Solvent Effects on the Aggregation and Reactivity of Lithium Enolates

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Supporting Information

Extinction Coefficient Measurements

Table S1. Spectral data for LiPhIBP in MTBE and DME.

MTBE			DME		
{PhIBP}[a] M	λ_{max}, nm	Absorbance (1 mm cell)	{PhIBP}[a] M	λ_{max}, nm	Absorbance (1 mm cell)
5.15E-03	328.0	2.20	4.47E-03	346.5	2.4
4.02E-03	331.0	1.67	3.18E-03	346.0	1.7
3.36E-03	329.0	1.40	2.61E-03	345.5	1.38
2.74E-03	330.5	1.23	2.07E-03	347.0	1.09
2.34E-03	330.5	0.95	1.68E-03	347.5	0.89
2.08E-03	331.0	0.84	1.35E-03	347.5	0.71
1.82E-03	330.0	0.74	1.06E-03	348.0	0.56
1.58E-03	330.5	0.64	8.38E-04	349.0	0.44
1.32E-03	331.5	0.53			
1.09E-03	331.0	0.43			
8.78E-04	330.0	0.35			
6.94E-04	331.5	0.27			

(a) Formal concentration

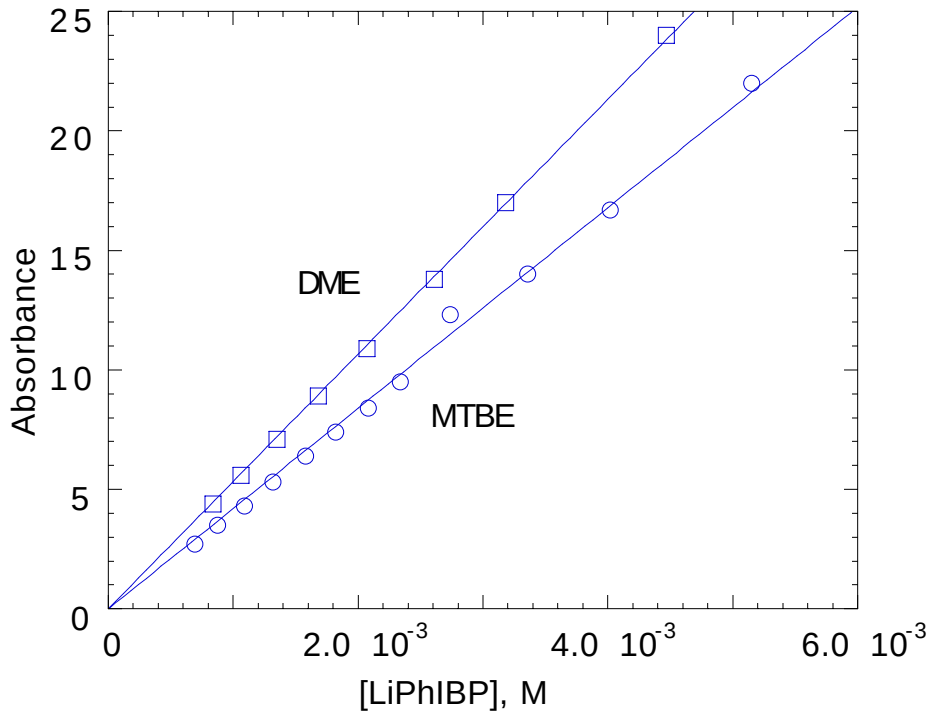


Figure S1. Extinction coefficient of LiPhIBP in MTBE and DME. Slopes of lines shown are MTBE, 4197 ± 39; DME, 5331 ± 16.

Table S2. Spectral data for LiPhAT in DME

{LiPhAT}[a] (M)	λ_{max} (nm)	Absorbance at 365 nm	absorbance at λ_{max}	[Monomer] from SVD	[Dimer] from SVD
Series 1	(1 mm cell)				
0.000961	362.5	1.6217	1.6244	3.02E-04	3.39E-04
0.000804	363	1.3619	1.3657	2.72E-04	2.75E-04
0.000674	363.5	1.1304	1.1322	2.45E-04	2.19E-04
0.000587	362.5	0.9876	0.9899	2.24E-04	1.86E-04
0.000522	364.5	0.8763	0.8763	2.08E-04	1.60E-04
0.000468	364	0.7903	0.7906	1.93E-04	1.41E-04
0.000427	364	0.7186	0.7192	1.82E-04	1.25E-04
0.000381	365.5	0.6347	0.6347	1.69E-04	1.07E-04
0.000335	364.5		0.5449	1.54E-04	8.78E-05
0.000291	364		0.4666	1.40E-04	7.15E-05
0.000240	365		0.3828	1.22E-04	5.43E-05
0.000181	365		0.2841	9.99E-05	3.60E-05
Series 2	(1 cm cell)				
8.8E-05	368.5		1.4202	5.88E-05	1.31E-05
6.8E-05	369		1.0940	4.74E-05	9.02E-06
6.4E-05	369		1.0345	4.54E-05	8.23E-06

(a) Formal concentration

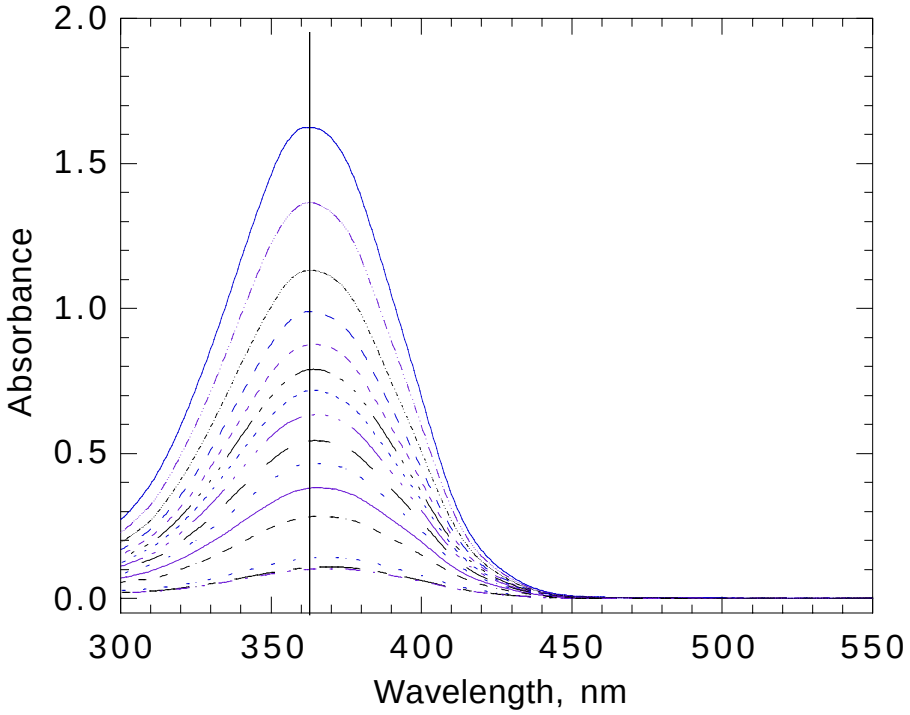


Figure S2. Spectra of LiPhAT in DME in 1 mm cell. Bottom three spectra were taken in a 1 cm cell. The vertical line shows the shift of λ_{max} to longer wavelength at lower concentration.

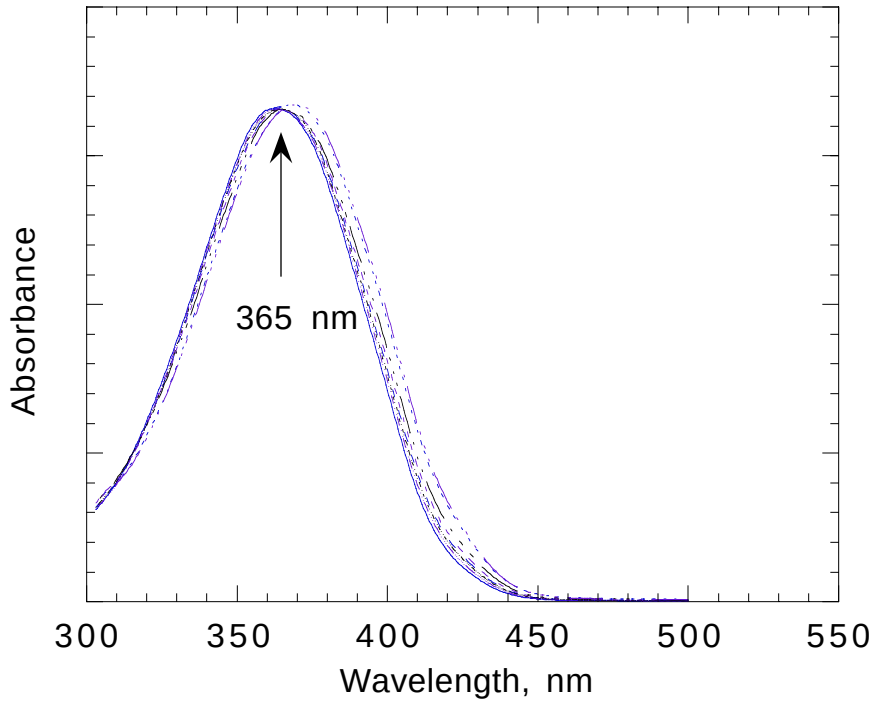


Figure S3. Normalized spectra of LiPhAT in DME showing isosbestic point at 365 nm. Only every other spectrum is shown for clarity.

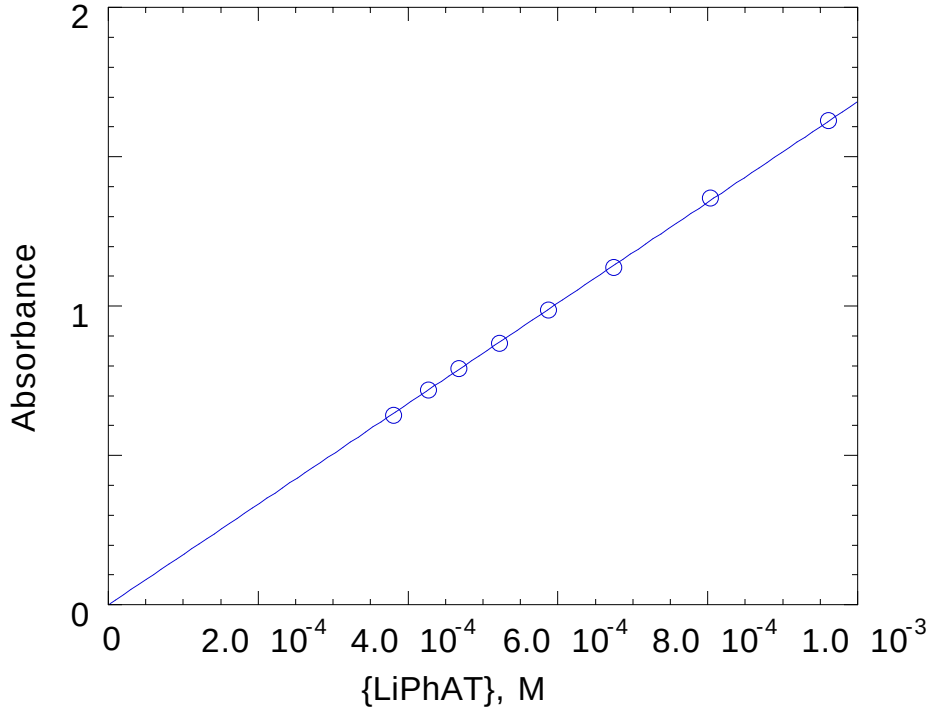


Figure S4. Extinction coefficient of LiPhAT in DME at isosbestic point. Slope of line shown is 1685 ± 3.

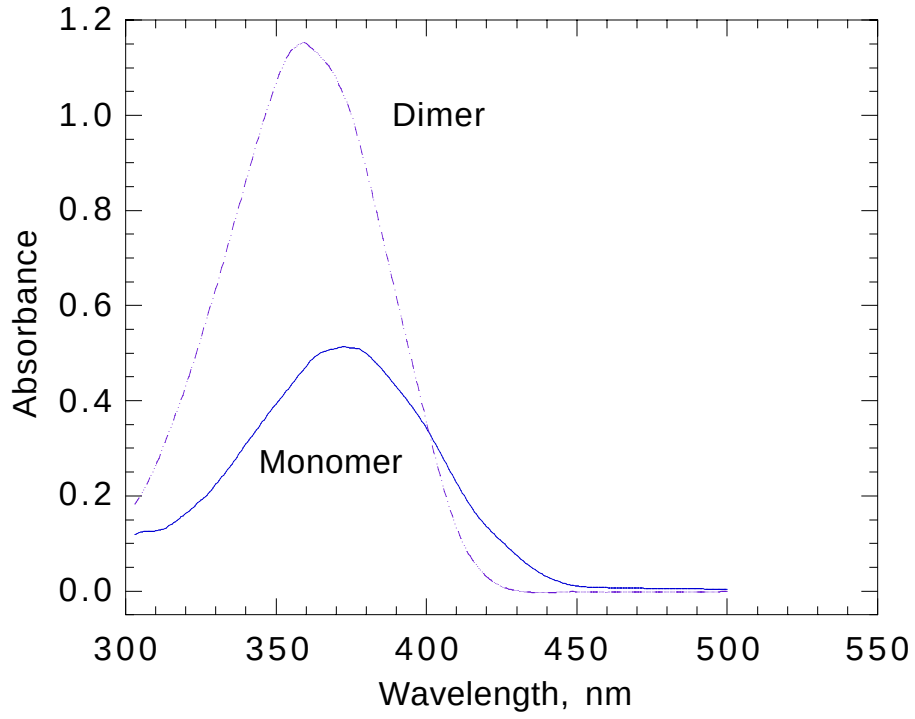


Figure S5. Spectra of monomer and dimer of LiPhAT in DME by SVD..

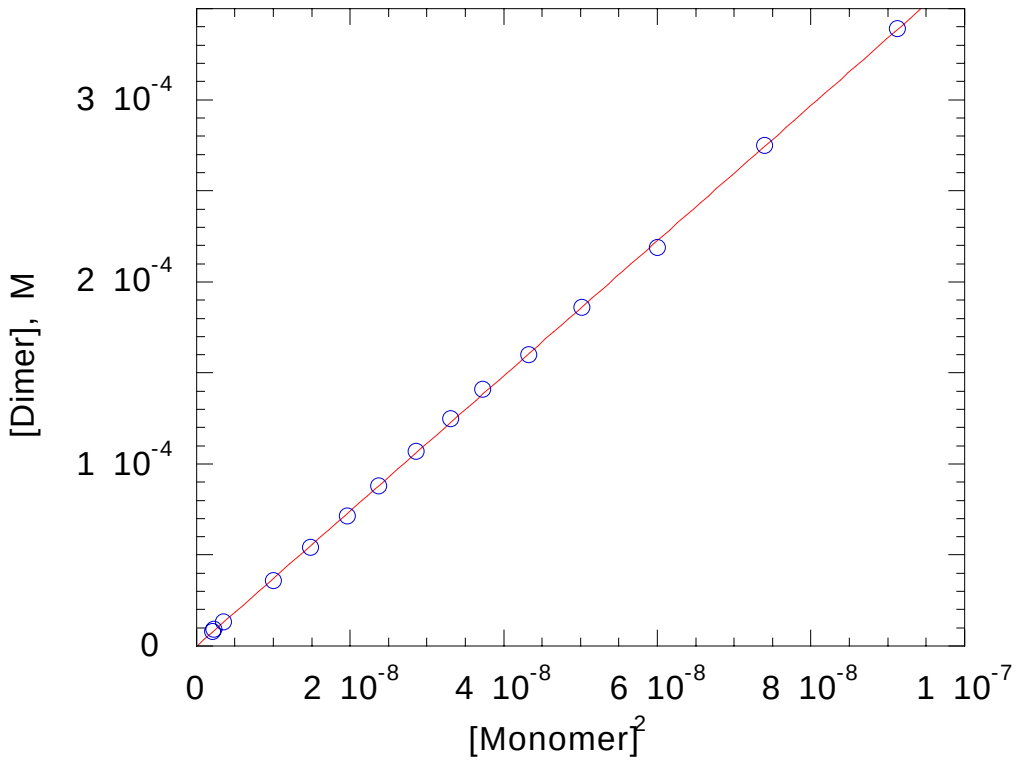


Figure S6. $K_{1,2}$ for LiPhAT in DME = [Dimer]/[Monomer]^2 = 3710 ± 9 M^{-1}. Data from Table S2.

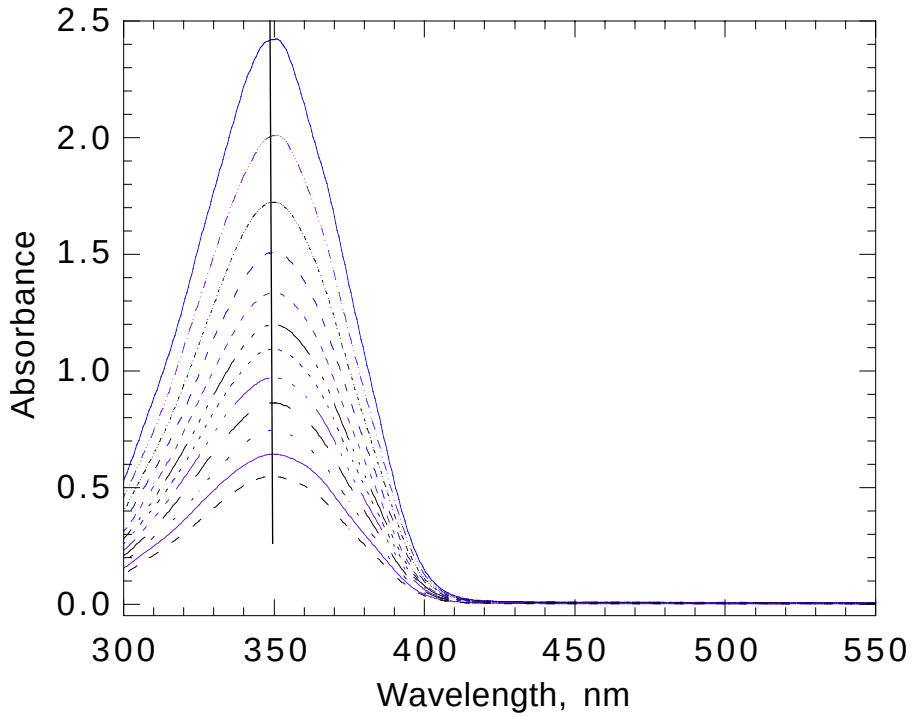


Figure S7. Spectra of LiPhAT in TBME showing constancy of λ_{max} at different concentrations.

Kinetic studies

The reaction of LiPhIBP with benzyl bromide (BnBr) in DME shows normal pseudo-first order behavior. Kinetic data are summarized in Table S3 and Figure S8. Rates are corrected for some independent quenching of the enolate. LiPhIBP is totally monomer in DME at these concentrations.

Table S3. Reaction of LiPhIBP with 0.0284M BnBr in DME.

Init {LiPhIBP} M	Rate M s^{-1}	Corr Rate M^{-1} s^{-1}
4.13E-03	5.93E-06	4.80E-06
2.82E-03	4.55E-06	3.42E-06
2.43E-03	3.95E-06	2.82E-06
1.56E-03	2.92E-06	1.79E-06
4.94E-03	6.89E-06	5.76E-06
1.87E-03	3.28E-06	2.16E-06

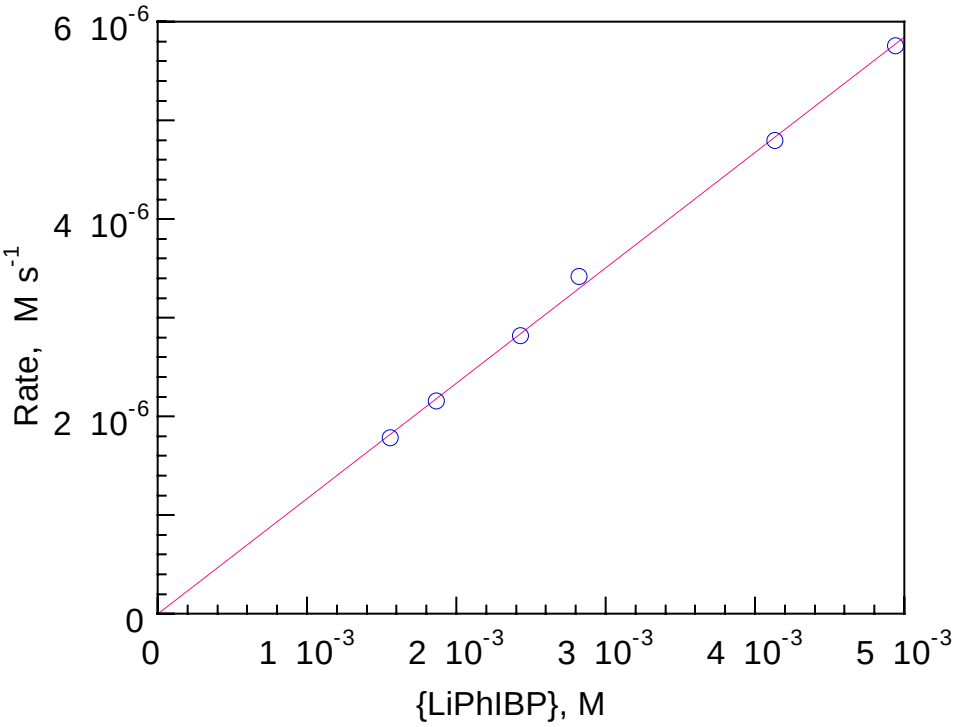
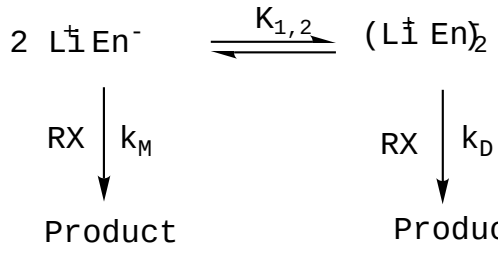


Figure S8. Corrected pseudo-first order initial rate of reaction of LiPhIBP with BnBr in DME at 25 °C. The slope of the line shown is (1.17 ± 0.02)E-3 s^{-1}. Divided by [BnBr] = 0.0284 gives k_2 = 0.0412 ± 0.0008 M^{-1} s^{-1}.

For a monomer-dimer equilibrium where En is the enolate, the reactions are:



(eq. 1)

where M = [LiEn] and D = $[(LiEn)_2]$.

$$-d\{LiEn\}/dt = k_M[M][RX] + k_D[D][RX] \quad \text{(eq. 2)}$$

where {LiEn} is the formal concentration of LiEn as measured by the absorbance at λ_{max}.

$$\frac{-d\{LiEn\}/dt}{[D][RX]} = k_M \frac{[M]}{[D]} + k_D \quad \text{(eq. 3)}$$

Such a plot is shown for the reaction of LiPhAT with benzyl bromide in DME at 25 °C in Figure S9 from data in Table S4.

Table S4. Reaction of LiPhAT with 0.0158M benzyl bromide in DME at 25 °C.

{LiPhAT} M	Initial Rate M s^{-1}	[Monomer][a] M	[Dimer][a] M
1.00E-03	1.75E-07	3.07E-04	3.48E-04
6.38E-04	1.44E-07	2.34E-04	2.02E-04
7.24E-04	1.59E-07	2.52E-04	2.36E-04
2.49E-04	5.93E-08	1.28E-04	6.05E-05
3.57E-04	1.17E-07	1.62E-04	9.75E-05
5.36E-04	1.09E-07	2.10E-04	1.63E-04
3.70E-04	9.35E-08	1.66E-04	1.02E-04
2.32E-04	7.85E-08	1.22E-04	5.52E-05

(a). From $K_{1,2}$ = 3700 M^{-1}.

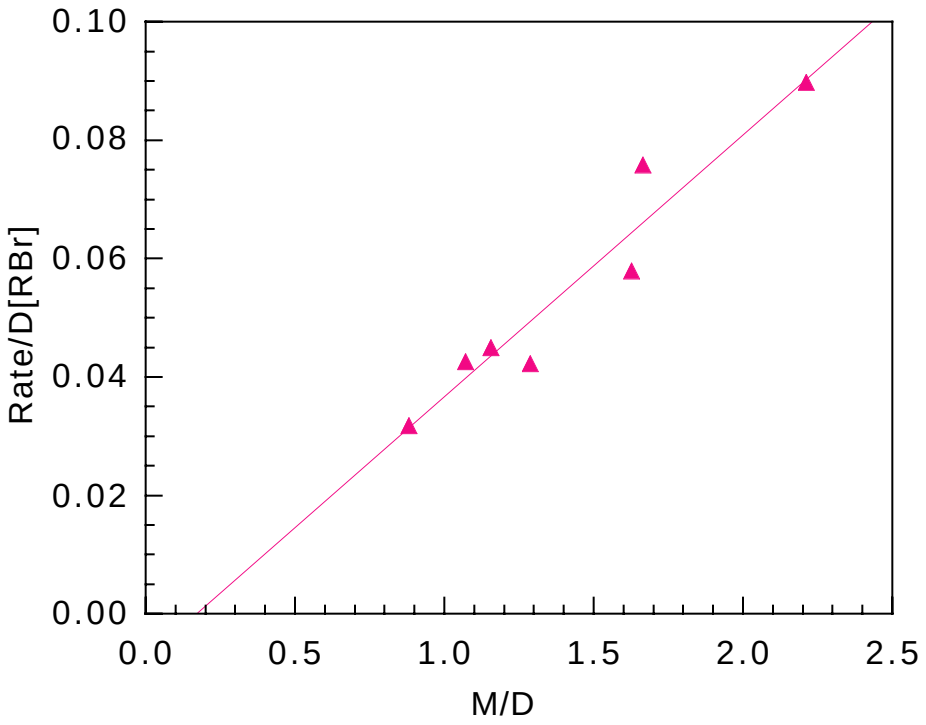


Figure S9. Plot of eq. 3 with the data in Table S4. The intercept, k_D = -7.7 ± 8.4; the slope, k_M = 4.42 ± 0.57.

Alternatively, since reaction is primarily with monomer, a plot of rate vs [Monomer] (Figure S10) gives directly, when divided by [BnBr], the second order rate constant k_M (eq. 4).

$$-d\{MPhPAT\}/dt = k_M [RX][M] \qquad \text{(eq. 4)}$$

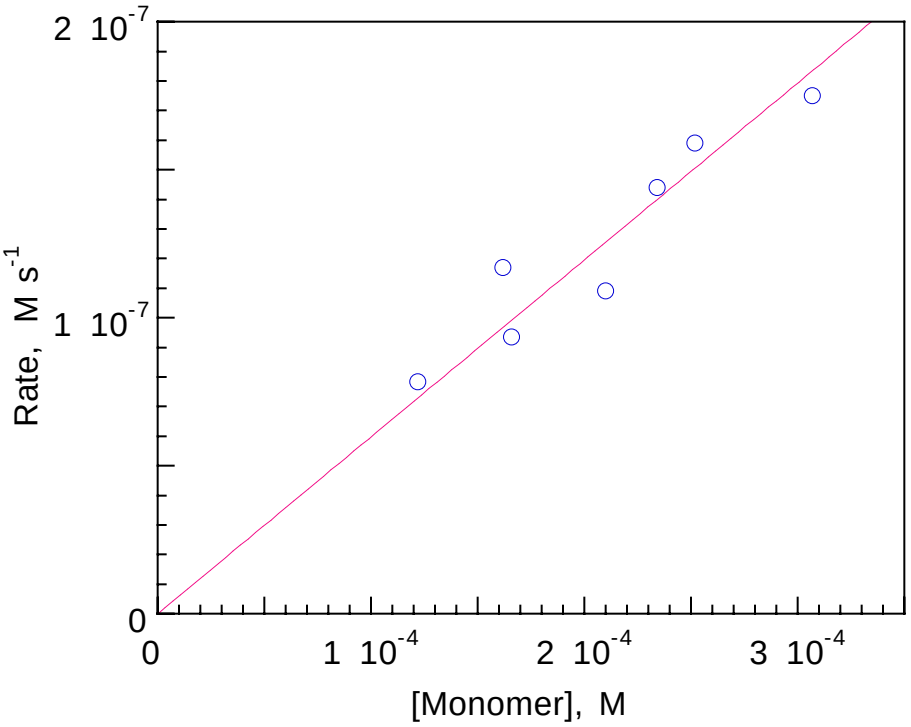


Figure S10. Rate vs [Monomer] for LiPhAT + BnBr in DME at 25 °C; Slope, (5.98 ± 0.22)E-4 gives k_2 = 0.0378 ± 0.0014 M^{-1} s^{-1}.

The Claisen reactions were treated similarly.

Table S5. Reaction of LiPhAT with 0.0096M p-chlorophenyl p-chlorobenzoate in THF at 25 °C.

{LiPhAT} M	Init Rate M s^{-1}	[Monomer]^a M	[Dimer]^a M
4.39E-04	1.24E-07	2.32E-04	1.04E-04
2.94E-04	7.82E-08	1.75E-04	5.92E-05
3.63E-04	9.13E-08	2.03E-04	7.99E-05
9.03E-04	2.15E-07	3.71E-04	2.66E-04
8.72E-04	1.69E-07	3.63E-04	2.54E-04
7.29E-04	1.54E-07	3.24E-04	2.03E-04
5.69E-04	1.30E-07	2.76E-04	1.47E-04
6.09E-04	1.52E-07	2.88E-04	1.60E-04

From $K_{1,2}$ = 1930 M^{-1}.

A plot according to eq. 3 gives Figure S11.

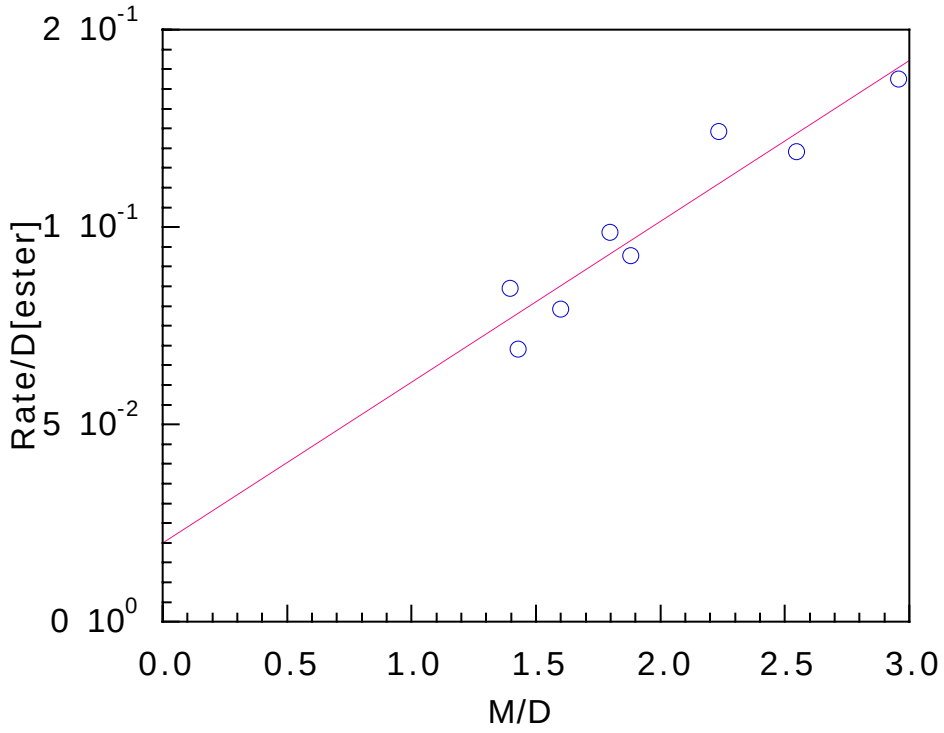


Figure S11. Reaction of LiPhAT with p-chlorophenyl p-chlorobenzoate in THF at 25 °C; k_D = 0.021 ± 0.011; k_M = 0.042 ± 0.006 M^{-1} s^{-1}.

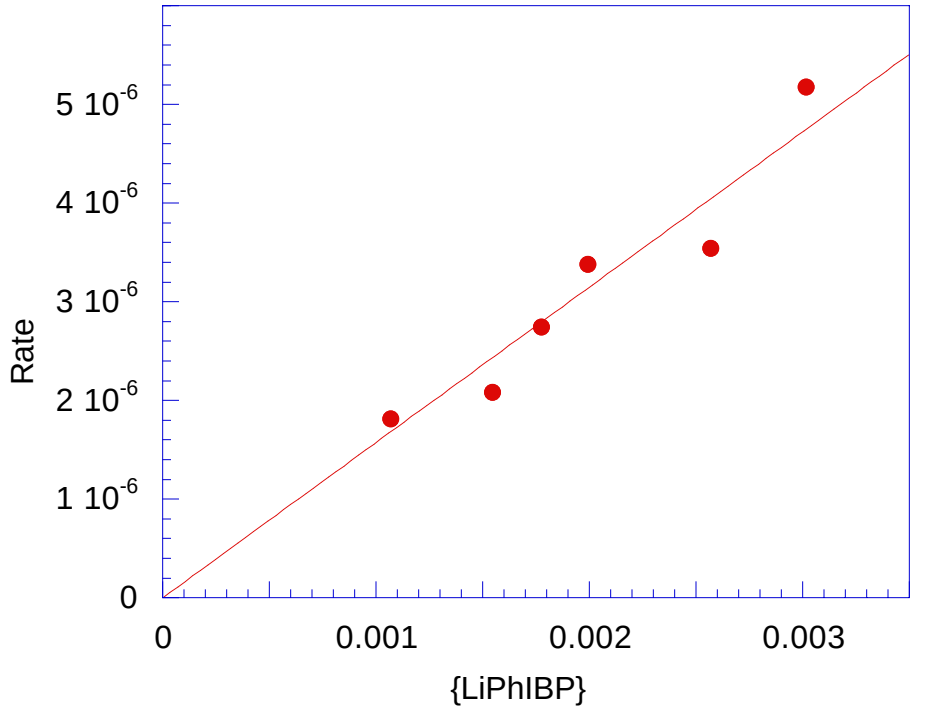


Figure S12. Initial rates of reaction of LiPhIBP with 0.020M PhCOSPh in DME at 25 °C. Line corresponds to k_2 = 0.078 ± 0.004 M^{-1} s^{-1}.

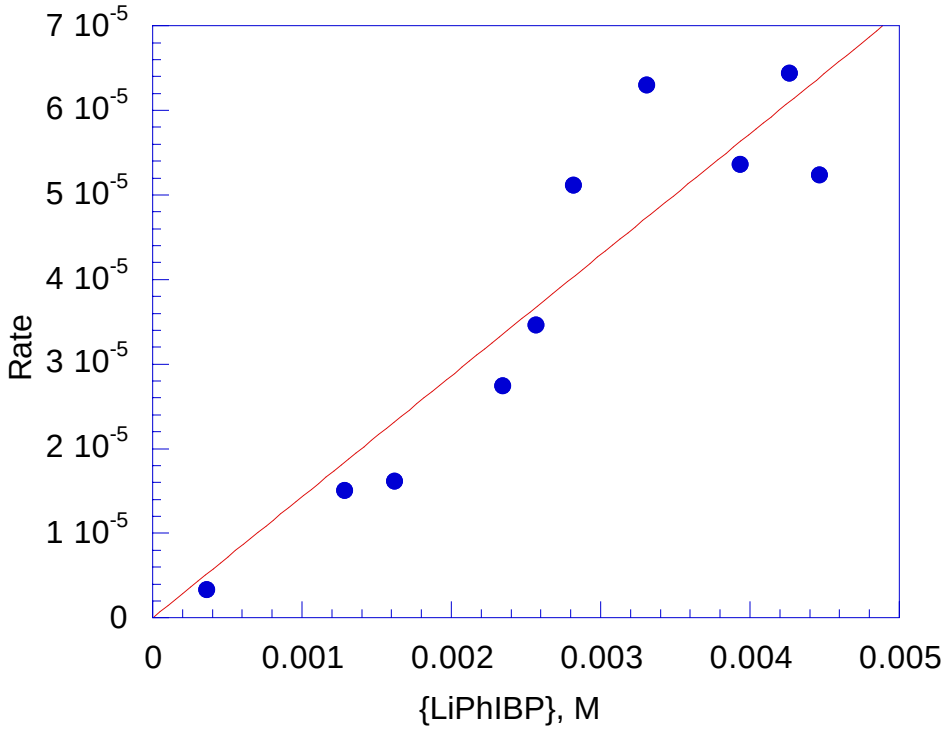


Figure S13. Initial rates of reaction of Initial rates of reaction of LiPhIBP with 0.047M PhCOpyrazole in MTBE at 25 °C. Line corresponds to k_2 = 0.31 ± 0.02 M^{-1} s^{-1}.

Note:

The reaction of LiPhIBP with p-t-butylbenzyl chloride and benzyl bromide in MTBE was found to be too slow. A precise value for these reaction rates could not be determined; however, curve fit analysis of signal versus time plots indicates that, relative to the reaction with benzoylpyrazole, reaction with p-t-butylbenzyl chloride is at least 1000 times slower, whereas reaction with benzyl bromide is at least 300 times slower.