Supporting Information for:

Artificial Enzymes with Thiazolium and Imidazolium Coenzyme Mimics

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Contents

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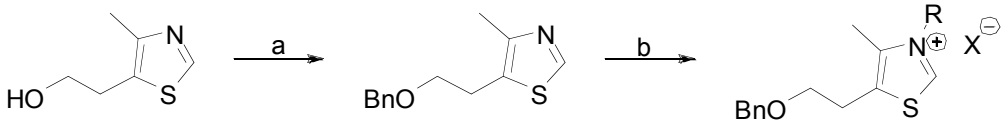
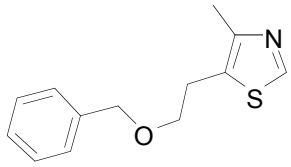
Chemicals were purchased from Sigma-Aldrich Co. (St. Louis, MO) and Fisher Scientific (Pittsburg, PA) and used without further purification, unless otherwise noted. EMD/Merck (San Diego, CA) pre-coated 250_m silica plates containing 254 nm fluorescence indicator were used for analytical thin-layer chromatography. Flash chromatography was performed on 230-400 mesh silica (Silica Gel 60) from EMD Chemicals (Gibbstown, NJ). NMR spectra were obtained on a Bruker DPX 300 or 400 MHz spectrometer. MS spectra were taken on JOEL LCmate. FAB MS spectra were taken on a JOEL JMS-DX-303 HF. Kinetics were followed by HPLC analysis of samples, using a Waters 600 controller and 2996 photodiode array UV detector (254 nm).

Synthesis of Thiazolium Catalysts

Some enzyme mimics reported below were not described in Table 1 of this work because they were insoluble in the reactions conditions described for the benzoin condensation. Their synthesis is included for those interested in the purification methods employed and the compounds' characterization.

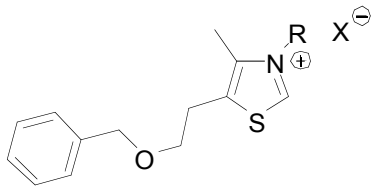


Reagents and Conditions: a.) NaH, BnBr, DMF, 0 °C, rt, 16h, 87%; b.) RX, MeCN, Δ, 24 to 48h .



To a suspension of 60% NaH (1.536 g, 38.41 mmol) in mineral oil and 45 mL of DMF, at 0 °C, was added dropwise benzylbromide (4.57 mL, 38.41 mmol) followed by a solution of 2-(4-methylthiazol-5-yl)ethanol (4.18 mL, 34.91 mmol) in 25 mL of DMF. The reaction mixture was allowed to slowly warm to room temperature overnight, becoming homogenous after 30 minutes. The reaction was diluted with EtOAc (50 mL) and washed exhaustively with saturated solutions of NH_4Cl aq (5x25 mL), brine (5X25 mL), and deionized H_2O (3x25 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and concentrated to yellow oil. Column chromatography (150 mL SiO_2; 1:4 EtOAc/Hexanes) yielded 7.098 g (87%) of clear liquid as the desired compound. Rf (1:4 EtOAc/Hexanes) = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 8.57 (s, 1H), 7.37- 7.26 (m, 5H), 4.54 (s, 2H), 3.66 (t, 2H, *J* = 6.6 Hz), 3.06 (t, 2H, J = 6.6 Hz) 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 149.59, 149.23, 138.02, 128.37, 127.98, 127.63, 127.57, 73.05,

70.06, 27.03, 14.94 ppm. MS (APCI+, *m/z*) = 150.3 (3%), 234.2 (100%), 235.2 (15%), 236.2 (5%).



The previous compound (1 eq.) and an appropriate alkyl halide (0.95 eq.) were dissolved in acetonitrile at room temperature and stirred under argon. The reaction vessel was heated between 85-90 °C for 24 hours, then at room temperature for 12 hours. The solvent was removed and the nearly pure material was further isolated as described.

(a) **RX = iodomethane** An oil was triturated from Et_2O (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.72 (s, 1H), 7.31 (m, 5H), 4.54 (s, 2H), 4.32 (s, 3H), 3.74 (t, 2H, J = 5.6 Hz), 3.14 (t, 2H, J = 5.6 Hz), 2.52 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.83, 142.22, 137.09, 135.12, 128.54, 127.98, 127.91, 73.40, 67.85, 41.77, 27.98, 12.91 ppm. MS (FAB+, *m/z*) = 248.00.

(b) **RX = 1-iodobutane** ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.86 (s, 1H), 7.31 (m, 5H), 4.67 (t, 2H, J = 7.7 Hz), 4.55 (s, 2H), 3.75 (t, 2H, J = 5.6 Hz), 3.17 (t, 2H, J = 5.6 Hz), 2.54 (s, 3H), 1.90 (dt, 2H, J = 7.6 Hz), 1.47 (m, 2H), 0.98 (t, 3H, J = 7.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.96, 141.55, 137.12, 125.73, 128.66, 128.13, 128.02, 73.55, 67.90, 53.78, 32.05, 28.11, 19.57, 13.67, 12.75 ppm. MS (FAB+, *m/z*) = 290.02.

(c) **RX = 1-bromohexane** An oil was triturated from Et_2O (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 11.23 (s, 1H), 7.34-7.21 (m, 5H), 4.67 (t, 2H, J = 7.7 Hz), 4.50 (s, 2H), 3.69 (t, 2H, J = 5.5 Hz), 3.13 (t, 2H, J = 5.5 Hz), 2.48 (s, 3H), 1.85 (dt, 2H, J = 8.1,7.3 Hz), 1.38 (m, 2H), 1.27 (m, 4H), 0.82 (t, 3H, J = 7.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 157.92, 141.12, 137.04, 135.55, 128.63, 128.13, 127.99, 73.53, 67.88, 53.73, 31.17, 30.28, 27.95, 25.89, 22.42, 13.99, 12.23 ppm. HRMS (FAB+, *m/z*) = 318.1908.

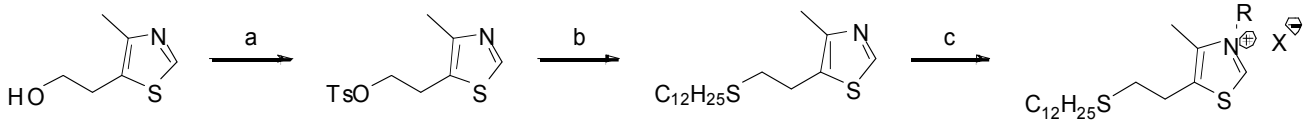
(d) **RX = benzyl chloride** An oil was triturated from Et_2O (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 11.73 (s, 1H), 7.37 – 7.24 (m, 10H), 6.10 (s, 2H), 4.51 (s, 2H), 3.68 (t, 2H, *J* = 5.5 Hz), 3.07 (t, 2H, *J* = 5.5 Hz), 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 158.60, 141.81, 136.93, 135.40, 132.14, 129.29, 129.07, 128.49, 128.16, 127.98, 127.81, 73.37, 67.68, 56.81, 27.64, 12.36 ppm. HRMS (FAB+, *m/z*) = 324.1446.

(e) **RX = 1-bromododecane** An oil was triturated from Et_2O (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 11.28 (s, 1H), 7.34-7.24 (m, 5H), 4.67 (t, 2H, J = 7.3 Hz), 4.50 (s, 2H), 3.70 (t, 2H, J = 5.3 Hz), 3.13 (t, 2H, J = 5.3 Hz), 2.49 (s, 3H),

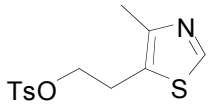
1.86 (dt, 2H, J = 7.3 Hz), 1.38 (m, 2H), 1.33-1.15 (m, 16H), 0.83 (t, 3H, J = 6.5 Hz) ppm. MS (FAB+, *m/z*) = 402.3.

(f) **RX = 1-iodohexadecane** A waxy solid was recrystallized from Et_2O ^1H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.93 (s, 1H), 7.40-7.28 (m, 5H), 4.67 (t, 2H, *J* = 7.9 Hz), 4.56 (s, 2H), 3.74 (t, 2H, *J* = 5.5 Hz), 3.12 (t, 2H, *J* = 5.5 Hz), 2.49 (s, 3H), 1.91 (dt, 2H *J* = 7.7 Hz), 1.43 (m, 2H), 1.34 (m, 2H), 1.25 (bs, 22H), 0.87 (t, 3H, *J* = 6.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C, δ) = 157.50, 141.35, 137.11, 135.67, 128.83, 128.37, 128.16, 73.78, 67.85, 54.09, 32.08, 30.44, 29.86 (b), 29.55, 29.25, 28.17, 26.38, 22.85, 14.30, 12.48 ppm. MS (FAB+, *m/z*) = 458.4.

(g) **RX = 1-iodooctadecane** A waxy solid was recrystallized from hot EtOAc/hexanes and washed with hexanes (3x) ^1H NMR (300 MHz, $CDCl_3$, 23 °C, δ) = 11.03 (s, 1H), 7.24-7.27 (m, 5H), 4.69 (t, 2H, J = 7.8 Hz), 4.56 (s, 2H), 3.74 (t, 2H, J = 5.5 Hz), 3.11 (t, 2H, J = 5.5 Hz), 2.48 (s, 3H), 1.92 (dt, 2H, J = 7.8 Hz), 1.44 (m, 2H), 1.37-1.2 (m, H), 0.88 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C, δ) = 157.49, 141.35, 137.15, 135.8, 128.91, 128.41, 128.22, 73.82, 67.91, 54.12, 32.13, 30.48, 29.90 (b), 29.73, 29.57, 29.28, 28.19, 26.42, 22.89, 14.32, 12.55 ppm. MS (FAB+, *m/z*) = 486.4.

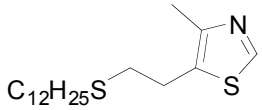


Reagents and Conditions: a.) p-tolylsulfonyl chloride, Et_3N, CH_2Cl_2, 2h, 85% b.) NaH, n-$C_{12}H_{25}SH$, DMF, 2h, rt; 50 °C, 24h, 87% c.) RX, 1:2 MeOH:MeCN, Δ, 24h

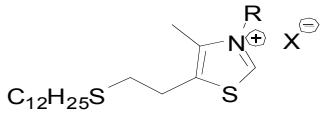


To a solution of 2-(4-methylthiazol-5-yl)ethanol (0.84 mL, 6.98 mmol) in 10 mL of CH_2Cl_2 at 0 °C, was added tosyl chloride (1.598 g, 8.38 mmol) followed by triethylamine (1.46 mL, 10.47 mmol) over two minutes. The ice bath was removed and the reaction was allowed to stir for two hours under argon. After 30 minutes, the ammonium chloride salt could be seen precipitating out of solution. The reaction was cooled in an ice water bath and 10 mL of H_2O was added. The layers were separated and the aqueous layer was extracted (3 x 10 mL) with CH_2Cl_2. The organic layers were dried with $MgSO_4$, filtered, and concentrated to an orange oil. The oil was purified by column chromatography (~150 mL of SiO_2; 1:9 EtOAC/hexanes (500 mL) then 1:1 EtOAc/hexanes (1500 mL) yielding clear oil, which became white needle-like crystalline material after cooling. A small sample of crude material was also purified by recrystallization from CH_2Cl_2/hexanes. R_f (50% EtOAc in hexanes) = 0.31. ^1H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 8.55 (s, 1H), 7.71 (d, 2H, *J* = 8.2 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 4.16 (t, 2H, *J* = 6.6 Hz), 3.11 (t, 2H, *J*

= 6.6 Hz), 2.44 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3, 23 °C, δ) = 150.66, 150.26, 145.16, 132.94, 130.06, 128.38, 69.47, 26.37, 21.83, 15.06 ppm. MS (FAB+, *m/z*) = 297.93 (100%), 298.93 (27%), 299.93 (20%).



To a slurry of 60% NaH (403 mg, 10.08 mmol) in 21 mL of DMF was added dodecane thiol (2.42 mL, 10.08 mmol) at 0 °C. After 15 minutes, the solution was warmed to room temperature. The mixture was stirred for 45 minutes to ensure formation of the thiolate. To the foamy mixture was added the previous tosylate (2.5 g, 8.406 mmol) in three 20 mL portions of DMF at room temperature. The reaction mixture was heated to 50 °C for 24 hours and cooled to room temperature. The reaction mixture was diluted with 75 mL of EtOAc and 150 mL of H_2O. The aqueous layer was separated and extracted with EtOAc (3x50 mL). The combined EtOAc layers were washed with $NaCl_{(aq)}$ (4x75 mL), and H_2O (3x25 mL) to effectively remove DMF. The EtOAc was dried ($Na_2SO_{4(s)}$), filtered, and concentrated to a nearly clear crude oil. The material was purified by column chromatography (250 mL SiO_2, 1:1 EtOAc/hexanes) to yield 2.440 g (87%) of clear oil. R_f (50% EtOAc in hexanes) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 8.56 (s, 1H), 3.02 (t, 2H, *J* = 7.7 Hz), 2.73 (t, 2H, *J* = 7.7 Hz), 2.52 (t, 2H, *J* = 7.3 Hz), 2.40 (s, 3H), 1.58 (tt, 2H, *J* = 7.3 Hz), 1.37 (m, 2H), 1.34-1.24 (m, 16H), 0.87 (t, 3H, *J* = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 149.73, 149.54, 130.21, 33.90, 32.85, 32.32, 30.06, 30.03, 30.01, 29.93, 29.75, 29.63, 29.28, 27.34, 23.09, 15.36, 14.52 ppm. MS (FAB+, *m/z*) = 215.31 (5%), 326.31(18%), 328.34 (100%), 329.32 (25%), 330.32 (17%).



The previous thiazolium compound (1 eq.) and an appropriate halide (0.95 eq.) were dissolved in a 1:1 mixture of methanol and acetonitrile at room temperature and stirred under argon in a high pressure tube with a Teflon screw top. The reaction vessel was heated between 60 -70 °C for 24 hours. The solvent was removed and the material was purified by precipitation and/or trituration as indicated.

(a) **RX = iodomethane** Oil obtained from EtOAc/Hexanes (heated, then cooled to rt); then washed with hexanes (3x) ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.93 (s, 1H), 4.39 (s, 3H), 3.14 (t, 2H, J = 6.6 Hz), 2.82 (t, 2H, J = 6.6 Hz), 2.54 (s, 3H), 2.53 (m, 2H), 1.57 (dt, 2H), 1.36 (m, 2H), 1.25 (bs, 16H), 0.87 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C, δ) = 156.84, 142.69, 136.13, 53.61,

42.19, 34.38, 32.51, 32.37, 31.98, 29.71, 29.68, 29.61, 29.41, 29.32, 28.94, 27.31, 22.75, 14.21, 13.09 ppm. HRMS (FAB+, *m/z*) = 342.2267.

(b) **RX = 1-iodobutane** Waxy solid obtained from EtOAc/hexanes precipitation, after filtration and washing with excess hexanes. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 11.00 (s, 1H), 4.69 (t, 2H, J = 7.8 Hz), 3.15 (t, 2H, J = 6.6 Hz), 2.84 (t, 2H, J = 6.6 Hz), 2.54 (s, 3H), 2.53 (t, 2H), 1.93, (dt, 2H, J = 7.7 Hz), 1.50 (m, 4H), 1.37 (m, 2H), 1.00 (t, 3H, J = 7.4 Hz), 0.87 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C, δ) = 157.27, 141.75, 136.81, 54.16, 32.79, 32.50, 32.21, 31.75, 29.86, 29.80, 29.73, 29.55, 29.44, 29.05, 27.42, 22.89, 19.77, 14.32, 13.80 ppm. HRMS (FAB+, *m/z*) = 384.2780.

(c) **RX = 1-iodohexane** Oil was triturated from EtOAc/hexanes and then from hexanes (2x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.81 (s, 1H), 4.63 (t, 2H, J = 7.7 Hz), 3.16 (t, 2H, J = 6.5 Hz), 2.81 (t, 2H, J = 6.5 Hz), 2.53 (s, 3H), 2.50 (t, 2H), 1.91 (dt, 2H, J = 7.6 Hz), 1.53 (dt, 2H, J = 7.5 Hz), 1.45-1.17 (m + bs, 21H), 0.84 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.76, 141.84, 136.72, 54.26, 53.62, 32.51, 32.39, 31.97, 31.20, 30.14, 29.70, 29.61, 29.41, 29.30, 29.16, 28.94, 27.34, 25.93, 22.75, 22.49, 14.21, 14.06 ppm. HRMS (FAB+, *m/z*) = 412.3058.

(d) **RX = 1-iodooctane** Oil was precipitated as a waxy solid from EtOAc/hexanes (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.66 (s, 1H), 4.61 (t, 2H, J = 7.7 Hz), 3.18 (t, 2H, J = 6.6 Hz), 2.86 (t, 2H, J = 6.6 Hz), 2.55 (s, 3H), 2.55 (t, 2H), 1.96 (dt, 2H, J = 7.5 Hz), 1.57 (dt, 2H, J = 7.5 Hz), 1.44 (m, 2H), 1.28 (m, 2H), 1.25 (bs, H), 0.86 (t, 3H, J = 7.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.61, 141.89, 134.53, 54.56, 32.71, 32.44, 32.08, 31.85, 30.27, 29.83, 29.80, 29.71, 29.52, 29.41, 29.25, 29.21, 29.18, 29.05, 22.85, 22.77, 14.29, 14.25 12.92 ppm (3 unresolved). HRMS (FAB+, *m/z*) = 440.3378.

(e) **RX = 1-iododecane** Waxy solid was triturated from EtOAc/hexane (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.84 (s, 1H), 4.63 (t, 2H, J = 7.7 Hz), 3.15 (t, 2H, J = 6.6 Hz), 2.81 (t, 2H, J = 6.6 Hz), 2.53 (s, 3H), 2.50 (t, 2H, J = 7.5 Hz), 1.90 (dt, 2H, J = 7.3 Hz), 1.53 (dt, 2H, J = 7.3 Hz), 1.39 (m, 2H), 1.31 (m, 2H), 1.28-1.15 (m + bs, ##H), 0.83 (t, 3H, J = 6.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.84, 141.85, 136.70, 54.27, 32.56, 32.43, 31.97, 31.90, 30.20, 29.71, 29.67, 29.60, 29.53, 29.45, 29.40, 29.32, 29.29, 29.14, 28.93, 27.36, 26.30, 22.74, 22.71, 14.18, 12.85 ppm (3 unresolved). HRMS (FAB+, *m/z*) = 468.3678.

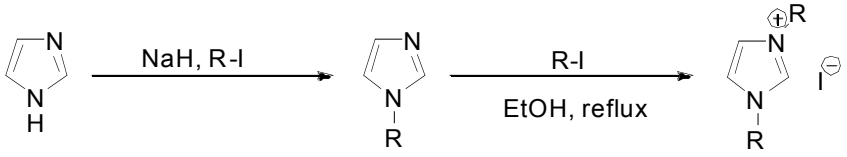
(f) **RX = 1-iodododecane** Oil was triturated with hexanes under sonication for 2 minutes (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.56 (s, 1H), 4.59 (t, 2H, J = 7.9 Hz), 3.18 (t, 2H, J = 6.6 Hz), 2.86 (t, 2H, J = 6.6 Hz), 2.55 (s, 3H), 2.54 (t, 2H, J = 7.4 Hz), 1.95 (dt, 2H, J = 7.5 Hz), 1.57 (dt, 2H, J = 7.5 Hz), 1.43 (m, 2H), 1.35 (m, 4H), 1.31-1.18 (m + bs, 30H), 0.85 (t, 6H, J = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.35, 141.94, 137.15, 54.59, 32.64, 32.40, 32.04,

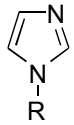
30.22, 29.79, 29.75, 29.68, 29.55, 29.47, 29.39, 29.22, 29.01, 27.56, 26.45, 22.81, 14.25, 13.00 ppm. HRMS (FAB+, *m/z*) = 496.3997.

(g) **RX = 1-iodohexadecane** Viscous oil was obtained by trituration with EtOAc/hexanes (3x). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, δ) = 10.56 (s, 1H), 4.61 (t, 2H, J = 7.7 Hz), 3.19 (t, 2H, J = 6.6 Hz), 2.87 (t, 2H, J = 6.6 Hz), 2.56 (s, 3H), 2.56 (t, 2H), 1.97 (dt, 2H, J = 7.5 Hz), 1.58 (m, 2H), 1.45 (m, 2H), 1.37 (m, 4H), 1.35-1.20 (m + bs, 38H), 0.87 (t, 6H, J = 6.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 23 °C, δ) = 156.41, 144.49, 137.24, 54.68, 32.78, 32.41, 32.13, 31.78, 30.27, 29.91, 29.87, 29.83, 29.75, 29.72, 29.69, 29.61, 29.56, 29.45, 29.28, 29.08, 27.58, 26.52, 22.89, 14.31, 12.92 ppm. HRMS (FAB+, *m/z*) = 552.4656.

(h) **RX = benzyl bromide** An oil was obtained by trituration with Et_2O (4x). ^{1}H NMR (300 MHz, $CDCl_3$, 23 °C, δ) = 11.37 (s, 1H), 7.35 (m, 5H), 6.15 (s, 2H), 3.11 (t, 2H, J = 6.6 Hz), 2.78 (t, 2H, J = 6.3 Hz), 2.48 (t, 2H), 2.47 (s, 3H), 1.53 (dt, 2H, J = 7.1 Hz), 1.40-1.20 (m+bs, 16H), 0.86 (t, 3H, J = 6.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C, δ) = 157.35, 142.41, 136.46, 131.86, 129.32, 129.18, 128.22, 57.03, 53.49, 32.31, 32.08, 31.77, 29.52, 29.46, 29.38, 29.21, 29.09, 28.71, 26.95, 22.55, 14.02, 12.73 ppm (1 unresolved). HRMS (FAB+, *m/z*) = 418.2607.

Synthesis of Imidazolium Catalysts





To a solution of imidazole (1 eq.) in DMF (0.5 M) was added 60% NaH (1.2 eq.) at 0 °C and the resulting mixture was stirred for 45min at that temperature. After bubbling off, an appropriate alkyl iodide was added at 0 °C and then the reaction was allowed to warm to room temperature and stirred overnight. The mixture was diluted with ether and washed by brine. The organic layer was dried over Na_2SO_4, filtered and concentrated to yellow oil. Column chromatography (SiO_2) was used to purify the product.

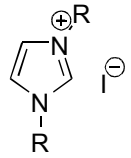
(a) **R = $C_{12}H_{25}$**, chromatography (15% EtOAc/Hexanes), ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 7.45 (s, 1H), 7.04 (s, 1H), 6.90 (s, 1H), 3.91 (t, 2H, *J* = 7.2Hz), 2.12 (m, 2H,), 1.28 (m, 18H), 0.87 (t, 3H, *J* = 6.3Hz) ppm. MS (APCI+, *m/z*) = 236.7 (100%), 472.3 (10%).

(b) **R= $C_{10}H_{21}$**, chromatography (15% EtOAc/Hexanes), ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 7.44 (s, 1H), 7.04 (s, 1H), 6.89 (s, 1H), 3.91 (t, 2H, *J* = 7.2Hz), 1.76 (m, 2H), 1.26 (m, 14H), 0.87 (t, 3H, *J* = 5.7Hz) ppm. MS (APCI+, *m/z*) = 209.5 (100%).

(c) **R = C_8H_{17}**, chromatography (CH_2Cl_2, 2% MeOH/CH_2Cl_2), ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 7.46 (s, 1H), 7.05 (s, 1H), 6.90 (s, 1H), 3.92 (t, 2H, *J* = 6.9Hz), 1.77 (m, 2H), 1.27 (m, 10H), 0.87 (t, 3H, *J* = 6.6 Hz) ppm. MS (APCI+, *m/z*) = 181.3 (100%), 361.1 (15%).

(d) **R = C_6H_{13}**, chromatography (CH_2Cl_2, 2% MeOH/CH_2Cl_2), ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 7.46 (s, 1H), 7.05 (s, 1H), 6.90 (s, 1H), 3.92 (t, 2H, *J* = 6.9Hz), 1.77 (m, 2H), 1.28 (m, 6H), 0.88 (t, 3H, *J* = 6.6Hz) ppm. MS (APCI+, *m/z*) = 153.1 (100%), 305.2 (30%).

(e) **R = C_4H_9**, chromatography (CH_2Cl_2, 5% MeOH/CH_2Cl_2), ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 7.43 (s, 1H), 7.03 (s, 1H), 6.88 (s, 1H), 3.91 (t, 2H, *J* = 7.2Hz), 1.74 (m, 2H), 1.32 (m, 2H), 0.92 (t, 3H, *J* = 7.5Hz) ppm. MS (APCI+, *m/z*) = 125.3 (100%), 249.7 (25%).



To a solution of 1-alkyl imidazole (1 eq.) from last step in absolute ethanol (0.5 M) was added the corresponding alkyl iodide (1 eq.). The resulting solution was refluxed overnight. After removing all the volatile material on rotary evaporator, the desired products were obtained without further purification.

(a) **R = $C_{12}H_{25}$**, ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 10.30 (s, 1H), 7.33 (s, 2H), 4.35 (t, 4H, *J* = 7.5Hz), 1.93 (m, 4H), 1.24 (m, 36H), 0.87 (t, 6H, *J* = 6.3Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 137.00, 122.39, 50.72, 32.28, 30.68, 29.91, 29.90, 29.78, 29.71, 29.37, 26.64, 23.06, 14.49ppm. MS (APCI+, *m/z*) = 404.45 (100%), 236.72 (15%).

(b) **R= $C_{10}H_{21}$**, ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 10.43 (s, 1H), 7.25 (s, 2H), 4.35 (t, 4H, *J* = 7.5Hz), 1.91 (m, 4H), ~1.25 (m, 28H), 0.87 (t, 6H, *J* = 6.3Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 136.92, 122.48, 50.70, 32.22, 30.68, 29.83, 29.76, 29.62, 29.37, 26.63, 23.03, 14.47 ppm. MS (APCI+, *m/z*) = 209.2 (100%), 349.3 (100%).

(c) **R = C_8H_{17}**, ^{1}H-NMR (300MHz, $CDCl_3$, 23°C, _) = 10.42 (s, 1H), 7.26 (s, 2H), 4.35 (t, 4H, *J* = 7.5Hz), 1.94 (m, 4H), ~1.26 (m, 20H), 0.87 (t, 6H, *J* = 6.6Hz)

ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 136.67, 122.67, 50.64, 32.03, 30.67, 29.39, 29.30, 26.59, 22.94, 14.42 ppm. MS (APCI+, *m/z*) = 181.3 (70%), 293.1 (100%).

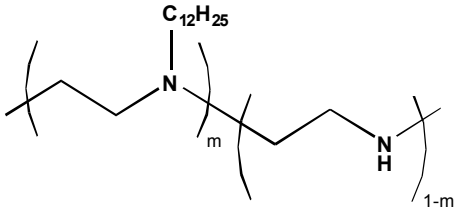
(d) **R = C_6H_{13}**, ^{1}H-NMR (300MHz, D_2O, 23°C, _) = 8.68 (s, 0.9H), 7.39 (s, 2H), 4.09 (t, 4H, *J* = 6.9Hz), 1.77 (m, 4H), 1.18 (m, 12H), 0.74 (t, 6H, *J* = 6.6Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 136.74, 122.64, 50.67, 31.42, 30.62, 26.23, 22.76, 14.23 ppm. MS (APCI+, *m/z*) = 153.0 (100%), 237.2 (75%).

(e) **R = C_4H_9**, ^{1}H-NMR (300MHz, D_2O, 23°C, _) = 8.69 (s, 1H), 7.40 (s, 2H), 4.12 (t, 4H, *J* = 6.6Hz), 1.76 (m, 4H), 1.21 (m, 4H), 0.82 (t, 6H, *J* = 7.5Hz) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 136.44, 122.86, 50.30, 32.54, 19.82, 13.87 ppm. MS (APCI+, *m/z*) = 125.2 (100%), 181.3 (60%).

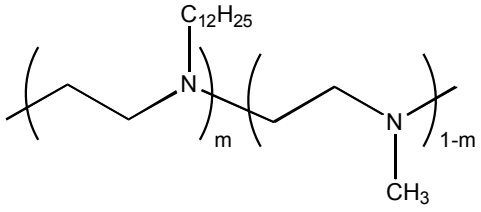
(f) **R = CH_3**, ^{1}H-NMR (300MHz, D_2O, 23°C, _) = 8.61 (s, 1H), 7.37 (s, 2H), 3.85 (s, 6H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 23 °C, _) = 136.94, 123.99, 37.77 ppm. MS (APCI+, *m/z*) = 97 (100%), 83 (80%).

* 1-Methylimidazole was directly purchased from Aldrich.

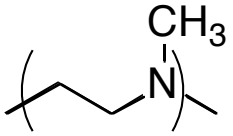
Modification of Polyethylenimine



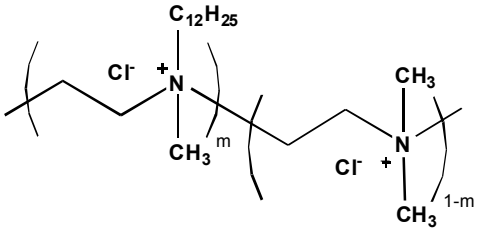
To a solution of polyethylenimine (Molecular Weight of PEI monomer (-NH-$(CH_2)_2$-) = 43.07, Sigma-Aldrich (408727), CAS 9002-98-6) (4 g) in 200 mL absolute ethanol was added 1.65 mL of bromododecane and 26 mL of triethylamine. The solution was refluxed for two days. After removing all the volatile materials by rotary evaporator, the yellow residue was put in a dialysis tube and dialyzed as follow (12 hours for each round): 50% absolute EtOH in 50mM HCl (2 rounds), 25% EtOH in 50 mM HCl (2 rounds), 10% EtOH in 50 mM HCl (2 rounds), 50 mM HCl (1 round), 50 mM aq. NaOH (1 round), deionized H_2O (1 round). 3.3g of product was obtained after lyophilizing. ^{1}H NMR (300 MHz, D_2O, 23°C, _) = 3.0-2.0 (m, 64.61H), 1.5-0.7 (s, 23H). Calculate from the NMR, 6.4% of the amine residues were laurylated.



A mixture of formaldehyde (37 wt. %, 54 mL) and formic acid (54 mL) was stirred at room temperature for one hour. A solution of laurylated PEI in distilled H_2O (42 mL) was added dropwise via addition funnel. The resulting solution was gently refluxed for four days. All the volatile materials were removed by rotary evaporator. The residue was put in a dialysis tube and dialyzed as follow (12 hours for each round): 50% absolute EtOH in 50mM HCl (2 rounds), 25% EtOH in 50mM HCl (2 rounds), 10% EtOH in 50mM HCl (2 rounds), 50mM HCl (1 round), 50mM aq. NaOH (1 round), deionized H_2O (1 round). 1.2 g of product was obtained after lyophilizing. ^{1}H NMR (300MHz, D_2O, 23°C, _) = 3.0-2.0 (m, 113.229H), 1.5-0.7 (m, 23H)



A mixture of formaldehyde (37 wt. %, 41 mL) and formic acid (45 mL) was stirred at room temperature for one hour. A solution of PEI (2.2 g) in distilled H_2O (35 mL) was added dropwise via addition funnel. The resulting solution was gently refluxed for 4 days. All the volatile materials were removed by rotary evaporator. The residue was put in a dialysis tube and dialyzed as follow (12 hours for each round): 50% absolute EtOH in 50mM HCl (2 rounds), 25% EtOH in 50mM HCl (2 rounds), 10% EtOH in 50mM HCl (2 rounds), 50mM HCl (1 round), 50mM aq. NaOH (1 round), deionized H_2O (1 round). 0.52 g of product was obtained after lyophilizing. ^{1}H NMR (300 MHz, D_2O, 23°C, _) = 2.7-2.3 (bm, 4H), 2.1 (bs, 3H)



To a suspension of cesium carbonate (32.6 g) and laurylated PEI (2.69 g) in anhydrous methanol (125 mL), 9.5 mL of dimethylsulfate was added at 0°C. The resulting suspension was stirred at 0 °C for one hour and then at r.t. for six days. The reaction was filtered and the filtrate was condensed on the rotavap. The residue was put in a dialysis tube and dialyzed as follow (12 hours for each round): 50% absolute EtOH in 50 mM HCl (2 rounds), 25% EtOH in 50 mM HCl (2 rounds), 10% EtOH in 50mM HCl (2 rounds), 50 mM HCl (1 round), 50 mM aq. NaOH (1 round), deionized H_2O (1 round). 0.8g of product was obtained after lyophilizing. ^{1}H NMR (300 MHz, D_2O, 23°C, _) = 4.3-2.2 (m, 107.18H), 0.6-1.7 (m, 23H)

Benzoin Condensation and Analysis

Instrumentation. A Waters XBridge™ phenyl 3.5_m column (4.6_150mm) was used at room temperature with eluant consisting of 40:60 (v/v) CH_3CN / 1 wt.% phosphoric acid pumped at 1.0 mL/min. Acetonitrile was purchased from Sigma Aldrich in HPLC grade. Typical retention times were 4 min for the catalysts, 10.5 min for benzaldehyde and 15.1 min for benzoin.

Kinetic Measurements. Benzaldehyde was distilled before use and was determined to be >99.5% pure by HPLC. Water was deionized and all solvents were degassed with argon prior to use. Briefly, a solution of PhCHO and the appropriate catalyst, and PEI in 10% (v/v) DMSO and buffer was degassed for one hour. During this time, the reaction vessel was brought to the reaction temperature and benzaldehyde was added. Aliquotes (0.1mL) were periodically removed, diluted with acetonitrile (0.9 mL) and injected into the HPLC. Chromatograms (see ***Figure 1***) revealed the increase of benzoin. Plotting [Benzoin] versus time gave straight lines, whose slopes were taken as the formation rate of benzoin. Slopes were calculated by OriginPro 7.0 (OriginLab Coorporation; Northampton, MA).

Imidazolium ions in aqueous solution. Initial concentrations of PhCHO, catalysts, and PEI were 40 mM, 8 mM, and 6 mM respectively. The buffer pH = 10 (K_2CO_3-K_3BO_3-KOH, Fisher product # SB116-500). Benzaldehyde was added to the refluxing solution (100 °C) under argon.

Imidazolium ions in THF. Initial concentrations of PhCHO and catalysts were 40 mM and 8 mM, respectively. The reaction solvent was THF. One normal NaOH (0.24 mL) was used in place of buffer. Benzaldehyde was added to the solution at 60 °C and under argon. The rates are plotted in Figure 2, below.

Thiazolium ions. Initial concentrations of PhCHO, catalysts, and PEI were 40 mM, 2 mM, and 6 mM respectively. The buffer pH = 8 (0.5M Na_2HPO_4). Benzaldehyde was added to the solution between 25 - 27 °C, under argon. The rate of benzoin formation for entry 1 in Table 1 of the communication was determined to be 0.014 μM/h.

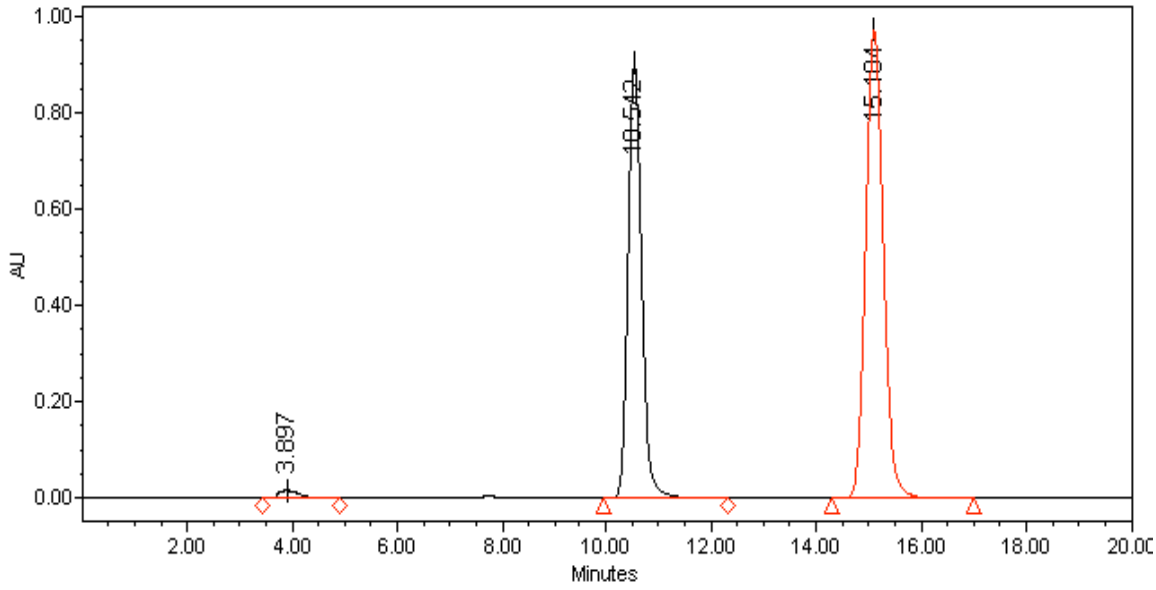


Figure 1. The standard output of HPLC for benzaldehyde and benzoin

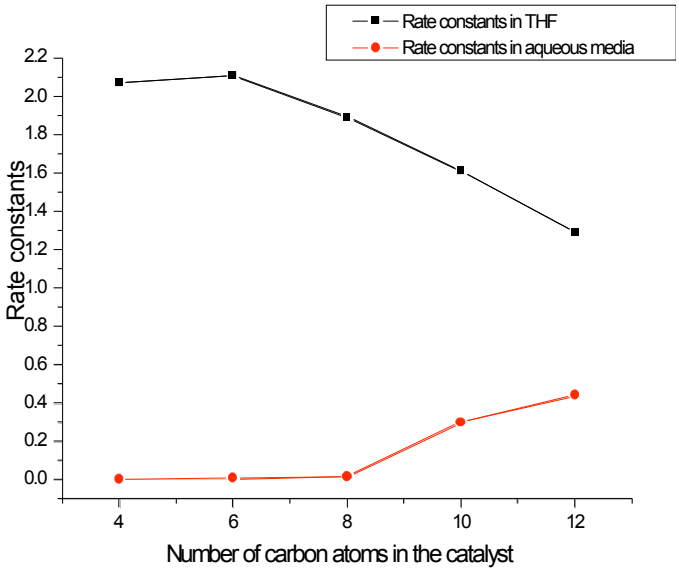


Figure 2. Trends comparison between in THF and in aqueous solution