Rapid Quantification of the Activating Effects of Hydrogen Bonding Catalysts with a Colorimetric Sensor

Phuong N. H. Huynh, Ryan R. Walvoord, and Marisa C. Kozlowski*

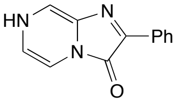
Department of Chemistry, Roy and Diana Vagelos Laboratories, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

Supporting information

1. General information

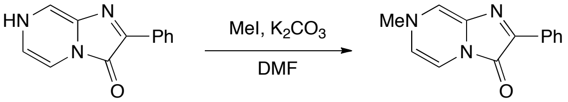
All non-aqueous reactions were carried out under an atmosphere of argon. All glassware was put in the oven at 85-90 °C overnight and flame-dried before use. The solvents for the reactions and all measurements were freshly distilled prior to use. ^{1}H-NMR spectra were recorded on Bruker AVII500B (500 MHz), Uni500 (500 MHz) or DMX-300 (300 MHz) spectrometers. NMR spectroscopic data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, b = broad, m = multiplet), coupling constants and number of protons and compared with the references. All the UV spectra were taken on a JASCO FT/IR-480 Plus from 700 nm – 380 nm.

2. Synthesis of the sensor



2-Phenylimidazo[1,2-a]pyrazin-3(7H)-one.

The title compound was prepared by a previously described procedure.[1] Spectral data are in good agreement with literature values. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.32 (bs, 1H), 8.47 (d, *J* = 7.7 Hz, 2H), 8.05 (s, 1H), 7.41-7.44 (m, 3H), 7.34 (t, *J* = 7.1 Hz, 1H), 6.89 (bd, *J* = 4.8 Hz, 1H).



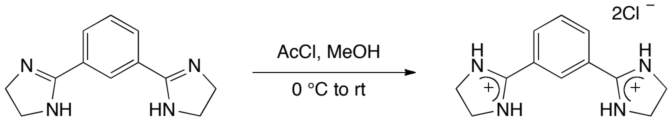
7-Methyl-2-phenylimidazo[1,2-a]pyrazin-3(7*H*)-one.

To a solution of 2-phenylimidazo[1,2-a]pyrazin-3(7H)-one (106 mg, 0.50 mmol) in DMF (0.6 mL) were added MeI (94 µL, 1.51 mmol) and K_2CO_3 (209 mg, 1.51 mmol), and the resulting solution was stirred at room temperature for 25 min. The reaction was then diluted with CH_2Cl_2 (20 mL), washed with H_2O (2 x 10 mL), brine (1 x 10 mL), dried over Na_2SO_4, filtered and concentrated. Purification by chromatography (gradient 4-10% MeOH:CH_2Cl_2) provided the title compound as a red solid (61 mg, 54%). Spectral data are in good agreement with literature values.[2] ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (d, *J* = 7.8 Hz, 2H), 8.08 (s, 1H), 7.50 (d, *J* = 5.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (td, *J* = 7.3, 1.2 Hz, 1H), 6.86 (dt, *J* = 5.8, 1.2 Hz, 1H), 3.64 (s, 3H).

3. Synthesis of catalysts

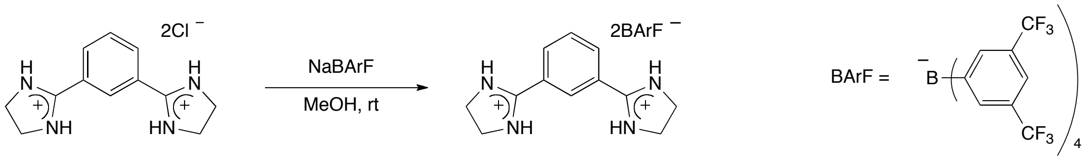
N,N'-diphenylthiourea (**2**) and (*R*)-BINOL (**3**) are commercially available.

N,N'-di(3,5-bis(trifluoromethyl)phenyl)thiourea[3] and monoaminidium BArFate salt[4] are known compounds. The ^{1}H-NMR specra matched those in reported.



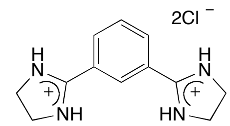
Bisamidinium Chloride.

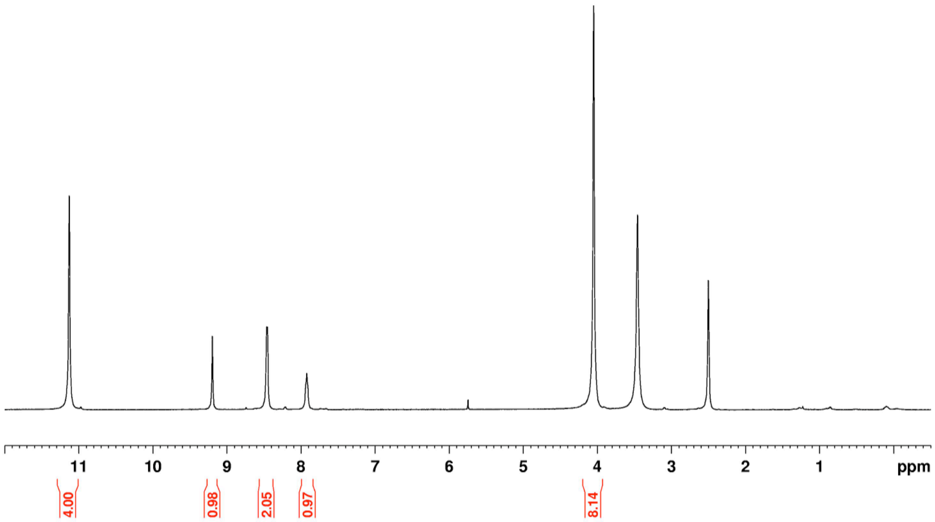
Dry MeOH (2.0 mL) was added to a dry flask under and cooled to 0 °C. Acetyl chloride (2.0 mL) was then added dropwise, and the solution was stirred for 1 h, warmed to rt and stirred for 1 h. After cooling back to 0 °C, the bisamidine substrate (150 mg, 0.7 mmol) was added and the reaction stirred for 1 h before warming to rt and stirring for an additional 17 h. Removal of the solvent afforded the product as a light tan solid (188 mg, 94%): mp: >250 °C; ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 11.13 (bs, 4H), 9.20 (s, 1H), 8.46 (bs, 2H), 7.92 (bs, 1H), 4.05 (bs, 8H); ^{13}C NMR (500 MHz, DMSO-*d*$_6$) δ 163.8, 133.8, 130.1, 130.0, 122.8, 44.5; IR (film) 3393, 1638, 1615, 1586, 1286 cm^{-1}.



Bisamidinium BArFate.

A dry flask was charged with bisamidinium chloride substrate (26 mg, 0.089 mmol), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[5] (150 mg, 0.169 mmol), and dry MeOH (1.5 mL). After stirring at rt for 21 h, the solvent was removed and dry CH_2Cl_2 (~2 mL) was added. The resulting mixture was passed through a plug of Celite and concentrated *in vacuo* to afford the product as a tan solid (157 mg, 96%): mp: 195-199 °C (dec); ^{1}H NMR (500 MHz, Acetone-*d*$_6$) δ 10.09 (b, 4H), 8.83 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 8.05 (t, *J* = 7.9 Hz, 1H), 7.79 (s, 16H), 7.67 (s, 8H), 4.39 (s, 8H); ^{13}C NMR (125 MHz, Acetone-*d*$_6$) δ 166.6, 162.7 (q, *J* = 50.0 Hz), 135.6, 135.1, 132.0, 130.1 (qq, *J* = 31.5, 2.7 Hz), 129.7, 125.4 (q, *J* = 272 Hz), 124.8, 118.5 (t, *J* = 3.7 Hz), 46.4; IR (film) 3460, 3237, 2998, 1357, 1279, 1124, 888 cm^{-1}.


2Cl −
H
N
+
NH
H
N
+
HN


11
10
9
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4
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2
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ppm
4.00
0.98
2.05
0.97
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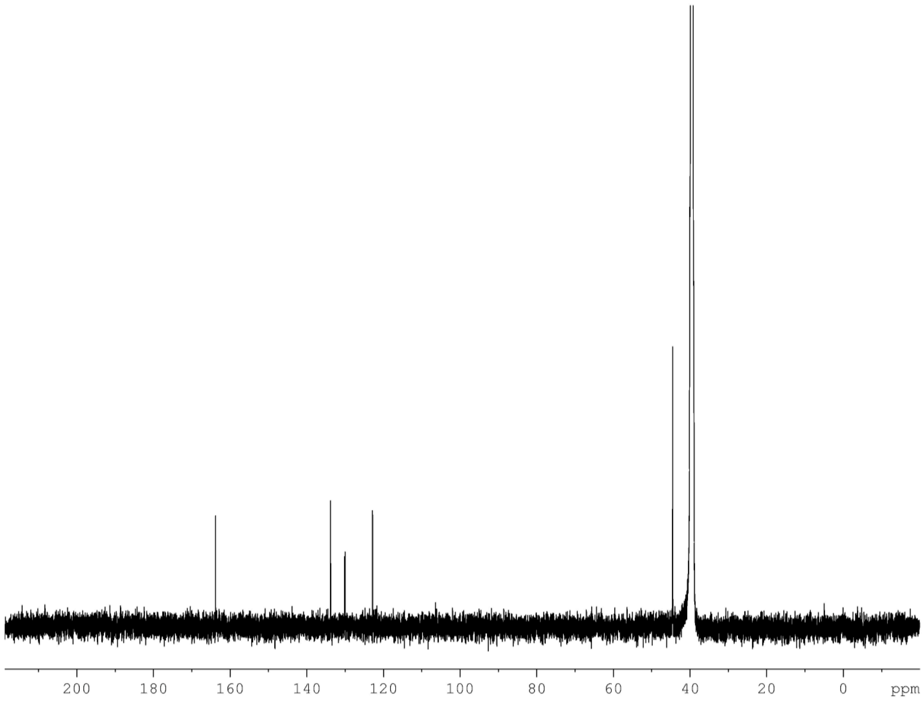
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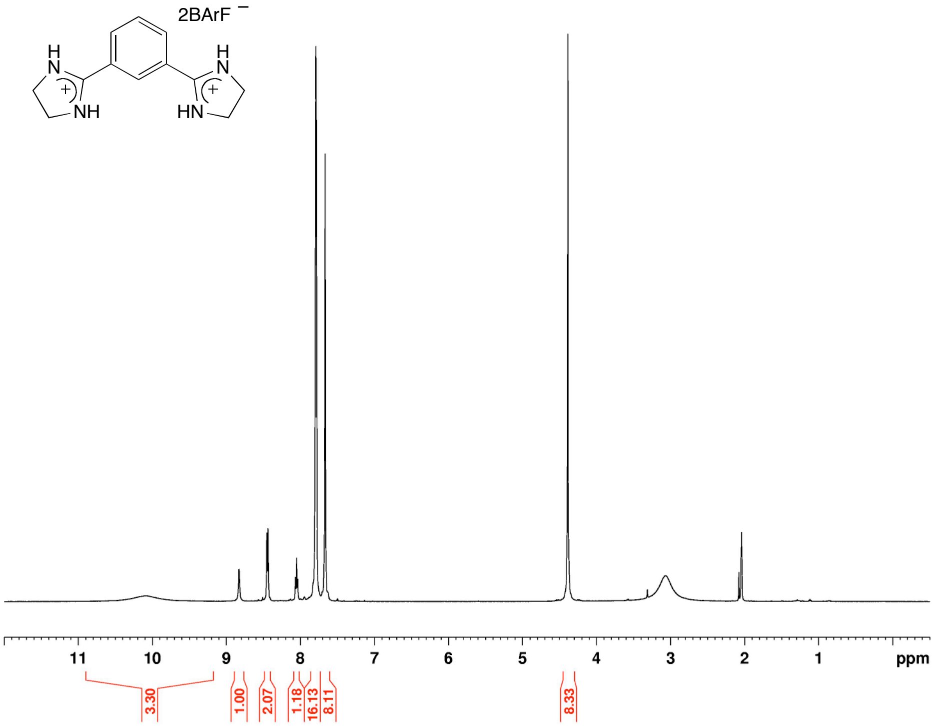
2BArF −
H
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H
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11
10
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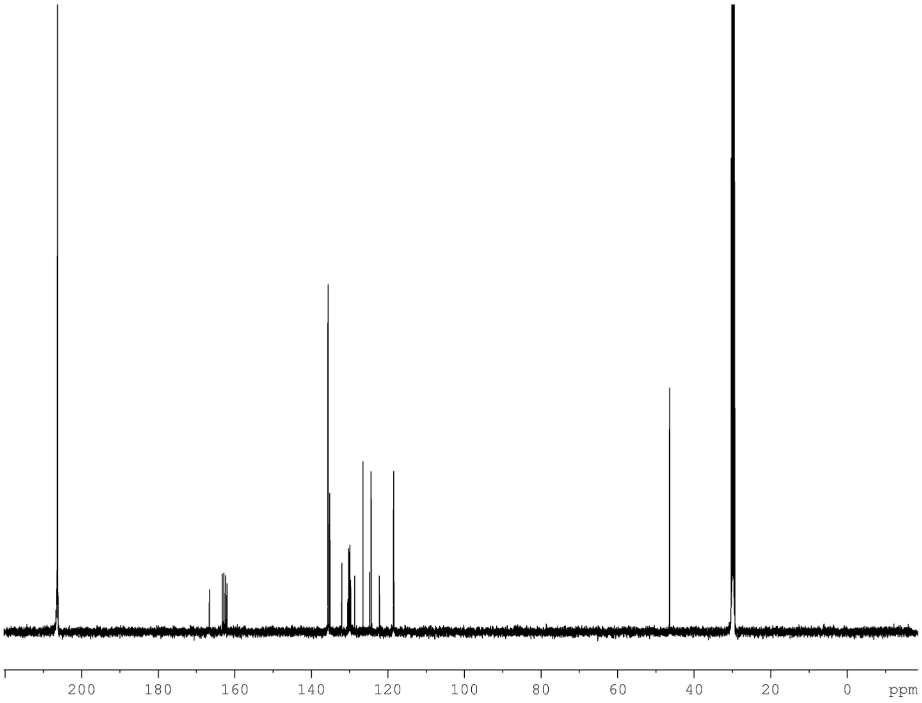
16.13
8.11
8.33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4. UV titration of sensor with different catalysts

General procedure

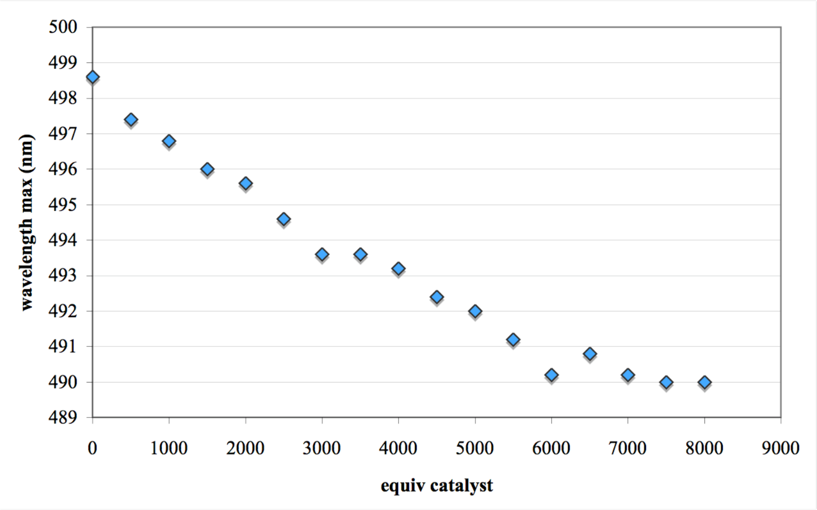
An oven-dried 10 mL volumetric flask was charged with sensor **1** (10.0 mg, 4.44×10^{-2} mmol) and diluted to the line with dichloromethane. The 2.22×10^{-5}M stock solution was prepared by transferring 50 µL of this initial solution to another 10 mL volumetric flask and diluting to the line with dichloromethane. For each UV titration experiment, 0.50 mL of the stock sensor solution was transferred to the UV cuvette.

To a Spectrosil Quartz Starna cell 2x10 mm, 0.50 mL of the 2.22×10^{-5} M sensor stock solution was added and the level of the solution was demarcated. Aliquots of the catalyst stock solution were sequentially added and the initial 0.5 mL volume was maintained by evaporation under an argon balloon to the demarcated line. The spectrum was measured after each addition and the λ_{max} was recorded. Aliquots of the catalyst stock solution were added until the λ_{max} did not change further. The titration curves of sensor with different catalysts were made by plotting the λ_{max} vs the concentration of catalyst added.

N,N'-diphenylthiourea (2)

To a oven-dried 2-dram vial, compound **2** (126.7 mg, 0.555 mmol) was added, followed by 3.0 mL dichloromethane to give a compound **2** stock solution of 0.185 M. The titration curve of compound **2** was made by adding 30.0 µL aliquots to the sensor solution (0.50 mL) in the UV cell, evaporating to constant volume (0.50 mL) with Ar, and recording the λ_{max}. Each addition increased the concentration of catalyst in the solution by 11.1×10^{-3} M.

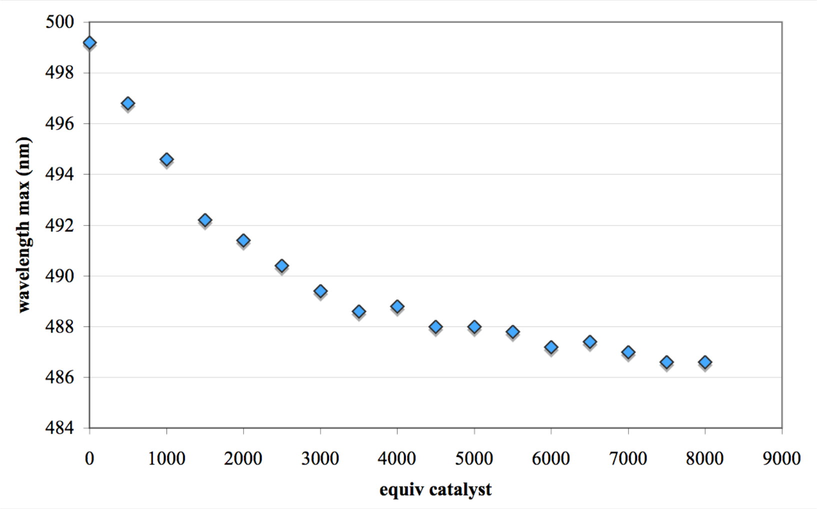
equiv catalyst	[catalyst] (10^{-3} M)	λ_{max} (nm)
0	0	498.6
500	11.1	497.4
1000	22.2	496.8
1500	33.3	496
2000	44.4	495.6
2500	55.5	494.6
3000	66.6	493.6
3500	77.7	493.6
4000	88.8	493.2
4500	99.9	492.4
5000	111	492
5500	122.1	491.2
6000	133.2	490.2
6500	144.3	490.8
7000	155.4	490.2
7500	166.5	490
8000	177.6	490



(*R*)-BINOL (3)

To an oven-dried 2-dram vial, compound **3** (158.9 mg, 0.555 mmol) was added, followed by 2 mL dichloromethane to give a compound **3** stock solution of 0.277 M. The titration curve of compound **3** was made by adding 20.0 μL aliquots to the sensor solution (0.50 mL) in the UV cell, evaporating to constant volume (0.50 mL) with Ar, and recording the λ_{max}. Each addition increased the concentration of catalyst in the solution by 11.1x10 $^{-3}$ M.

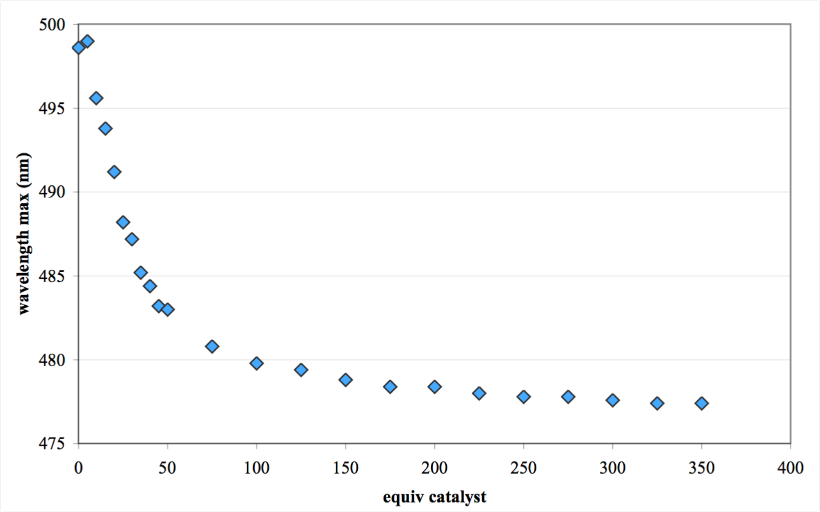
equiv catalyst	[catalyst] (10^{-3} M)	λ_{max} (nm)
0	0	499.2
500	11.1	496.8
1000	22.2	494.6
1500	33.3	492.2
2000	44.4	491.4
2500	55.5	490.4
3000	66.6	489.4
3500	77.7	488.6
4000	88.8	488.8
4500	99.9	488
5000	111	488
5500	122.1	487.8
6000	133.2	487.2
6500	144.3	487.4
7000	155.4	487
7500	166.5	486.6
8000	177.6	486.6



N,N'-di(3,5-bis(trifluoromethyl)phenyl)thiourea (4)

To a flame-dried 2-dram vial, compound **4** (5.6 mg, 11.1x10^{-3} mmol) was added, followed by 0.80 mL dichloromethane to give a compound **4** stock solution of 14.0x10^{-3} M. The titration curve of compound **4** was made by adding 4.0 µL aliquots 10 times, increasing the concentration of catalyst by 0.111x10^{-3} M with each addition, followed by 20 µL aliquots, increasing the concentration of catalyst by 0.555x10^{-3} M with each addition, until the λ_{max} did not change further not changed. The λ_{max} was recorded after evaporation with Ar to a constant volume (0.50 mL) subsequent to each addition.

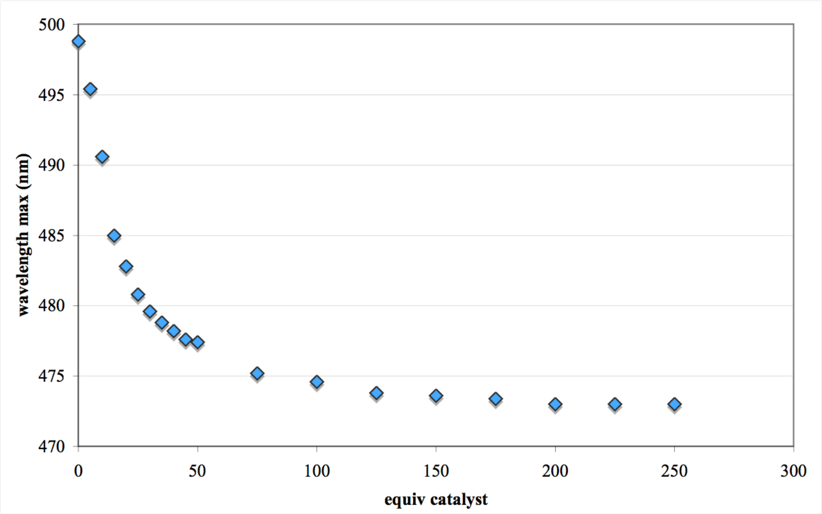
equiv catalyst	[catalyst] (10^{-3} M)	λ_{max} (nm)
0	0	498.6
5	0.111	499
10	0.222	495.6
15	0.333	493.8
20	0.444	491.2
25	0.555	488.2
30	0.666	487.2
35	0.777	485.2
40	0.888	484.4
45	0.999	483.2
50	1.11	483
75	1.665	480.8
100	2.22	479.8
125	2.775	479.4
150	3.33	478.8
175	3.885	478.4
200	4.44	478.4
225	4.995	478
250	5.55	477.8
275	6.105	477.8
300	6.66	477.6
325	7.215	477.4
350	7.77	477.4



Monoaminidium BArFate salt (5)

To a flame-dried 2-dram vial, compound **5** (5.6 mg, 5.54x10^{-3} mmol) was added, followed by 0.4 mL dichloromethane to give a compound **5** stock solution of 13.9x10^{-3} M. The titration curve of compound **5** was made by adding 4.0 µL aliquots 10 times, increasing the concentration of catalyst by 0.111x10^{-3} M with each addition, followed by 20 µL aliquots, increasing the concentration of catalyst by 0.555x10^{-3} M with each addition, until the λ_{max} did not change further not changed. The λ_{max} was recorded after evaporation with Ar to a constant volume (0.50 mL) subsequent to each addition.

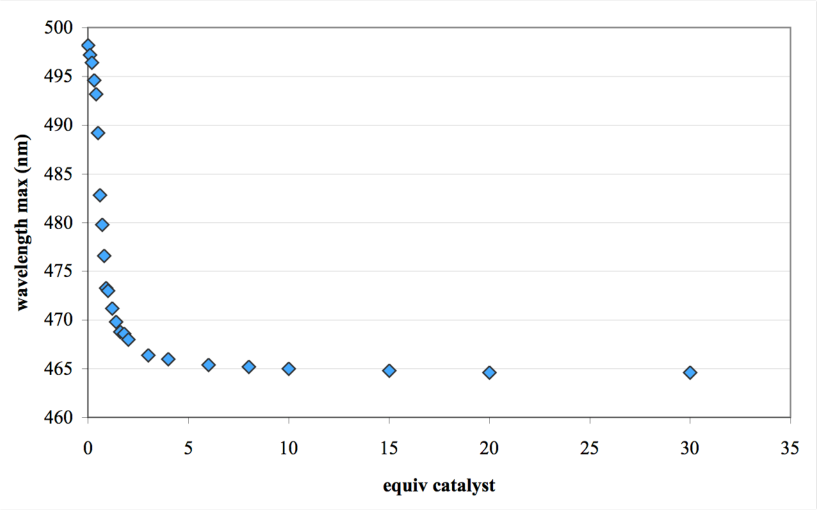
equiv catalyst	[catalyst] (10^{-3} M)	λ_{max} (nm)
0	0	498.8
5	0.111	495.4
10	0.222	490.6
15	0.333	485
20	0.444	482.8
25	0.555	480.8
30	0.666	479.6
35	0.777	478.8
40	0.888	478.2
45	0.999	477.6
50	1.11	477.4
75	1.665	475.2
100	2.22	474.6
125	2.775	473.8
150	3.33	473.6
175	3.885	473.4
200	4.44	473
225	4.995	473
250	5.55	473



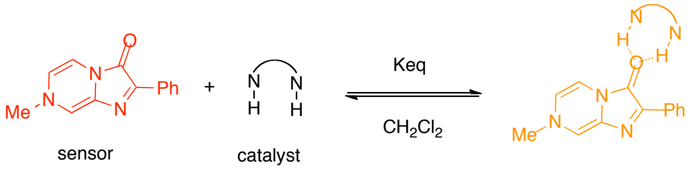
Bisamidinium BArFate salt (6)

To an oven-dried 2-dram vial, compound **6** (4.3 mg, 2.21×10^{-3} mmol) was added, followed by 1.0 mL dichloromethane to give a 2.21×10^{-3} stock solution (S1). A 1.11×10^{-4} M stock solution of compound **6** (S2) was prepared by adding 50.0 µL of S1 and diluting to 1.0 mL with dichloromethane. The titration curve of compound **6** was made by adding 10.0 µL aliquots of S2 to the sensor solution (0.50 mL) in the UV cell, evaporating to constant volume (0.50 mL) with Ar, and recording the λ_{max}. Each addition increased the concentration of catalyst in the solution by 0.00222×10^{-3} M. Additional points were made by adding 20.0 µL of S2 (1.2-2 equiv catalyst) or 5.0-100.0 µL of S1 (3-30 equiv catalyst), appropriately.

equiv catalyst	[catalyst] (10^{-3} M)	λ_{max} (nm)
0	0	498.2
0.1	0.00222	497.2
0.2	0.00444	496.4
0.3	0.00666	494.6
0.4	0.00888	493.2
0.5	0.0111	489.2
0.6	0.01332	482.8
0.7	0.01554	479.8
0.8	0.01776	476.6
0.9	0.01998	473.3
1	0.0222	473
1.2	0.02664	471.2
1.4	0.03108	469.8
1.6	0.03552	468.8
1.8	0.03996	468.6
2	0.0444	468
3	0.0666	466.4
4	0.0888	466
6	0.1332	465.4
8	0.1776	465.2
10	0.222	465
15	0.333	464.8
20	0.444	464.6
30	0.666	464.6



Calculation of the equilibrium constants (K_{eq})

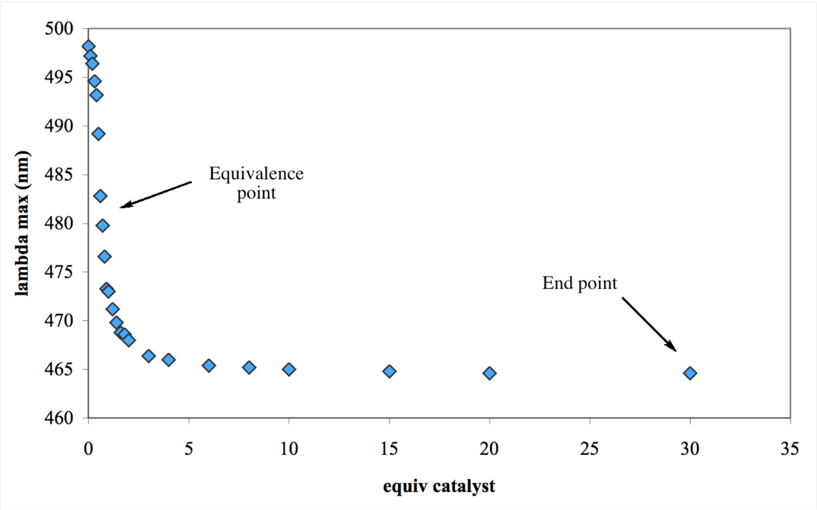


The equilibrium constants were calculated based on the equivalence points and the end points, which were determined from the UV titration curves.

$$K_{eq} = \frac{[\text{sensor} \bullet \text{catalyst}]}{[\text{sensor}] \bullet [\text{catalyst}]} \tag{1}$$

$[\text{sensor}\bullet\text{catalyst}] + [\text{sensor}] = [\text{sensor}]_{\text{total}}$

$[\text{catalyst}] + [\text{sensor}\bullet\text{catalyst}] = [\text{catalyst}]_{\text{total}}$



At the end point, all of the sensor is bound in the sensor•catalyst complex. At the equivalence point, half of the sensor is bound with the catalyst and half is unbound.

Equation (1) became: $K_{eq} = \dfrac{[\text{sensor} \bullet \text{catalyst}]_{eq}}{[\text{sensor}]_{eq} \bullet [\text{catalyst}]_{eq}}$ (2)

In this equation: $[\text{sensor}\bullet\text{catalyst}]_{eq}$ is the concentration of sensor•catalyst complex at the equivalence point

$[\text{sensor}]_{eq}$ is the concentration of sensor at the equivalence point

$[\text{catalyst}]_{eq}$ is the concentration of catalyst at the equivalence point

$[\text{sensor}\bullet\text{catalyst}]_{eq} + [\text{sensor}]_{eq} = [\text{sensor}]_{total} = 0.022\text{x}10^{-3}$ M

$[\text{sensor}\bullet\text{catalyst}]_{eq} = [\text{sensor}]_{eq} = 0.011\text{x}10^{-3}$ M

$[\text{catalyst}]_{eq} + [\text{sensor}\bullet\text{catalyst}]_{eq} = [\text{catalyst}]_{total}$

$[\text{catalyst}]_{eq} = ([\text{catalyst}]_{total} - [\text{sensor}\bullet\text{catalyst}]_{eq}) = [\text{catalyst}]_{total} - 0.011\text{x}10^{-3}$ (M)

Substitute into equation (2)

$$K_{eq} = \frac{1}{[\text{catalyst}]_{eq}} \ (\text{M}^{-1})$$

Catalyst	$[\text{catalyst}]_{total}$ (M)	$[\text{catalyst}]_{eq}$ (M)	K_{eq}
N,N’-diphenylthiourea	$5.99\text{x}10^{-2}$	$5.99\text{x}10^{-2}$	1.67x10
R-BINOL	$3.11\text{x}10^{-2}$	$3.11\text{x}10^{-2}$	3.22x10
N,N’-di(3,5-bis(trifluoromethyl)phenyl)thiourea	$5.77\text{x}10^{-4}$	$5.66\text{x}10^{-4}$	$1.77\text{x}10^{3}$
Monoaminidium BArFate salt	$3.11\text{x}10^{-4}$	$3.00\text{x}10^{-4}$	$3.34\text{x}10^{3}$
Bisamidinium BArFate salt	$1.40\text{x}10^{-5}$	$2.89\text{x}10^{-6}$	$3.47\text{x}10^{5}$

5. Rate measurements of Diels-Alder reactions of methyl vinyl ketone (MVK) and cyclopentadiene (Cp) with different catalysts

General procedure

All reagents (MVK and Cp) and internal standard (toluene) were freshly distilled before using for the reaction. All reactions were conducted with 0.1 M of MVK, 1 M (10 equiv.) of Cp, 0.1 M of internal standard and 1 mol % catalyst loading unless stated otherwise. Stocks solutions of MVK (0.75 M), Cp (7.5 M), toluene (0.75 M) and the catalysts (0.0075 M) in deuterated benzene were prepared in flame dried vials. An NMR tube was charged with 0.35 mL deuterated benzene followed by 0.10 mL of toluene solution, 0.10 mL MVK solution and 0.10 mL of catalyst solution. After adding 0.10 mL Cp solution, the solutions were mixed. The first NMR spectrum was taken after 6 minutes after the addition of Cp and additional NMR spectra were recorded every 5 minutes for 95 minutes. The methyl peak of toluene (2.12, s, 3H) was calibrated as 100. The methyl peaks of the exo product and MVK, which overlapped (1.75, s, 3H), the methyl peak of endo product (1.71, s, 3H), and the vinyl peak of MVK (5.20, d, J = 10 Hz, 1H) were integrated. The integration of the methyl peak of the exo product was calculated by subtracting three times the vinyl peak from the total of the peak from the overlapping exo product and MVK methyl signals (in the tables below corresponds to: column6 = column4 – 3*column3). The concentration of the product (total of the endo and exo products) was calculated based on the known concentration of internal standard (toluene) in the reaction using:

[product] = {(endo Me + exo Me)/100} x [toluene].

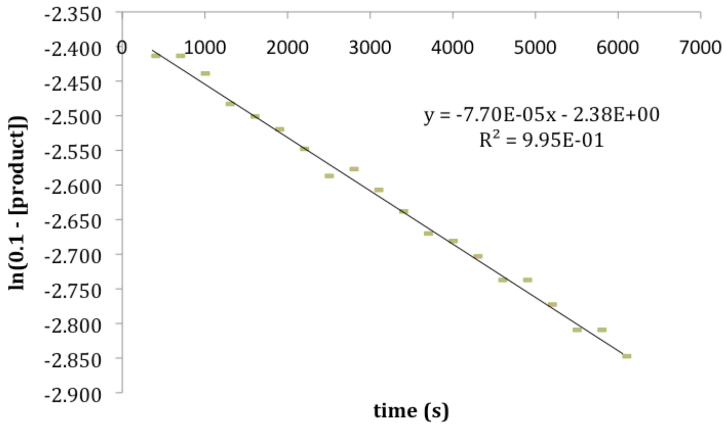
The concentration of MVK at each time point was calculated by subtracting the concentration of product from 0.1 M. The k_{obs} of each reactions was determine using the slope of the plot of the ln(0.1 – [product]) vs time. Most catalysts were subject to 2 trials and the reported k_{obs} is the average of the k_{obs} values from the 2 trials.

Background reaction (uncatalyzed reaction)

For the background reaction, 0.10 mL of deuterated benzene was added instead of 0.10 mL of catalyst solution.

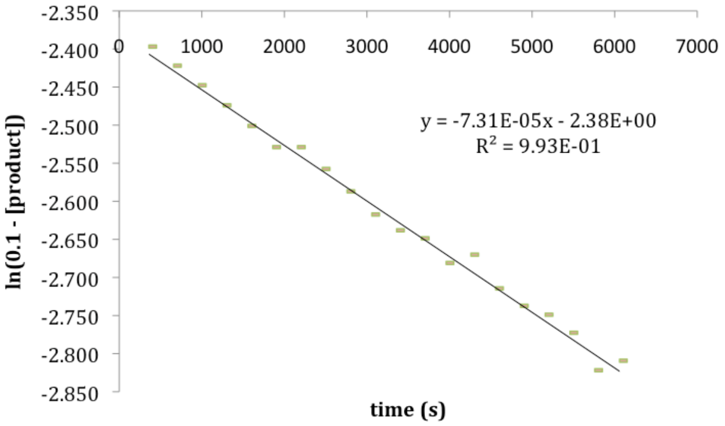
Trial 1

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	33	106	7	7	0.0105	0.0895	-2.414
660	11	33	105	8	6	0.0105	0.0895	-2.414
960	16	32	103	10	7	0.0128	0.0873	-2.439
1260	21	30	99	13	9	0.0165	0.0835	-2.483
1560	26	30	98	16	8	0.0180	0.0820	-2.501
1860	31	29	96	17	9	0.0195	0.0805	-2.519
2160	36	28	94	19	10	0.0218	0.0783	-2.548
2460	41	27	92	22	11	0.0248	0.0753	-2.587
2760	46	27	90	23	9	0.0240	0.0760	-2.577
3060	51	26	88	25	10	0.0263	0.0738	-2.607
3360	56	25	86	27	11	0.0285	0.0715	-2.638
3660	61	24	84	29	12	0.0308	0.0693	-2.670
3960	66	24	83	31	11	0.0315	0.0685	-2.681
4260	71	23	81	32	12	0.0330	0.0670	-2.703
4560	76	22	79	34	13	0.0353	0.0648	-2.737
4860	81	22	77	36	11	0.0353	0.0648	-2.737
5160	86	21	76	37	13	0.0375	0.0625	-2.773
5460	91	20	75	38	15	0.0398	0.0603	-2.809
5760	96	20	73	40	13	0.0398	0.0603	-2.809
6060	101	19	72	41	15	0.0420	0.0580	-2.847



Trial 2

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	32	102	6	6	0.0090	0.0910	-2.397
660	11	31	100	8	7	0.0113	0.0888	-2.422
960	16	30	97	11	7	0.0135	0.0865	-2.448
1260	21	29	95	13	8	0.0158	0.0843	-2.474
1560	26	28	93	15	9	0.0180	0.0820	-2.501
1860	31	27	91	17	10	0.0203	0.0798	-2.529
2160	36	27	89	19	8	0.0203	0.0798	-2.529
2460	41	26	87	21	9	0.0225	0.0775	-2.557
2760	46	25	85	23	10	0.0248	0.0753	-2.587
3060	51	24	83	25	11	0.0270	0.0730	-2.617
3360	56	23	81	26	12	0.0285	0.0715	-2.638
3660	61	23	80	28	11	0.0293	0.0708	-2.649
3960	66	22	78	30	12	0.0315	0.0685	-2.681
4260	71	22	76	31	10	0.0308	0.0693	-2.670
4560	76	21	75	33	12	0.0338	0.0663	-2.714
4860	81	20	73	34	13	0.0353	0.0648	-2.737
5160	86	20	72	36	12	0.0360	0.0640	-2.749
5460	91	19	70	37	13	0.0375	0.0625	-2.773
5760	96	18	69	39	15	0.0405	0.0595	-2.822
6060	101	18	67	40	13	0.0398	0.0603	-2.809

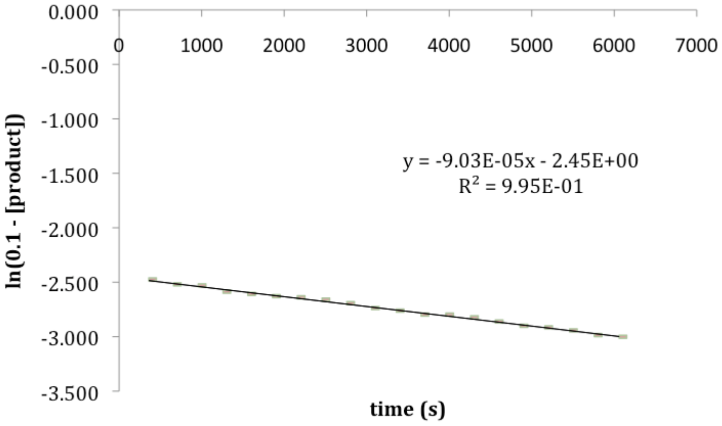


***N,N'*-diphenylthiourea (2)**

This catalyst was used at 10 mol% loading, so the concentration of catalyst stock solution was prepared at 0.0075 M.

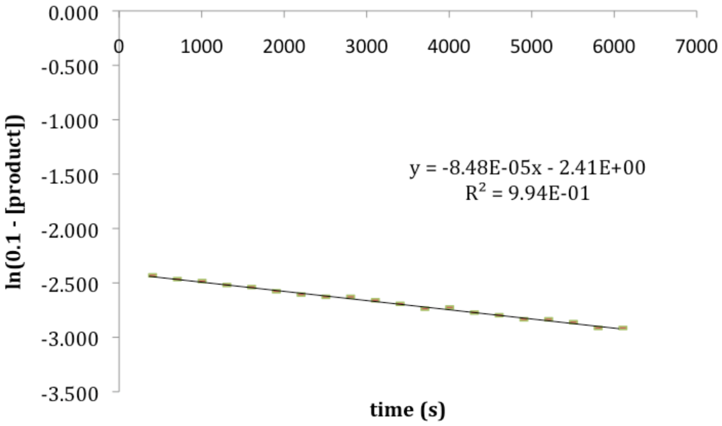
Trial 1

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	36	122	7	14	0.0158	0.0843	-2.474
660	11	34	118	10	16	0.0195	0.0805	-2.519
960	16	34	117	12	15	0.0203	0.0798	-2.529
1260	21	32	113	16	17	0.0248	0.0753	-2.587
1560	26	31	110	18	17	0.0263	0.0738	-2.607
1860	31	30	107	20	17	0.0278	0.0723	-2.628
2160	36	30	105	23	15	0.0285	0.0715	-2.638
2460	41	29	102	25	15	0.0300	0.0700	-2.659
2760	46	28	99	28	15	0.0323	0.0678	-2.692
3060	51	27	98	30	17	0.0353	0.0648	-2.737
3360	56	26	95	32	17	0.0368	0.0633	-2.761
3660	61	25	93	34	18	0.0390	0.0610	-2.797
3960	66	25	91	36	16	0.0390	0.0610	-2.797
4260	71	24	88	38	16	0.0405	0.0595	-2.822
4560	76	23	86	40	17	0.0428	0.0573	-2.860
4860	81	22	85	41	19	0.0450	0.0550	-2.900
5160	86	22	83	44	17	0.0458	0.0543	-2.914
5460	91	21	81	45	18	0.0473	0.0528	-2.942
5760	96	20	79	47	19	0.0495	0.0505	-2.986
6060	101	20	78	49	18	0.0503	0.0498	-3.001



Trial 2

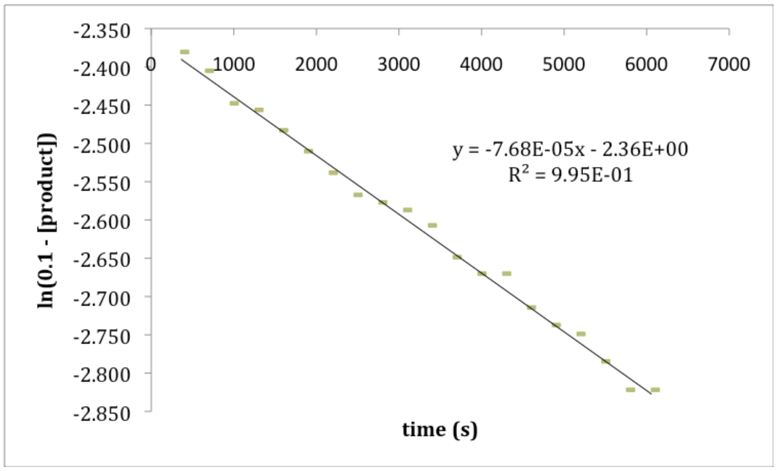
Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	33	108	7	9	0.0120	0.0880	-2.430
660	11	32	108	8	12	0.0150	0.0850	-2.465
960	16	31	104	11	11	0.0165	0.0835	-2.483
1260	21	30	103	13	13	0.0195	0.0805	-2.519
1560	26	29	100	15	13	0.0210	0.0790	-2.538
1860	31	28	98	18	14	0.0240	0.0760	-2.577
2160	36	27	96	20	15	0.0263	0.0738	-2.607
2460	41	26	93	22	15	0.0278	0.0723	-2.628
2760	46	26	91	24	13	0.0278	0.0723	-2.628
3060	51	25	89	26	14	0.0300	0.0700	-2.659
3360	56	24	87	28	15	0.0323	0.0678	-2.692
3660	61	23	86	30	17	0.0353	0.0648	-2.737
3960	66	23	83	32	14	0.0345	0.0655	-2.726
4260	71	22	82	34	16	0.0375	0.0625	-2.773
4560	76	21	80	35	17	0.0390	0.0610	-2.797
4860	81	20	78	37	18	0.0413	0.0588	-2.834
5160	86	20	76	39	16	0.0413	0.0588	-2.834
5460	91	19	74	40	17	0.0428	0.0573	-2.860
5760	96	18	73	42	19	0.0458	0.0543	-2.914
6060	101	18	72	43	18	0.0458	0.0543	-2.914



R-BINOL (3)

Trial 1

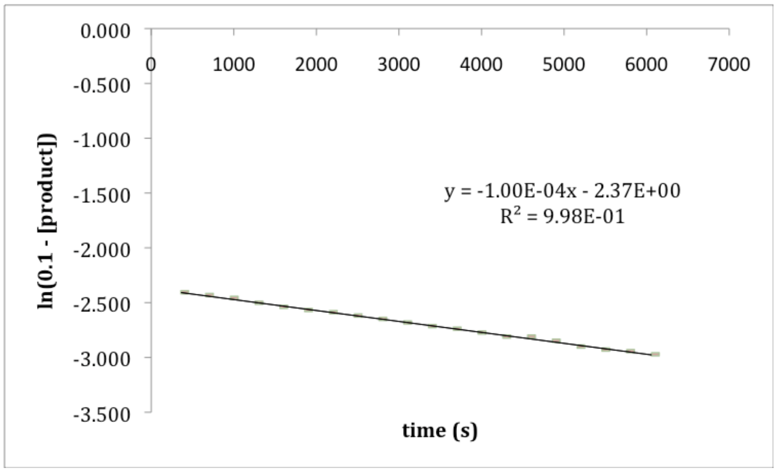
Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	34	107	5	5	0.0075	0.0925	-2.381
660	11	33	104	8	5	0.0098	0.0903	-2.405
960	16	31	101	10	8	0.0135	0.0865	-2.448
1260	21	31	100	12	7	0.0143	0.0858	-2.456
1560	26	30	98	14	8	0.0165	0.0835	-2.483
1860	31	29	95	17	8	0.0188	0.0813	-2.510
2160	36	28	93	19	9	0.0210	0.0790	-2.538
2460	41	27	92	20	11	0.0233	0.0768	-2.567
2760	46	26	88	22	10	0.0240	0.0760	-2.577
3060	51	26	86	25	8	0.0248	0.0753	-2.587
3360	56	25	84	26	9	0.0263	0.0738	-2.607
3660	61	24	83	28	11	0.0293	0.0708	-2.649
3960	66	23	80	30	11	0.0308	0.0693	-2.670
4260	71	23	79	31	10	0.0308	0.0693	-2.670
4560	76	22	78	33	12	0.0338	0.0663	-2.714
4860	81	21	76	34	13	0.0353	0.0648	-2.737
5160	86	21	75	36	12	0.0360	0.0640	-2.749
5460	91	20	74	37	14	0.0383	0.0618	-2.785
5760	96	19	72	39	15	0.0405	0.0595	-2.822
6060	101	19	71	40	14	0.0405	0.0595	-2.822



***N,N'*-di(3,5-bis(trifluoromethyl)phenyl)thiourea (4)**

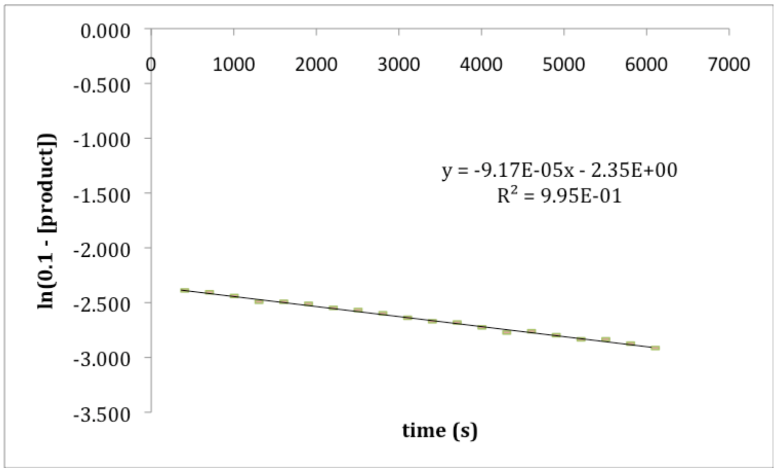
Trial 1

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	35	110	8	5	0.0098	0.0903	-2.405
660	11	34	107	11	5	0.0120	0.0880	-2.430
960	16	33	104	14	5	0.0143	0.0858	-2.456
1260	21	31	100	17	7	0.0180	0.0820	-2.501
1560	26	30	98	20	8	0.0210	0.0790	-2.538
1860	31	29	95	23	8	0.0233	0.0768	-2.567
2160	36	28	92	25	8	0.0248	0.0753	-2.587
2460	41	27	90	27	9	0.0270	0.0730	-2.617
2760	46	26	87	30	9	0.0293	0.0708	-2.649
3060	51	25	85	32	10	0.0315	0.0685	-2.681
3360	56	24	83	34	11	0.0338	0.0663	-2.714
3660	61	23	80	36	11	0.0353	0.0648	-2.737
3960	66	22	78	38	12	0.0375	0.0625	-2.773
4260	71	21	76	40	13	0.0398	0.0603	-2.809
4560	76	21	74	42	11	0.0398	0.0603	-2.809
4860	81	20	72	44	12	0.0420	0.0580	-2.847
5160	86	19	71	46	14	0.0450	0.0550	-2.900
5460	91	18	69	47	15	0.0465	0.0535	-2.928
5760	96	18	68	49	14	0.0473	0.0528	-2.942
6060	101	17	65	51	14	0.0488	0.0513	-2.971



Trial 2

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	33	103	7	4	0.0083	0.0918	-2.389
660	11	32	100	9	4	0.0098	0.0903	-2.405
960	16	31	98	12	5	0.0128	0.0873	-2.439
1260	21	29	95	15	8	0.0173	0.0828	-2.492
1560	26	29	93	17	6	0.0173	0.0828	-2.492
1860	31	28	90	19	6	0.0188	0.0813	-2.510
2160	36	27	89	21	8	0.0218	0.0783	-2.548
2460	41	26	85	24	7	0.0233	0.0768	-2.567
2760	46	25	83	26	8	0.0255	0.0745	-2.597
3060	51	24	81	29	9	0.0285	0.0715	-2.638
3360	56	23	79	31	10	0.0308	0.0693	-2.670
3660	61	22	76	32	10	0.0315	0.0685	-2.681
3960	66	21	74	35	11	0.0345	0.0655	-2.726
4260	71	20	73	37	13	0.0375	0.0625	-2.773
4560	76	20	71	38	11	0.0368	0.0633	-2.761
4860	81	19	69	40	12	0.0390	0.0610	-2.797
5160	86	18	67	42	13	0.0413	0.0588	-2.834
5460	91	18	66	43	12	0.0413	0.0588	-2.834
5760	96	17	64	45	13	0.0435	0.0565	-2.874
6060	101	16	63	46	15	0.0458	0.0543	-2.914

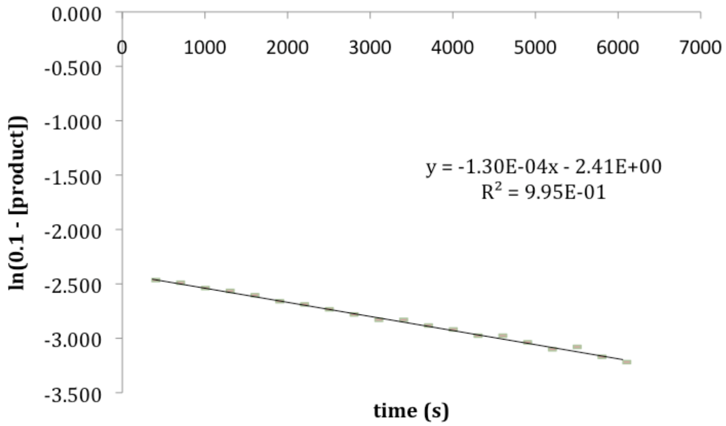


Monoaminidium BArFate salt (5)

The internal standard was used in the reaction at 0.1 M. The stock solution of toluene in dichloromethane was prepared at 0.075 M.

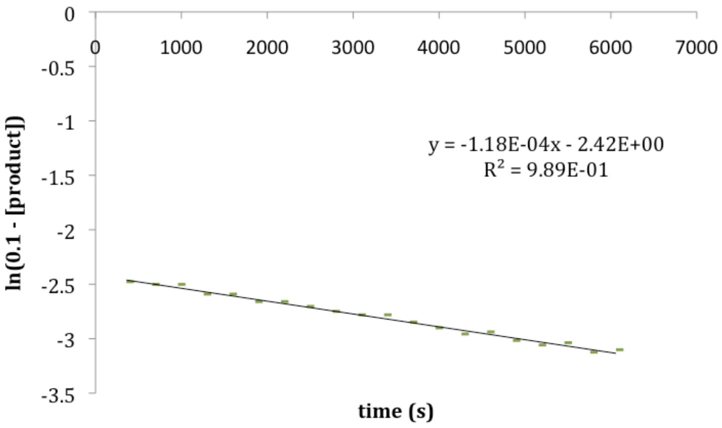
Trial 1

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	33	107	7	8	0.0150	0.0850	-2.465
660	11	32	103	10	7	0.0170	0.0830	-2.489
960	16	31	101	13	8	0.0210	0.0790	-2.538
1260	21	30	98	15	8	0.0230	0.0770	-2.564
1560	26	29	96	17	9	0.0260	0.0740	-2.604
1860	31	28	94	20	10	0.0300	0.0700	-2.659
2160	36	27	91	22	10	0.0320	0.0680	-2.688
2460	41	26	89	24	11	0.0350	0.0650	-2.733
2760	46	25	87	26	12	0.0380	0.0620	-2.781
3060	51	24	85	28	13	0.0410	0.0590	-2.830
3360	56	24	83	30	11	0.0410	0.0590	-2.830
3660	61	23	81	32	12	0.0440	0.0560	-2.882
3960	66	22	79	33	13	0.0460	0.0540	-2.919
4260	71	21	77	35	14	0.0490	0.0510	-2.976
4560	76	21	75	37	12	0.0490	0.0510	-2.976
4860	81	20	74	38	14	0.0520	0.0480	-3.037
5160	86	19	72	40	15	0.0550	0.0450	-3.101
5460	91	19	70	41	13	0.0540	0.0460	-3.079
5760	96	18	69	43	15	0.0580	0.0420	-3.170
6060	101	17	67	44	16	0.0600	0.0400	-3.219



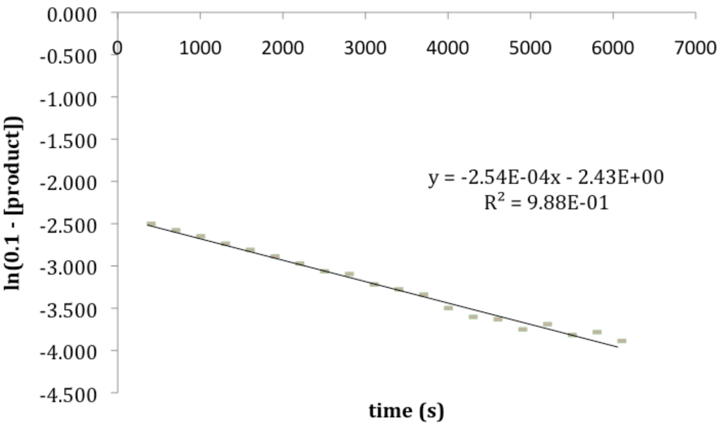
Trial 2

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	32	105	7	9	0.0160	0.0840	-2.477
660	11	31	102	9	9	0.0180	0.0820	-2.501
960	16	31	99	12	6	0.0180	0.0820	-2.501
1260	21	29	98	14	11	0.0250	0.0750	-2.590
1560	26	29	96	16	9	0.0250	0.0750	-2.590
1860	31	27	93	18	12	0.0300	0.0700	-2.659
2160	36	27	90	21	9	0.0300	0.0700	-2.659
2460	41	26	89	22	11	0.0330	0.0670	-2.703
2760	46	25	86	25	11	0.0360	0.0640	-2.749
3060	51	24	84	26	12	0.0380	0.0620	-2.781
3360	56	24	82	28	10	0.0380	0.0620	-2.781
3660	61	23	81	30	12	0.0420	0.0580	-2.847
3960	66	22	79	32	13	0.0450	0.0550	-2.900
4260	71	21	77	34	14	0.0480	0.0520	-2.957
4560	76	21	75	35	12	0.0470	0.0530	-2.937
4860	81	20	74	37	14	0.0510	0.0490	-3.016
5160	86	19	72	38	15	0.0530	0.0470	-3.058
5460	91	19	70	39	13	0.0520	0.0480	-3.037
5760	96	18	69	41	15	0.0560	0.0440	-3.124
6060	101	18	67	42	13	0.0550	0.0450	-3.101



Bisamidinium BArFate salt (6)

Time (s)	Time (min)	MVK vinyl(1H)	MVK + exo product Me (3H)	Endo product Me (3H)	Exo product Me (3H)	[product] (M)	0.1-[product] (M)	ln(0.1-[product])
360	6	33	104	19	5	0.0180	0.0820	-2.501
660	11	30	96	26	6	0.0240	0.0760	-2.577
960	16	28	90	33	6	0.0293	0.0708	-2.649
1260	21	25	82	40	7	0.0353	0.0648	-2.737
1560	26	23	77	45	8	0.0398	0.0603	-2.809
1860	31	21	71	51	8	0.0443	0.0558	-2.887
2160	36	19	66	56	9	0.0488	0.0513	-2.971
2460	41	17	61	61	10	0.0533	0.0468	-3.063
2760	46	16	57	64	9	0.0548	0.0453	-3.096
3060	51	14	54	68	12	0.0600	0.0400	-3.219
3360	56	13	50	72	11	0.0623	0.0378	-3.277
3660	61	12	47	75	11	0.0645	0.0355	-3.338
3960	66	11	46	80	13	0.0698	0.0303	-3.498
4260	71	10	43	84	13	0.0728	0.0273	-3.603
4560	76	8	39	83	15	0.0735	0.0265	-3.631
4860	81	8	38	88	14	0.0765	0.0235	-3.751
5160	86	7	34	87	13	0.0750	0.0250	-3.689
5460	91	6	33	89	15	0.0780	0.0220	-3.817
5760	96	6	31	90	13	0.0773	0.0228	-3.783
6060	101	5	29	92	14	0.0795	0.0205	-3.887



Equations

Based on the UV measurements:

$K_{eq} = e^{-\Delta G/RT} \Rightarrow \Delta G \propto \ln(K_{eq})$

$E = h\upsilon$, h = Planck constant $\Rightarrow \Delta E = h(\upsilon_1 - \upsilon_2) = h(1/\lambda_1 - 1/\lambda_2)$

λ_1 = maximum wavelength of the sensor•catalyst complex in dichloromethane (read at the end point of each titrations)

λ_2 = maximum wavelength of the sensor in dichloromethane (498.6 nm)

Based on the rate measurements:

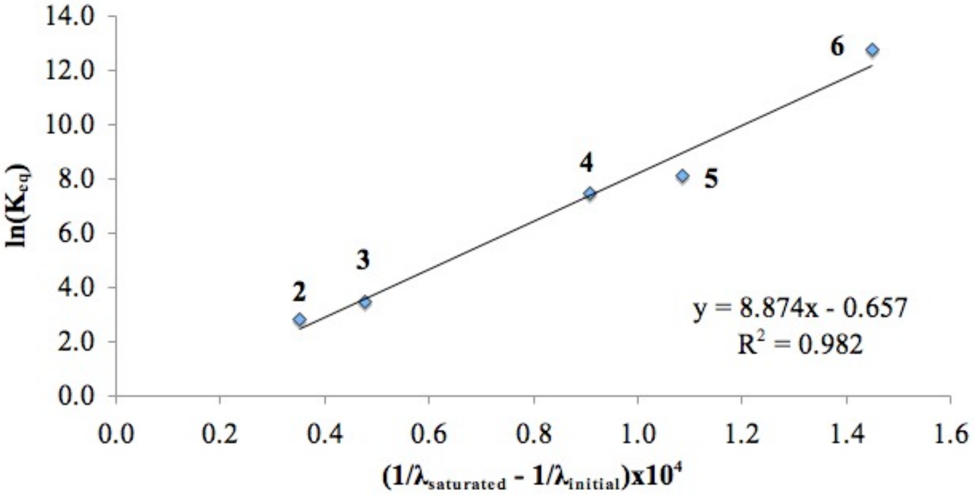
rate = k_{obs}[cat]

Arrhenius equation: $k_{obs} = Ae^{-Ea/RT}$

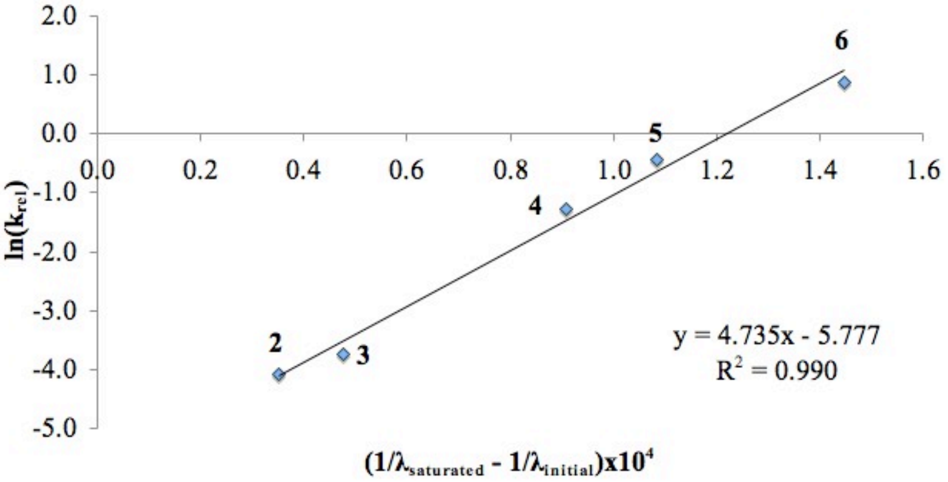
$k_{rel} = k_{cat}/k_{uncat} = Ae^{(Ea\ uncat - Ea\ cat)/RT} \Rightarrow \Delta E_a \propto \ln(k_{rel})$

$k_{cat} = k_{obs} - k_{uncat}$

catalyst	λ_1 (nm)	K_{eq} (M^{-1})	k_{obs} (10^{-5} s^{-1})	cat loading	k_{cat} (10^{-5} s^{-1})	k_{rel}	$\Delta(1/\lambda_{max})$ x10^4	ln(K_{eq})	ln(k_{rel})
uncat			7.50						
2	490	1.67x10	8.76	10	0.126	0.0168	0.352	2.815	-4.086
3	487	3.22x10	7.68	1	0.180	0.0240	0.478	3.472	-3.730
4	477	1.77x10^3	9.59	1	2.09	0.279	0.908	7.477	-1.278
5	473	3.34x10^3	12.4	1	4.90	0.653	1.09	8.113	-0.426
6	465	3.47x10^5	25.4	1	17.9	2.39	1.45	12.76	0.870



Correlation between wavelength shift and K_{eq}.



Correlation of Diels-Alder k_{rel} values from different hydrogen bonding catalysts with their wavelength shifts of sensor **1.**

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