Electronic Supplementary Material (ESI) for ChemComm.

A Highly Efficient Thiazolylidene Catalyzed Acetoin Formation: Reaction, Tolerance and Catalyst Recycling

Experimental section

General information

All starting materials are commercially available and were used as received, unless otherwise indicated. ^1H and ^{13}C NMR spectra were obtained using a Brucker AV-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm with reference to tetramethylsilane with the solvent resonance as the internal standard. **SB1**, Poly(4-vinylpyridine), Sigma-Alrich, product No: 547697-100G; **SB2**, Ion exchanger II, Merck, product No: 104768; **SB3**, Ion exchanger III, Merck, product No: 104767; **SB4**, Silica bond diethylamine, SiliCycle, product No: R76530B; **SB5**, Poly(acrylic acid sodium salt), Sigma-Alrich, product No: 447013; **(**Chloromethyl)polystyrene (porus, extent of labeling: ~5.5 mmol/g Cl loading), Sigma-Alrich, product No: 63868.

General procedure in acetoin formation via condensation of acetaldehyde

To a 4 mL thick wall glass tube with stirring bar was added the precatalyst and the base, acetaldehyde (2 ml, 35.5 mmol), and then the tube was sealed. After the reaction mixture was stirred at indicated temperature and hours, the mixture was cooled to room temperature subjected to ^1H NMR analysis. Yield was measured via ^1H NMR with mesitylene or 1,10-phenathroline as the internal standard. The Spectrum is consistent with the analytical standard purchased (*Sigma-Aldrich*): ^1H NMR (400 MHz, $CDCl_3$) δ 4.25 (q, *J* = 7.2 Hz, 1H), 3.48 (br, 1H), 2.21 (s, 3H), 1.40 (d, *J* = 7.2 Hz, 3H).

Procedure for ethanol to acetaldehyde

Ethanol to acetaldehyde was carried out under atmospheric pressure in a conventional fixed-bed Pyrex tubular reactor (Φ = 6 mm) at 300°C. Self-synthesized CuO/SiO_2 (0.2 g, 60 mesh) [11] was used as catalyst. The reactant was fed by bubbling liquid ehtanol with high purity He carrier gas (flow rate 20 ml min^{-1}). The feed composition was ethanol/ He(v/v) =

9/20. The effluent gas from the reactor was cooled by dry ice and the collected liquid was analyzed by a Shimadzu GC2010 gas chromatograph with FID and HP-FFAP capillary column (30 m × 0.32 mm × 0.5 μm). The product contains 83% of acetaldehyde with unreacted ethanol as major impurity and trace amount of acetic acid.

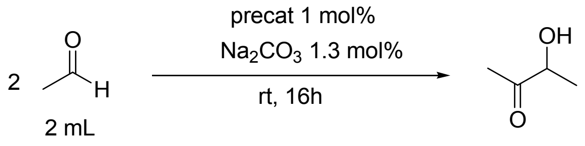
Synthesis of polystyrene supported thiazolium salt 2

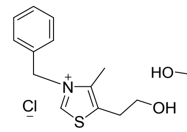
To a dried two-necked round flask with a condenser were added (chloromethyl)polystyrene (1.8 g, Cl^- ~ 9.9 mmol), anhydrous acetonitrile (30 mL), 1,4-dioxane (30 mL) and 4-methyl-5-thiazoleethanol (2.85 mL,23.8 mmol). The mixture was refluxed for 2 days, following the filtration to remove unreacted 4-methyl-5-thiazoleethanol and solvents. Then the solid was washed with acetonitrile (10 mL), 1,4-dioxane (10 mL) and ethanol (10 mL). After dried under vaccum, the precatalyst **2** was ready for use (3.036g, loading of precatalyst: 2.84 mmol/g).

General procedures for catayst recyclings

To a 4 mL thick wall dry glass tube with stirring bar was added the precatalyst, the base, and acetaldehyde. After the reaction mixture was stirred at the indicated temperature and hours, it was cooled down to room temperature and kept standing for 2 hours to allow the complete precipitation. The liquid was decanted out to another tube, from which small amount was transferred to NMR tube for ^{1}H NMR analysis. The sealed tube with the precipitate was added another round of acetaldehyde and then sealed immediately for the 2nd running.

Table S1. Screening of precatalysts in acetoin formation via self-condensation of acetaldehyde. [a]





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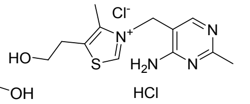

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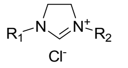
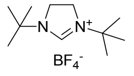


3a: $R_1 = R_2 = 2,4,6\text{-triMeC}_6H_2$
3b: $R_1 = R_2 = 2\text{-}^{i}PrC_6H_4$



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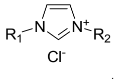
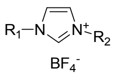
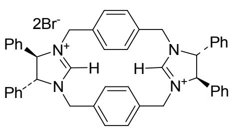


5a: $R_1 = R_2 = 2,,6\text{-di-}^{i}PrC_6H_3$
5b: $R_1 = R_2 = 2\text{-}^{i}PrC_6H_4$
5c: $R_1 = R_2 = (CH_2)_3CN$
5d: R_1 = *n*-Butyl, R_2 = Me



6a: $R_1 = R_2 = {}^{i}Pr$
6b: $R_1 = R_2$ = Cyclohexyl



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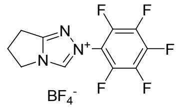

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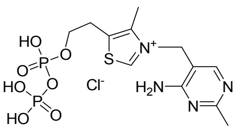

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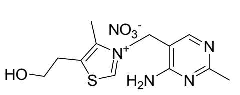

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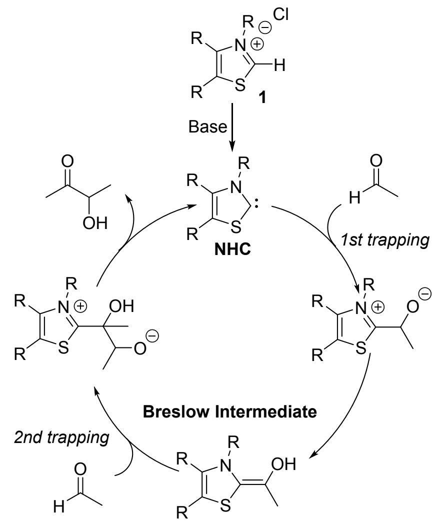
Entry	Precatalyst	Yield (^{1}H NMR)	Entry	Precatalyst	Yield (^{1}H NMR)
1	**1**	21% [b, c]	9	**5d**	N.R.
2	**2**	7%	10	**6a**	N.R.
3	**3a**	< 17% [b,d]	11	**6b**	N.R.
4	**3b**	Trace [d]	12	**7**	N.R.
5	**4**	N.R.	13	**8**	< 9% [b,d]
6	**5a**	N.R. [d]	14	**9**	N.R. [d]
7	**5b**	N.R.	15	**10**	10%[b, d]
8	**5c**	N.R.			

[a] Reaction conditions: A mixture of precatalyst (0.355 mmol), Na_2CO_3 (0.5 mmol) and 2 mL acetaldehyde (35.5 mmol) were stirred in a sealed tube at the room temperature for 16h. [b] K_2CO_3 (0.35 mmol) was used. [c] Reaction was run for 2 days. [d] Some complex by-products were observed.



Scheme S1. Possible reaction pathway explains the high efficiency of this system.