Predicting Counterion Effects Using a Gold Affinity Index and a Hydrogen Bonding Basicity Index

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Supporting Information

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1. General

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively, using $CDCl_3$, CD_2Cl_2 , d-THF as a solvent. The chemical shifts are reported in δ (ppm) values relative to CH_2Cl_2 (δ 5.33 for ^{1}H NMR and δ 54.2 ppm for ^{13}C NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. All air and/or moisture sensitive reactions were carried out under argon atmosphere.

Solvents (tetrahydrofuran, ether, dichloromethane and DMF) were chemically dried using a commercial solvent purification system. All other reagents and solvents were employed without further purification. The products were purified using a CombiFlash system or a regular glass column. TLC was developed on Merck silica gel 60 F254 aluminum sheets. $KCTf_3$ was purchased from Synquest Labs, $Ag^{+}[Al[(CF_3)_3C\text{-}O)]_4]^{-}$ was purchased from IoLiTec. All NMR solvents were from Cambridge Isotope Laboratories, Inc. All other chemicals like catalysts and ligands were purchased from Aldrich, Alfa Aesar or Strem.

2. General procedure for kinetic measurements

In some cases, 1,3,5-tri-tert-butylbenzene (internal standard) was used. The reactions were monitored with ^{1}H NMR (single pulse or 1 scan for fast reactions, 8 scans for slow reactions). Some NMR measurements were conducted using a NMR experiment array (a series of spectra measured at predetermined time intervals over a period by adjusting the pre-acquisition delay). NMR experiment array gives better precision for both concentration (*via* integration) and reaction time, because each measurement is conducted at almost identical shimming and temperature conditions.

3. Synthesis of starting materials

3.1 Synthesis of JohnPhosAuCl

JohnPhosAuCl were synthesized using a slightly modified version of a literature method.[1]

Sodium tetrachloroaurate(III) dihydrate (1 mmol) was dissolved in water, and the orange solution was cooled in ice. To this solution, 2,2'-thiodiethanol (3 mmol) was slowly added (ca. 45 min) with stirring. A solution of the Johnphos ligand (1 mmol) in EtOH (if the ligand could not be dissolved, more EtOH was used) was added dropwise to yield a white solid. The solid was filtered off, washed with water followed by EtOH, and ultimately dried in vacuum.

3.2 Synthesis of Tris(1,1,1-trifluoromethanesulfonyl)methyl silver(I)

In the suspension of water with silver carbonate (1.38 g, 5 mmol), tris[(trifluoromethyl)sulfonyl]methane (2.06 g, 5 mmol) was slowly added into the flask. After vigorous stirring for 2 hours, the product was collected by filtration and washed with water. Trace amount of water was removed by high vacuum.

3.3 Preparation of JohnPhosAuCl stock solution in CD_2Cl_2 or $CDCl_3$

The desired amount of L-AuCl was dissolved in corresponding amount of CD_2Cl_2 and then kept in freezer (-20 ^oC) until it was used.

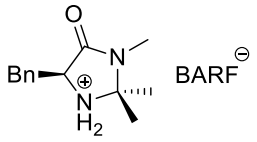
3.4 Synthesis and preparation of starting material stock solution

All reaction starting materials were synthesized according to related reference paper.[2] The starting materials were then used for the preparation of 0.1 M or 0.2 M stock solution in CD_2Cl_2.

3.5 Preparation of cationic gold stock solution (using JohnPhosAu$^+$OTf$^-$ as example)

Standard stock solutions of cationic gold catalyst were made when it was needed and were usually used in the same day. Weighing the L-Au(I)Cl complex into a vial and adding corresponding $CDCl_3$ or CD_2Cl_2, then 1.5 equiv of AgOTf was added and the vial was sonicated for 3 min at 0-5 ^oC. The vial was centrifuged and the clear solution was transferred to a clean glass vial with a screw cap. The solution was kept in freezer (-20 ^oC) until it was used.

3.6 Preparation of stock solution of organocatalyst



Stock solution (0.02 M) of MacMillan imidazolidinone organocatalyst with 1.5 equivalent NaBARF were made by weighting into a vial using tetrahydrofuran-d^8 as solvent. Sonication of mixed solution followed by filtration gave the standard stock solution. The solution was kept in the freezer (-20°C) until it was needed.

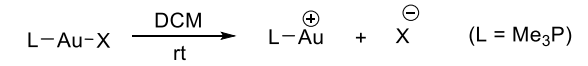
4. Gold affinity index and hydrogen bond basicity index

4.1 Gold affinity index

The affinity of the counterion towards cationic gold will depends on the size and charge distribution of the counterion. However, comprehensive data about counterions' gold affinity is not available, only a limited set is available in the literature.[3] We used calculated gold-counterion dissociation energies to describe the bonding affinity.[4] In our calculations, among common counterions, iodide (I^-) is the strongest

cationic gold binder and SbF_6^- is the weakest counterion. For convenience, we set up the gold affinity index of counterions (GAI) by assign GAI (I^-) = 10 and GAI (SbF_6^-) = 0.

Table S 1. Gold affinity scale of counterions.



counterion	dissociation energy ΔE (kJ/mol)[a]	gold affinity index (GAI)
Cl^-	53.9	5.2
Br^-	67.7	6.0
I^-	143.8	10
TFA^-	74	6.3
OAc^-	70.6	6.1
OTs^-	28	3.8
NTf_2^-	10.4	2.9
OTf^-	0	2.4
BF_4^-	-35.1	0.5
CTf_3^-	-40.5	0.2
SbF_6^-	-44.3	0
$Al[(CF_3)_3C\text{-}O)]_4^-$	<-45	<0
$BArF_4^-$	<-45	<0

[a] Theoretical calculation using B3LYP[5] hybrid functional and Lanl2DZ[6] with pseudo potential for Au, an all electron QZP[7] basis set for Sb and 6-311++g(d.p)[8] for remains atoms, solvent effect was included using SMD[9] model for DCM. All calculation were performed using Gaussian09.[10]

Table S 2. Theoretical calculation using B3LYP hybrid functional and Lanl2DZ with pseudo potential for Au, an all electron QZP basis set for Sb and 6-31g(d,p) for remains atoms:

complex	E (Complex)	E (Au^+)	E (counterion)	$\Sigma(E_{Au+} + E_{counterion})$	dissociation Energy (a.u)	relative Dissociation energy (kcal mol^{-1})
$(CH_3)_3P$-Au-Cl	-1056.8614	-596.370514	-460.2522334	-1056.622747	149.756893	35.7
$(CH_3)_3P$-Au-BF_4	-1021.056207	-596.370514	-424.4990705	-1020.869585	117.1071712	3.0
$(CH_3)_3P$-Au-OAc	-825.1183349	-596.370514	-228.5021965	-824.8727105	154.1317672	40.0
$(CH_3)_3P$-Au-OTs	-1491.406712	-596.370514	-894.8430369	-1491.213551	121.2105219	7.1
$(CH_3)_3P$-Au-OTf	-1558.050317	-596.370514	-961.4979922	-1557.868506	114.0882206	0.0
$(CH_3)_3P$-Au-NTf2	-2423.744338	-596.370514	-1827.20535	-2423.575864	105.7191825	-8.4
$(CH_3)_3P$-Au-BArf4	-4244.347863	-596.370514	-3647.877069	-4244.247583	62.92638905	-51.2
$(CH_3)_3P$-Au-CTf3	-3293.234021	-596.370514	-2696.726866	-3293.09738	85.74390767	-28.3
$(CH_3)_3P$-Au-SbF6	-7511.448345	-596.370514	-6914.906983	-7511.277497	107.2090795	-6.9

The energies are in a.u. (atomic unit), expect otherwise stated.

Table S 3. Theoretical calculation using B3LYP hybrid functional and Lanl2DZ with pseudo potential for Au, an all electron QZP basis set for Sb and 6-311++g(d.p) for remains atoms.

complex	E (Complex)	E (Au^+)	E (counterion)	dissociation energy	dissociation Energy (kcal/mol)	relative Dissociation energy (kcal mol^{-1})
$(CH_3)_3P$-Au-Cl	-1056.953825	-596.427412	-460.3037273	-1056.731139	139.7375664	31.8
$(CH_3)_3P$-Au-BF_4	-1021.2671	-596.427412	-424.679694	-1021.107106	100.3979604	-7.6
$(CH_3)_3P$-Au-OAc	-825.2508789	-596.427412	-228.6024863	-825.029898	138.6677246	30.7
$(CH_3)_3P$-Au-OTs	-1491.631388	-596.427412	-895.0145449	-1491.441957	118.8697841	10.9
$(CH_3)_3P$-Au-OTf	-1558.329903	-596.427412	-961.7304094	-1558.157821	107.9829248	0.0
$(CH_3)_3P$-Au-NTf2	-2424.206358	-596.427412	-1827.61046	-2424.037872	105.7264616	-2.3
$(CH_3)_3P$-Au-BArf4	*					
$(CH_3)_3P$-Au-CTf3	-3293.874231	-596.427412	-2697.305526	-3293.732937	88.66346069	-19.3
$(CH_3)_3P$-Au-SbF6	-7511.727824	-596.427412	-6915.159662	-7511.587074	88.321907	-19.7

The energies are in a.u. (atomic unit), except the relative energy which is in kcal mol^{-1}.

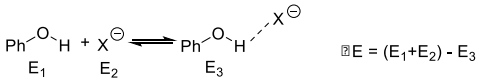
Table S 4. Theoretical calculation using B3LYP hybrid functional and Lanl2DZ with pseudo potential for Au, an all electron QZP basis set for Sb and 6-311++g(d.p) for remains atoms, solvent effect was included using SMD model for DCM.

Complex	E (Complex)	E (Au^+)	E (counterion)	dissociation energy	dissociation Energy (a.u)	relative Dissociation energy (kcal mol^{-1})
$(CH_3)_3P$-Au-Cl	-1056.981007	-596.522897	-460.4002443	-1056.923141	36.31124266	12.9
$(CH_3)_3P$-Au-BF_4	-1021.311095	-596.522897	-424.7642585	-1021.287156	15.02208739	-8.4
$(CH_3)_3P$-Au-OAc	-825.2776554	-596.522897	-228.690414	-825.213311	40.37675444	16.9
$(CH_3)_3P$-Au-OTs	-1491.672795	-596.522897	-895.1018309	-1491.624728	30.16258592	6.7
$(CH_3)_3P$-Au-OTf	-1558.361856	-596.522897	-961.8016013	-1558.324498	23.44276958	0.0
$(CH_3)_3P$-Au-NTf2	-2424.233873	-596.522897	-1827.669696	-2424.192593	25.90398931	2.5
$(CH_3)_3P$-Au-BArf4					Not converge	
$(CH_3)_3P$-Au-CTf3	-3293.904531	-596.522897	-2697.359714	-3293.882611	13.7548937	-9.7
$(CH_3)_3P$-Au-SbF6	-7511.773802	-596.522897	-6915.230429	-7511.753326	12.8484555	-10.6

4.2 Hydrogen bond basicity index

Because the measurement of pK_{BHX} is based on the complexation of a hydrogen bond acceptor with a substituted phenol.[11] We calculated the H-bonding bonding energies of phenol with various anions, and these energies correlated very well with the experimental pK_{BHX} of the corresponding *n*-Bu_4N^+ salts ([11] In our calculations, among common counterions, acetate (OAc-) is the strongest hydrogen bonding acceptor and CTf_3^- is the weakest. For convenience, we set up a hydrogen bonding basicity index of counterions (HBI) by assign HBI (OAc^-) = 10 and HBI (CTf_3^-) = 0. In this scale, HBI of strong bases like OH^- will be greater than 10.

Table S 5. Hydrogen bond basicity index.



(X^-)	H-bonding energy ΔE (kJ/mol) [a]	hydrogen bond basicity ind (HBI)
OAc^-	149.7	10
TFA^-	122.1	7.2
TsO^-	93.1	4.3
Cl^-	115.3	6.5
Br^-	91.1	4.1
I^-	76.9	2.6
OTf^-	83.9	3.4
PF_6^-	82.2	3.2
BF_4^-	102.2	5.2
SbF_6^-	78.5	2.8
NTf_2^-	60.6	1.0
CTf_3^-	50.7	0

[a] Bonding energies were calculated at B3LYP/6-31g.

Table S 6. Theoretical calculation using B3LYP hybrid functional for hydrogen bonding energies.

counterion	**phenol**	**H-bond acceptor**	**phenol-acceptor complex**	**H-bond bonding energy Kcal/mol**
OAc-	-307.464905	-228.497887	-536.019828	149.7
TsO	-307.464905	-894.832407	-1202.332758	93.1
TFA	-307.464905	-526.237588	-833.748981	122.1
Cl	-307.464905	-460.252232	-767.761034	115.3
Br	-307.464905	-2573.958562	-2881.458166	91.1
I	-307.464905	-11.472208	-318.966388	76.9
OTf	-307.464905	-961.497969	-1268.994838	83.9
PF6	-307.464905	-940.642767	-1248.138966	82.2
BF4	-307.464905	-424.499245	-732.003091	102.2
SbF6	-307.464905	-604.709546	-912.204364	78.5
CTf3	-307.464905	-2696.727262	-3004.211485	50.7
NTf2	-307.464905	-1827.205401	-2134.69339	60.6

4.3 Correlation between gold affinity and hydrogen bonding basicity

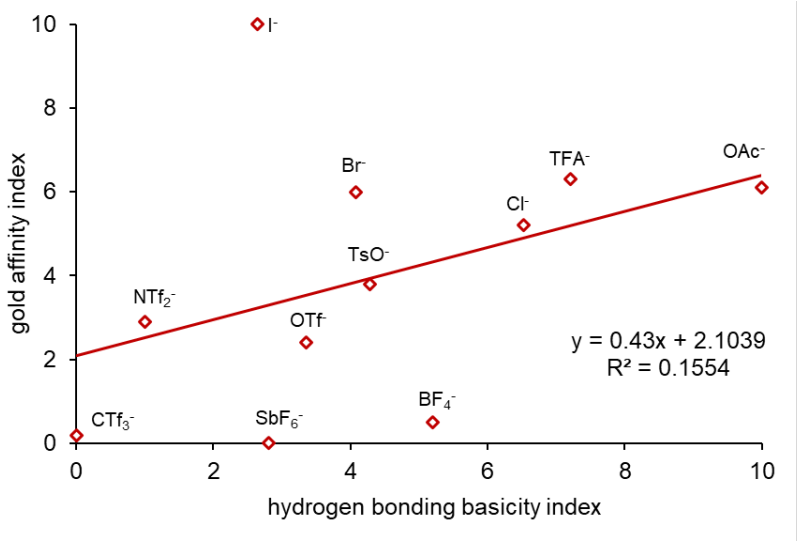
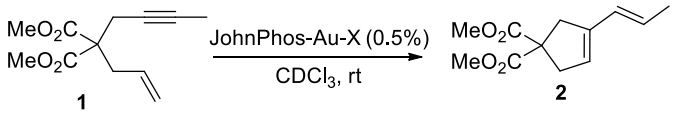


Figure S1. Lack of correlation between gold affinity and hydrogen bond basicity.

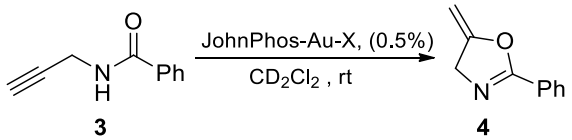
5. General procedures for model reactions

General procedure for cycloisomerization of 1,6-enyne



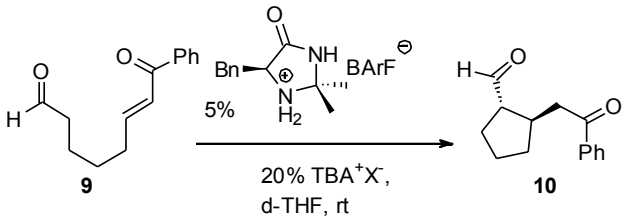
The model reaction was conducted in a NMR tube: 50 µl standard stock solution of cationic gold catalyst ($JohnPhosAu^{+}X^{-}$, 0.01 mol/L) was directly added into NMR tube. Then 1,6-enyne (0.1 mmol, 22 mg) in 0.45 mL $CDCl_3$ was transferred into the tube. All reactions were conducted at room temperature and the progress of the reaction was monitored by ^{1}H NMR.

General procedure for cycloisomerization of propargyl amide



The model reaction was conducted in a NMR tube: 50 µl standard stock solution of cationic gold catalyst ($JohnPhosAu^{+}X^{-}$, 0.01 mol/L) was directly added into NMR tube. Then propargyl amide (0.1 mmol, 15.9 mg) in 0.45 mL CD_2Cl_2 was transferred into tube. All reactions were conducted at room temperature and the progress of the reaction was monitored by ^{1}H NMR.

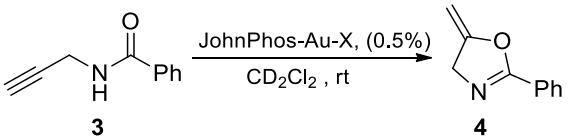
General procedure for organo-enamine catalysis



The model reaction was conducted in a NMR tube. Ketoaldehyde **9** (10.8 mg, 0.05 mmol) was dissolved in 0.375 mL tetrahydrofuran-d_8 and 0.125 mL stock solution of catalyst and was introduced to a NMR tube. After a short time sonification (about 1 min), corresponding hydrogen bonding acceptor (TBA^+X^-) was added into the NMR tube at room temperature, and the mixture was sonicated for 1 min. All reactions were kept at room temperature and the progress of the reaction was monitored by ^{1}H NMR.

6. Spectrum for ^{1}H NMR monitoring of model reactions

Cycloisomerization of propargyl amide



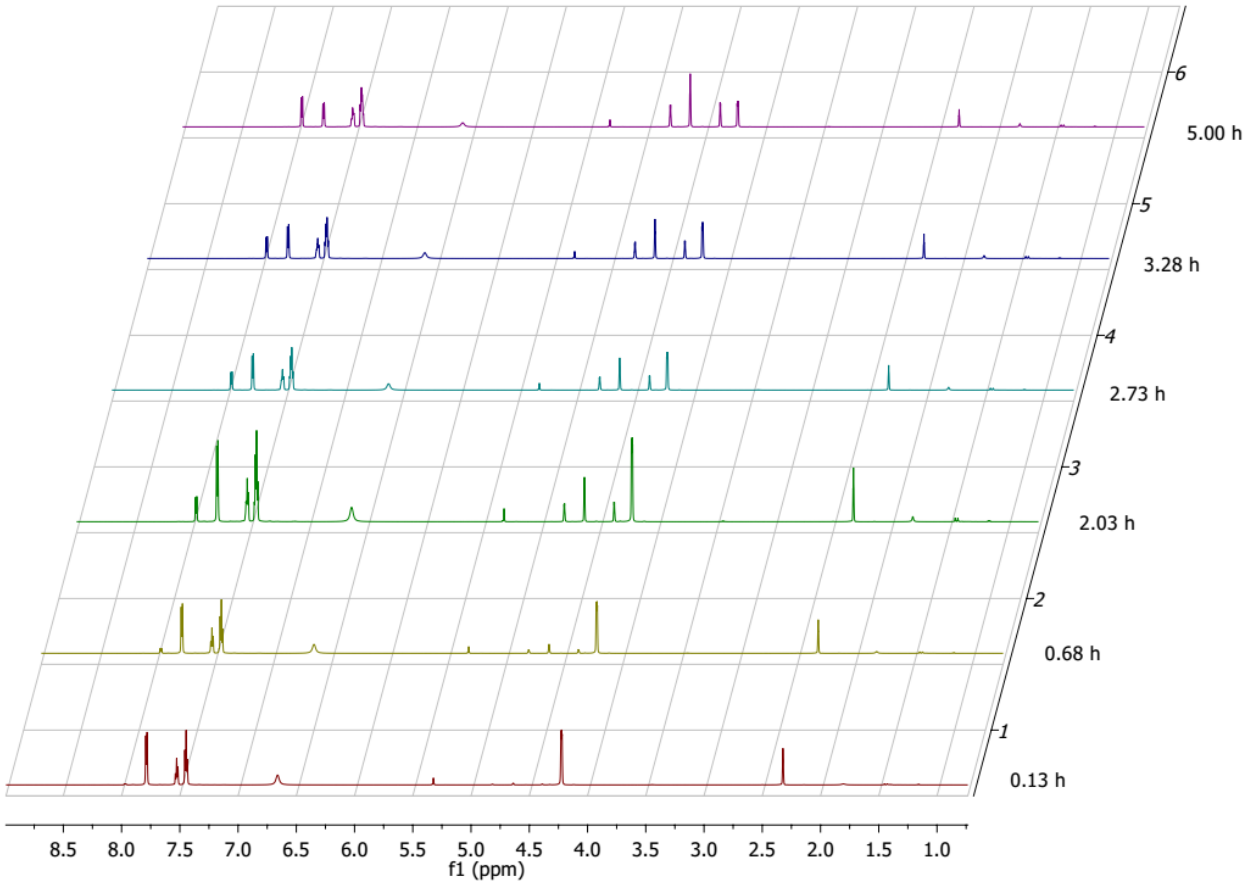
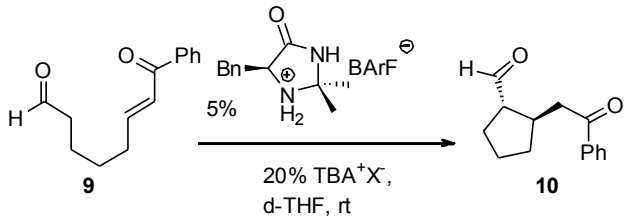


Figure S2. Monitoring of organo-enamine catalysis using NMR (OTf^- as counterion)

Organo-enamine catalysis



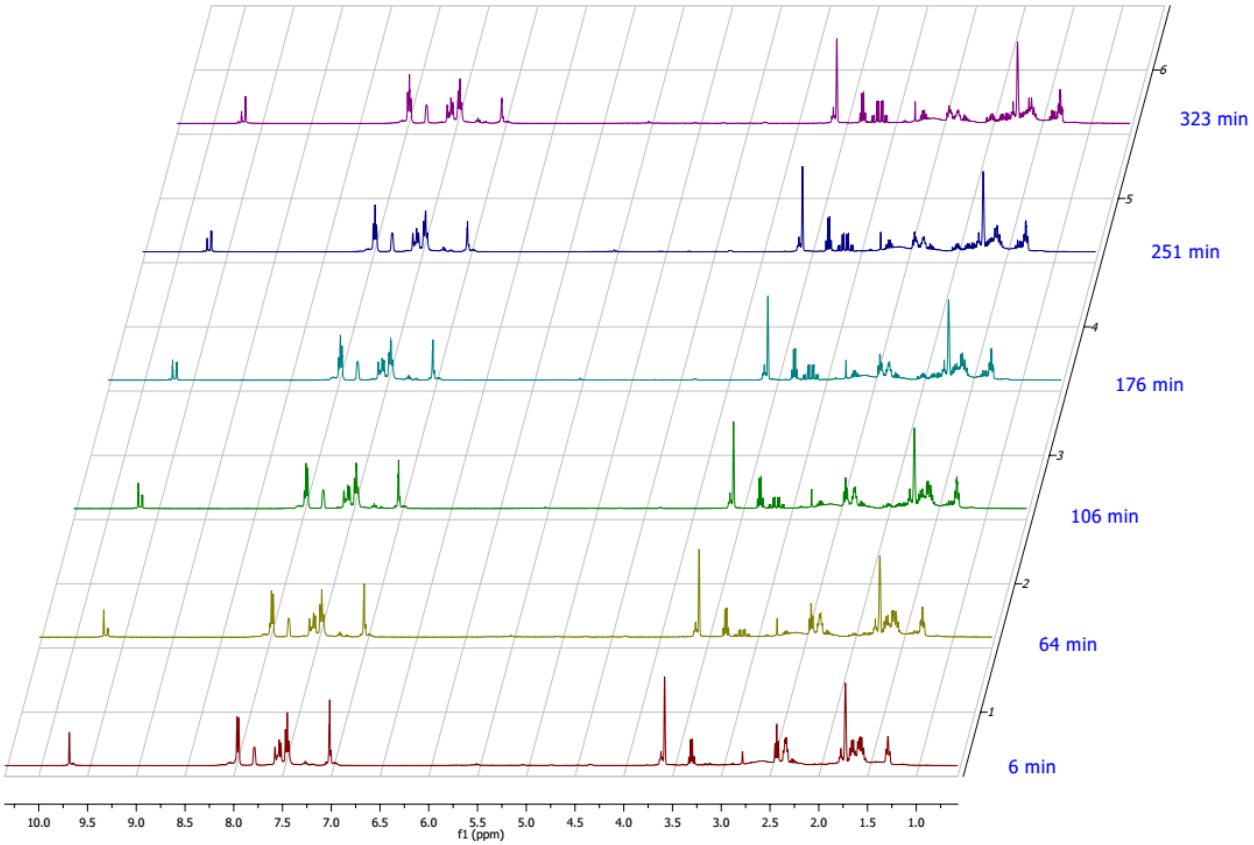


Figure S3. Monitoring of organo-enamine catalysis using NMR (Cl^- as counterion)

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