0.068	12.6 ± 0.1
3109			25 μL	0.34	1.438 ± 0.009
3111			55 μL	0.75	0.95 ± 0.04
3113	CH ₂ Cl ₂	acetic acid	5 μL	0.12	16.4 ± 0.3
3115			25 μL	0.62	13.4 ± 0.2
3117			55 μL	1.4	12.22 ± 0.07
3121	CH ₂ Cl ₂	DMSO	5 μL	0.1	57 ± 2
3123			25 μL	0.5	66 ± 2
3125			55 μL	1.1	51 ± 1
3131	CH ₂ Cl ₂	1,4-dioxane	5 μL	0.08	40 ± 1
3133			25 μL	0.34	39 ± 1
3135			55 μL	0.75	35.2 ± 0.9
3139	CH ₂ Cl ₂	THF	5 μL	0.9	42 ± 1
3141			25 μL	0.44	43 ± 1
3143			55 μL	0.97	42 ± 1
3153	CH ₂ Cl ₂	acetonitrile	5 μL	0.14	8.28 ± 0.08
3149			25 μL	0.69	4.76 ± 0.02
3151			55 μL	1.5	2.34 ± 0.09

Order in Catalyst (Figure 8 in Paper)



Procedure with 10 μ L MeOH. A stock solution of catalyst (0.018 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 5.0 mL of CH₂Cl₂. Urea Alkene (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in 0.64 mL or 0.67 mL or 0.68 mL of CH₂Cl₂ with 10 μ L of CH₃OH and the solution transferred to an NMR tube. Variable amounts of catalyst stock solution were added to initiate the reaction and bring the total volume to 0.7 mL (substrate concentration is 0.05 M). The sample was immediately transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 80%.

	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/s^{-1}$
BRL 2101	0.01 mL	0.00018 mmol	0.5 mol %	36.9 \pm 0.7
BRL 2103	0.02 mL	0.00036 mmol	1 mol %	71 \pm 2
BRL 2105	0.05 mL	0.0009 mmol	2.5 mol %	125 \pm 7

Procedure without MeOH. A stock solution of catalyst (0.018 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 5.0 mL of CH₂Cl₂. Urea Alkene (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in 0.69 mL or 0.68 mL or 0.65 mL of CH₂Cl₂ and transferred to an NMR tube. Variable amounts of catalyst stock solution were added to initiate the reaction and bring the total volume to 0.7 mL (substrate concentration is 0.05 M). The sample was transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 50%.

	Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/s^{-1}$
BRL 2107	0.01 mL	0.00018 mmol	0.5 mol %	6.39 \pm 0.04
BRL 2109	0.02 mL	0.00036 mmol	1 mol %	12.9 \pm 0.2
BRL 2111	0.05 mL	0.0009 mmol	2.5 mol %	29 \pm 0.6

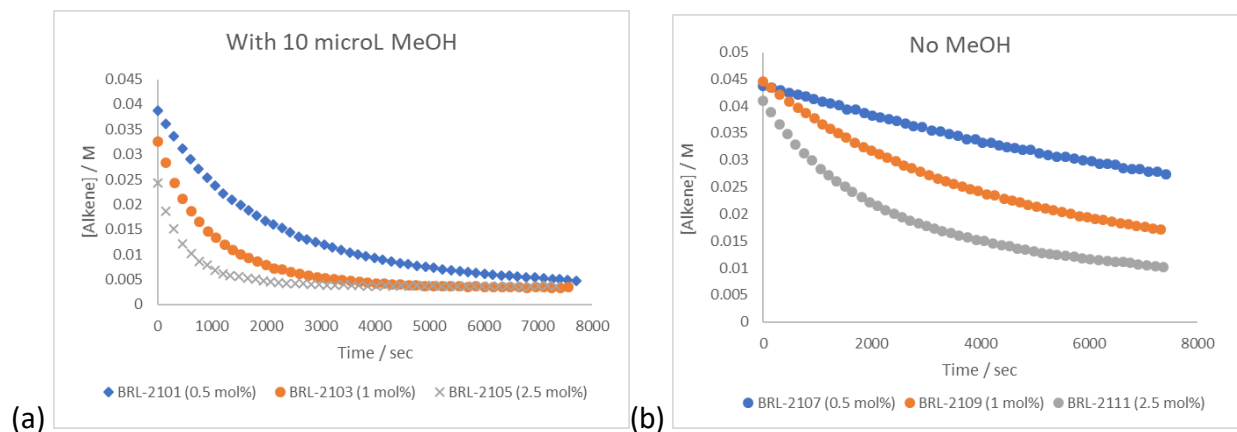


Figure S33. Raw plots showing urea alkene decay (0.05 M) in (a) 0.69 mL CH₂Cl₂/0.01 mL MeOH or (b) 0.7 mL CH₂Cl₂ with variable amounts of [JPhosAu(CNCH₃)]Sbf₆.

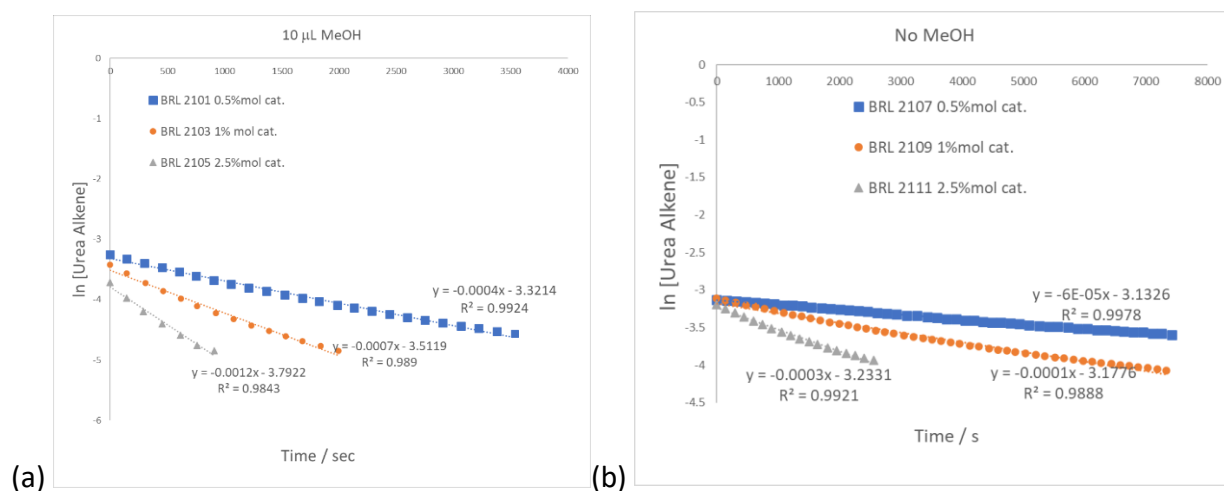


Figure S34. First order plots of urea alkene decay (0.05 M) in (a) 0.69 mL CH₂Cl₂/0.01 mL MeOH or (b) 0.7 mL CH₂Cl₂ with variable amounts of [JPhosAu(CNCH₃)]Sbf₆.

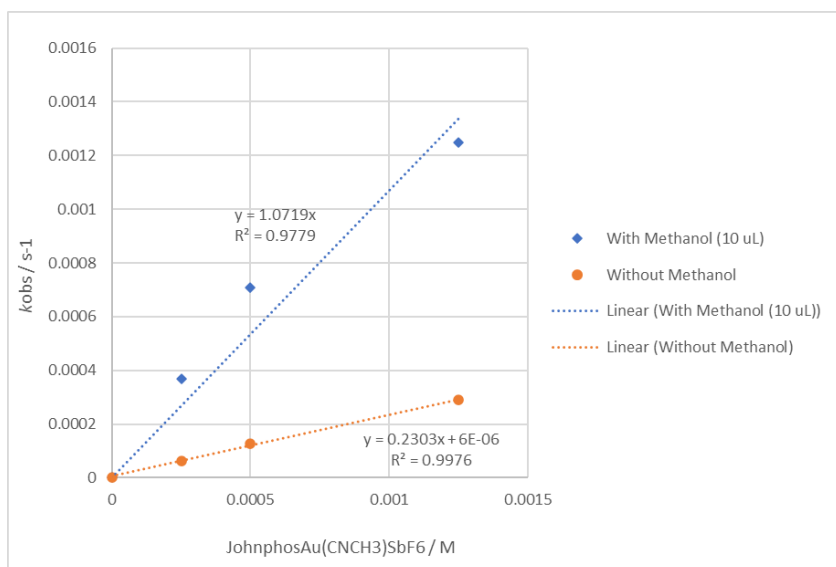


Figure S35. Plots of k_{obs} versus catalyst **5** concentration (0.5 mol %, 1 mol %, 2.5 mol % [JPhosAu(CNCH₃)]SbF₆) for the urea alkene **1a** cyclization (0.05 M) in CH₂Cl₂ with or without 10 μ L methanol additive (total volume 0.7 mL).

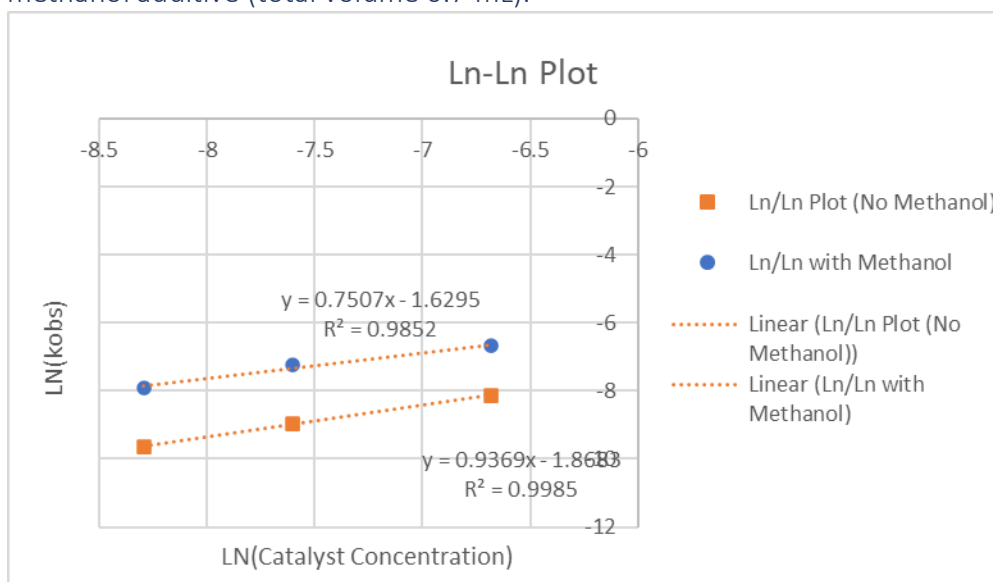
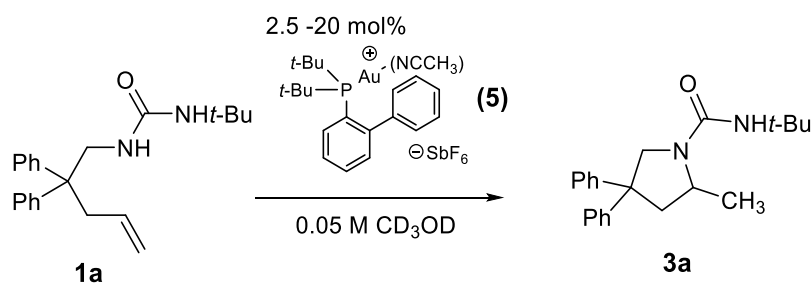


Figure S36. Plots of LN(k_{obs}) versus LN(catalyst concentration) at 0.5 mol %, 1 mol %, 2.5 mol % [JPhosAu(CNCH₃)]SbF₆ for the urea alkene **1a** cyclization (0.05 M) in CH₂Cl₂ with or without 10 μ L methanol additive (total volume 0.7 mL).



Order in Catalyst in CD_3OD

A similar procedure to the previous section was followed.

	$10^5 \times k_{obs}/s^{-1}$
BRL-4035	4.42 ± 0.06
BRL-6063	21.5 ± 0.6
BRL-6065	36 ± 1

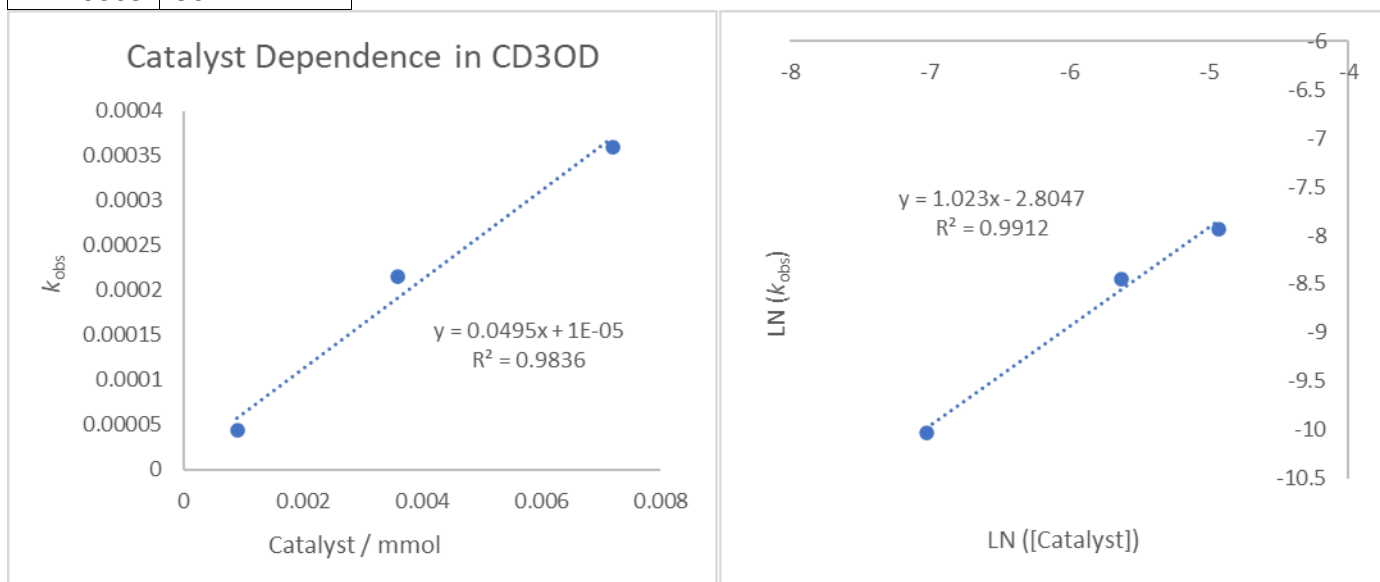
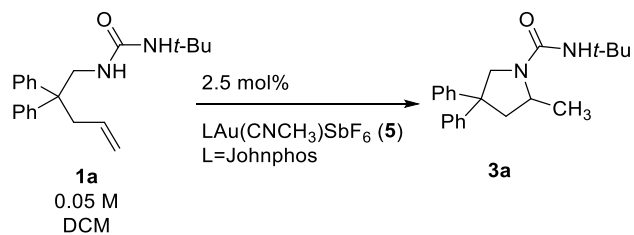


Figure S37. Plots of k_{obs} versus catalyst concentration (2.5 mol %, 10 mol %, 20 mol %) [$JPhosAu(CNCH_3)SbF_6$] for the urea alkene cyclization (0.05 M **1a**) in CD_3OD and corresponding plot of $LN(k_{obs})$ versus $LN(catalyst\ concentration)$.

Order in Urea



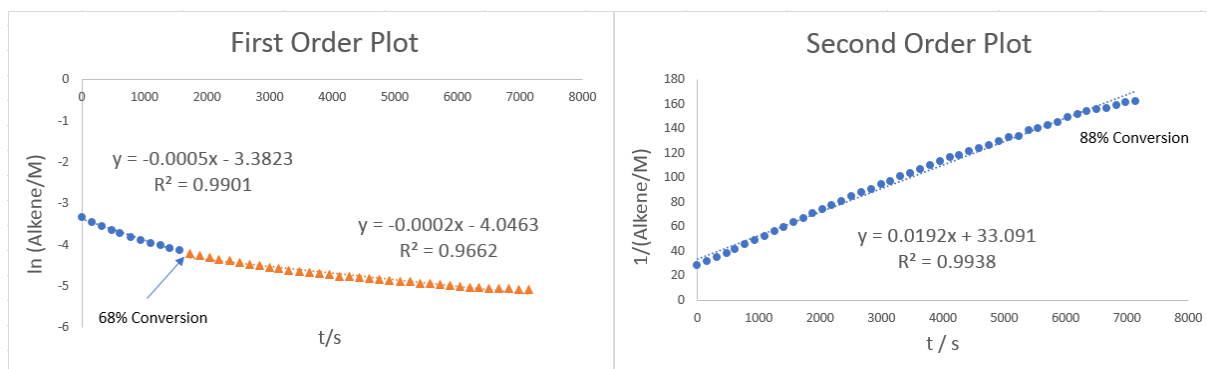


Figure S38. First and second order plots of urea alkene decay (0.05 M) in 0.7 mL of CH_2Cl_2 with $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (0.0009 mmol, 2.5 mol %).

Variable Urea Concentration in CDCl_3 : The t-butyl urea (0.005 g, 0.01 g, 0.03 g, 0.06 g) was dissolved in CDCl_3 (0.5 mL) with 1.5 μL 1,1,2,2-Tetrachloroethane. In a separate vial, the catalyst (0.0039 g, 0.005 mmol) was dissolved in CDCl_3 (0.1 mL). A ^1H NMR spectrum was collected to check the concentration of alkene by comparison to the TCE standard. The catalyst solution was added to the NMR tube and spectra collected immediately. Plots of $\text{Ln}(\text{Alkene})$ were linear up to 80% conversion. A plot of $\text{Ln}(\text{Alkene})$ versus $\text{Ln}(k_{\text{obs}})$ gives a slope of 0.55.

	1a / M	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
YSJ1133	0.0105 M	42 ± 1
YSJ1137	0.016 M	65 ± 2
YSJ1141	0.054 M	105 ± 3
YSJ1145	0.075 M	139 ± 3

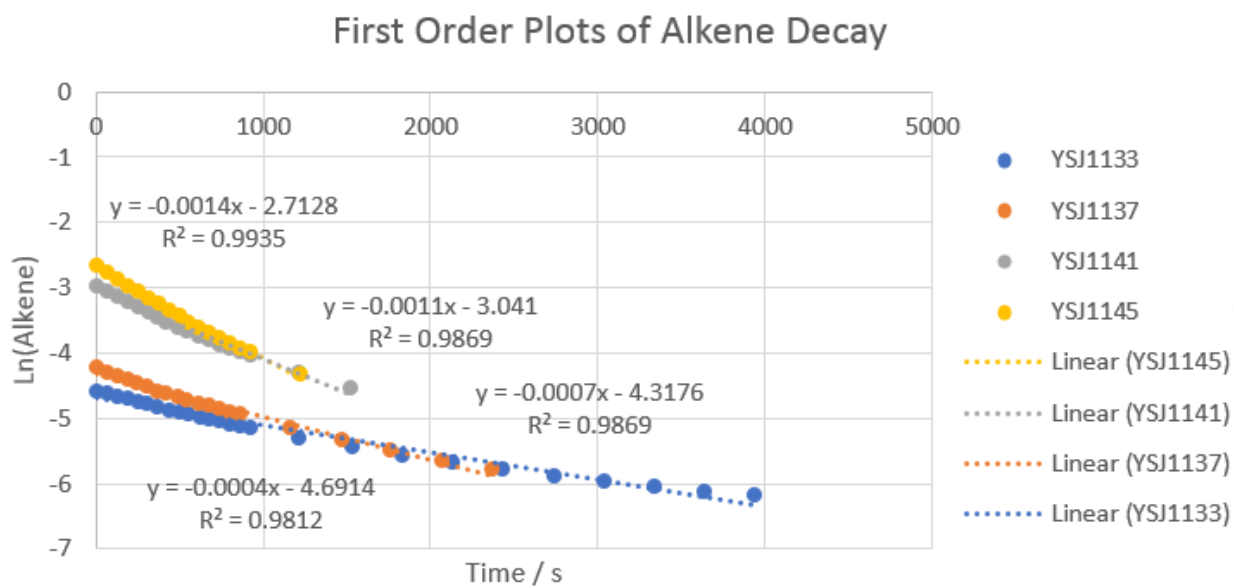


Figure S39. First order plots of urea alkene (**1a**) decay in CDCl_3 at various concentrations of **1a**.

Variable Urea Concentration in CH₂Cl₂. A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH₃)SbF₆ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CH₂Cl₂. Variable amount of Urea Alkene (336.48 g/mol, 6 mg, 6 mg, 12 mg, 36 mg) was dissolved in 0.675 mL of CH₂Cl₂, with 1.5 μL of 1,1,2,2-tetrachloroethane infused as the internal standard, and then the solution was transferred to an NMR tube. Catalyst solution (25 μL, 0.000892 mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL (substrate was at a concentration of 0.05 M). The sample was immediately transferred to the NMR spectrometer and ¹H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots were linear up to at least 48% conversion. Concentrations calculated relative to TCE.

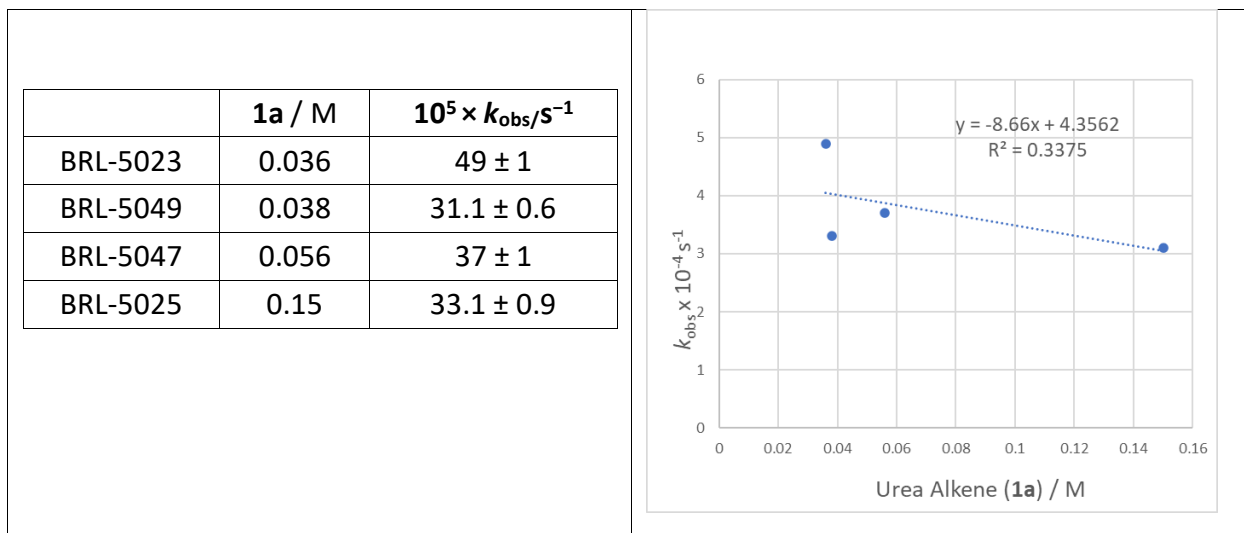
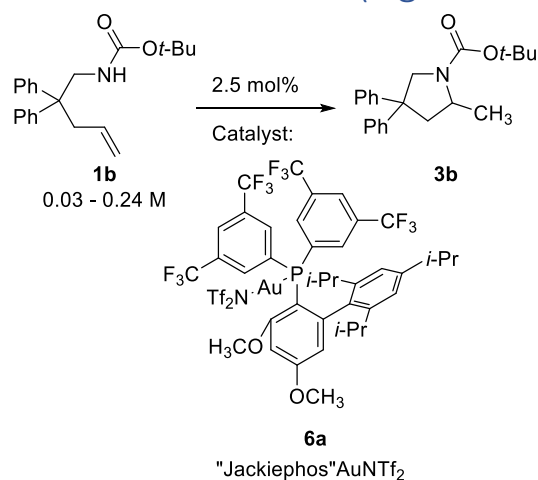


Figure S40. First order rate constants for urea alkene (**1a**) decay in (CH₂Cl₂) showing non-linear dependence on substrate concentration.

Order in Carbamate (Figure 7 in Paper)



A stock solution of catalyst (0.022 M) was prepared by dissolving Jackiephos-Au-(NTf₂)₂ (1273.78 g/mol, 56.7 mg, 0.045 mmol) in 2 mL of CH₂Cl₂. Alkene carbamate (337.46 g/mol), ranging in mass, was dissolved in 0.660 mL of CH₂Cl₂ and transferred to an NMR tube. Catalyst solution (40 μL, 0.000 89mmol) was injected to initiate the reaction and to bring the total volume to 0.7 mL; the sample was transferred to

the NMR spectrometer and ^1H NMR spectra collected. The time from injection to spectrum #1 was approximately 5 minutes. Pseudo first order plots maintained their linearity until the end of acquisition of data (80% conversion at the higher concentrations of carbamate).

	Alkene carbamate		Catalyst Solution	Catalyst Amount	Catalyst Loading	$10^5 \times k_{\text{obs}}/\text{s}^{-1}$
	Mass(mg)	C(M)				
BRL 5051	12	0.05	0.040mL	0.00089 mmol	2.5 mol %	9.73 ± 0.02
BRL 5053	6	0.03				6.96 ± 0.02
BRL 5055	36	0.14				29.5 ± 0.1
BRL 5057	72	0.24				19.6 ± 0.1

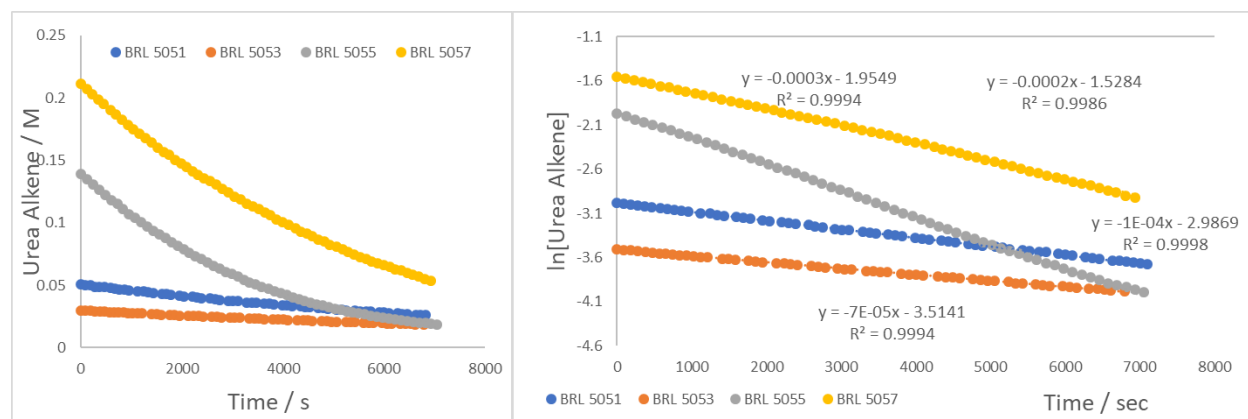
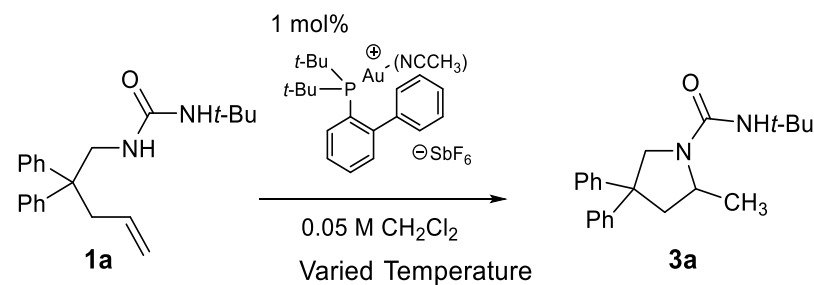


Figure S41. Raw plots of alkene carbamate decay at variable concentrations in 0.7 mL of CH_2Cl_2 with 0.00089 mmol of Jackiephos-Au-(NTf) $_2$ catalyst and the corresponding first order plots.

Activation Parameters



A stock solution of catalyst (0.036 M) was prepared by dissolving JPhosAu(NCCH $_3$)SbF $_6$ (772.17 g/mol, 68.9 mg, 0.0892 mmol) in 2.5 mL of CH_2Cl_2 . Urea alkene (336.48 g/mol, 12 mg, 0.036 mmol) was dissolved in 0.690 mL of CH_2Cl_2 and transferred to an NMR tube. If the necessary temperature of a reaction was lower than 20 °C, the NMR sample was pre-cooled in a chiller set to the target temperature. Once the spectrometer temperature and chiller reached the desired temperature (after a 0.5-1 hr pre-cooling period), the catalyst solution (10 μL , 0.00036 mmol) was injected to the NMR tube to bring the total volume to 0.7 mL (the substrate was at a concentration of 0.05 M); the sample tube was immediately transferred to the NMR spectrometer and ^1H NMR spectra collected. If the reaction ought to be conducted at or over 20 °C, the catalyst solution was injected directly into a room temperature NMR sample and transferred instantly to the spectrometer, pre-set to the desired temperature. The time from injection to spectrum #1 was

approximately 5 minutes, during which time temperature fluctuations were expected. The spectrometer also re-established the set temperature within that time. In the absence of MeOH, hydroamination was shown to be first order in catalyst. Thus, second order rate constants were calculated by dividing the observed rate constant by the catalyst concentration.

T/°C	T/K	$k_{\text{obs}}(\text{s}^{-1}) \times 10^5$	Cat. (M)	$k_2 (\text{s}^{-1} \text{M}^{-1})$		$\ln(k_2/T)$	1000/T
-5	267	6.12 ± 0.04	0.00051	0.118	BRL 3021	-7.71	3.745
5	278.1	11.9 ± 0.2	0.00051	0.196	BRL 3023	-7.08	3.596
15	288.1	12.2 ± 0.2	0.00051	0.196	BRL 3017	-7.09	3.471
30	303.1	25.9 ± 0.8	0.00051	0.588	BRL 3015	-6.39	3.299

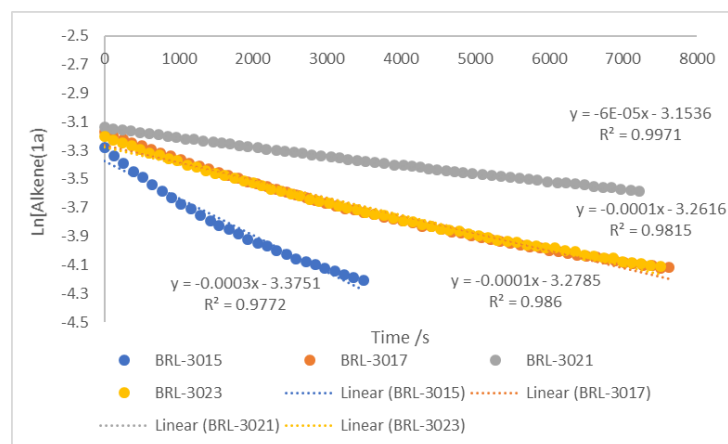


Figure S42. First order plots of urea alkene decay (0.05 M) in 0.7 mL of CH_2Cl_2 and with 0.00036 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (1 mol %) at variable temperatures.

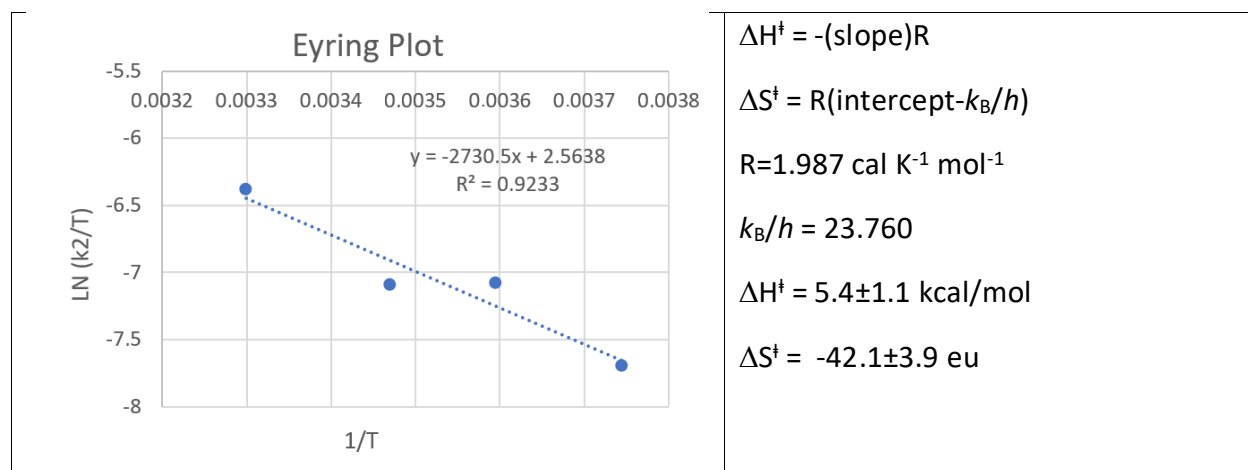


Figure S43. The plot of $\ln(k_{\text{obs}})$ versus $1/T$ for urea alkene decay (0.05 M) in 0.7 mL of CH_2Cl_2 and with 0.00036 mmol of $[\text{JPhosAu}(\text{NCCH}_3)]\text{SbF}_6$ (1 mol %)

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