Supplementary Tables

Table S1

Kinetic data for the reactions of **5a-f** with LiOEt and KOEt in anhydrous ethanol at $25^{\circ}C$

Substrate	MOEt	$10^2[MOEt]_o/M$	$10^2[EtO^-]_{eq}/M$	k_{obs}/s^{-1}	$k_{obs}/[EtO^-]_{eq}$ $(M^{-1}s^{-1})$
5a	LiOEt	0.496	0.303	0.955	316
		0.993	0.488	2.390	490
		1.986	0.761	5.590	735
		3.103	0.997	10.34	1037
		4.219	1.19	14.35	1201
		5.460	1.39	20.14	1452
	KOEt	0.532	0.393	0.508	129
		1.063	0.665	1.064	160
		2.126	1.08	2.476	230
		3.037	1.36	3.660	269
		4.100	1.65	5.354	325
		5.315	1.94	7.477	386
5b	LiOEt	0.869	0.446	0.912	204
		2.110	0.789	2.765	350
		3.103	0.997	4.516	453
		4.220	1.19	6.461	541
		5.335	1.37	8.525	623
	KOEt	0.532	0.393	0.238	60.6
		1.063	0.665	0.507	76.3
		2.126	1.08	1.033	95.8
		3.037	1.36	1.686	124
		4.100	1.65	2.467	150
		5.315	1.94	3.656	189
5c	LiOEt	0.441	0.278	0.117	42.0
		1.241	0.565	0.402	71.2
		2.482	0.872	0.955	110
		3.723	1.11	1.576	142
		4.964	1.31	2.173	166
		6.205	1.49	2.867	192

	KOEt	0.454	0.346	0.0606	17.5
		1.049	0.658	0.151	22.9
		1.748	0.944	0.276	29.2
		2.098	1.07	0.337	31.6
		3.007	1.35	0.586	43.2
		4.196	1.67	0.917	54.8
		5.245	1.92	1.074	55.9
5d	LiOEt	0.482	0.296	0.0220	7.43
		0.720	0.393	0.0331	8.42
		1.008	0.493	0.0537	10.9
		2.110	0.789	0.125	15.8
		3.103	0.997	0.202	20.3
		4.220	1.19	0.283	23.6
		5.335	1.37	0.374	27.4
	KOEt	0.474	0.358	0.0147	4.11
		1.041	0.655	0.0430	6.56
		1.997	1.03	0.0829	8.02
		3.037	1.36	0.126	9.23
		4.100	1.65	0.197	11.9
		5.315	1.94	0.267	13.8
5e	LiOEt	1.179	0.546	0.00881	1.61
		1.620	0.670	0.0128	1.91
		2.045	0.774	0.0166	2.15
		2.504	0.876	0.0230	2.62
		3.041	0.985	0.0281	2.85
	KOEt	0.553	0.405	0.00269	0.663
		1.080	0.673	0.00651	0.969
		2.248	1.12	0.0166	1.49
		3.380	1.46	0.0267	1.83
5f	LiOEt	0.426	0.271	0.00128	0.474
		1.007	0.493	0.00370	0.751
		1.936	0.749	0.00888	1.19
		2.942	0.966	0.0135	1.40
		4.120	1.18	0.0198	1.68
		5.332	1.37	0.0272	1.99
		6.411	1.52	0.0333	2.19

KOEt	0.553	0.405	0.00142	0.351
	1.080	0.673	0.00335	0.499
	2.156	1.09	0.00773	0.710
	3.297	1.44	0.0125	0.870
	4.393	1.72	0.0182	1.06

Table S2

Kinetic data for the reactions of **5a-f** with KOEt in anhydrous ethanol at 25°C in the presence of excess complexing agents

Substrate	Complexing agent	10^2[KOEt]/M	10^2[Complexing agent]/M	k_{obs}/s^{-1}
5a	[2.2.2] cryptand	0.494	0.939	0.2699
		1.025	1.861	0.6171
		2.051	3.717	1.271
		3.038	5.308	2.070
		4.177	5.666	2.715
5b	[2.2.2] crptand	1.025	1.861	0.2620
		2.051	3.717	0.5978
		3.038	5.308	0.8871
		4.177	5.666	1.288
5c	[2.2.2] cryptand	0.515	0.981	0.0416
		1.041	1.836	0.0899
		2.098	4.280	0.187
		3.007	6.134	0.274
		4.196	8.560	0.392
5d	[2.2.2] cryptand	0.515	0.981	0.00949
		1.041	1.836	0.0204
		2.071	3.068	0.0439
		2.916	6.170	0.0675
		3.817	6.461	0.0958
5e	[2.2.2] cryptand	0.494	0.973	0.00129
		1.043	2.055	0.00290
		1.913	3.768	0.00565
		3.446	6.974	0.0126
		4.133	8.141	0.0134
		5.100	10.46	0.0182
	DC-18-C-6	1.195	5.114	0.00341
		2.214	9.255	0.00676
		2.736	11.38	0.00891
		3.211	13.69	0.00987
		4.292	18.33	0.0144
		5.327	22.91	0.0194

	18-C-6	0.780	1.609	0.00201
		1.077	2.222	0.00289
		1.309	2.736	0.00366
		1.532	3.159	0.00443
		1.940	4.001	0.00652
		2.969	6.124	0.00898
		4.847	9.998	0.0150
5f	[2.2.2] cryptand	0.488	0.973	0.000682
		1.031	2.055	0.00153
		1.891	3.768	0.00287
		3.056	6.088	0.00495
		4.086	8.141	0.00664
		5.042	10.46	0.00864
	DC-18-C-6	1.201	3.112	0.00185
		2.090	5.412	0.00331
		2.986	7.735	0.00488
		4.179	10.82	0.00727

Table S3

Kinetic data for the reaction of **5e** with KOEt in anhydrous ethanol at 25°C at varying concentrations of [2.2.2] cryptand[a] and 18-C-6[b]

Macrocycle	10^2[Macrocycle]/M	[Macrocycle]/[KOEt]	$10^3 k_{obs}$/s^{-1}	k_{obs}/[KOEt] (M^{-1}s^{-1})[c]
[2.2.2] cryptand	0.000	0.000	2.285	0.4630
	0.226	0.458	1.854	0.3756
	0.452	0.916	1.410	0.2857
	0.904	1.832	1.286	0.2606
	1.848	3.745	1.318	0.2671
	2.670	5.410	1.339	0.2713
	3.696	7.489	1.372	0.2780
18-C-6	0.000	0.000	2.176	0.4576
	0.262	0.550	1.810	0.3807
	0.458	0.963	1.278	0.2688
	0.915	1.925	1.210	0.2545
	1.961	4.125	1.219	0.2564
	2.877	6.051	1.223	0.2572
	3.923	8.251	1.245	0.2618
	5.231	11.00	1.265	0.2660

[a] Initial [Substrate] = 2.30 x 10^{-4}M; initial [KOEt] = 4.94 x 10^{-3}M.

[b] Initial [Substrate] = 3.30 x 10^{-4}M; initial [KOEt] = 4.78 x 10^{-3}M.

[c] The limiting value of this quantity (= k_{EtO^-}) of 0.28 ± 0.01, 0.26 ± 0.01 and 0.26 ± 0.01 M^{-1}s^{-1} obtained from these experiments in the presence of [2.2.2] cryptand, DC-18-C-6 and 18-C-6, respectively (see Fig. 2), may be compared with k_{EtO^-} = 0.37 ± 0.02, 0.38 ± 0.02 and 0.32 ± 0.01 M^{-1}s^{-1} derived by linear regression of the data in Table S2 for the reaction of **5e** with KOEt in the presence of excess [2.2.2] cryptand, DC-18-C-6 and 18-C-6, respectively (see text and Table 1).

Table S4

Kinetic data for the reaction of **5e** with LiOEt in anhydrous ethanol at 25°C at varying concentrations of [2.1.1] cryptand[a]

10^2[Macrocycle]/M	[Macrocycle]/ [LiOEt]	$10^3 k_{obs}$/s^{-1}	k_{obs}/[LiOEt] (M^{-1}s^{-1})[b]
0.000	0.000	2.781	0.5726
0.225	0.464	2.215	0.4561
0.451	0.928	1.383	0.2847
0.902	1.856	1.270	0.2615
1.691	3.482	1.267	0.2609
3.381	6.961	1.329	0.2736

[a] Initial [Substrate] = 3.30 x 10^{-4}M; initial [KOEt] = 4.86 x 10^{-3}M.
[b] The limiting value of this quantity (= k_{EtO^-}) of 0.27 ± 0.01 M^{-1}s^{-1} reproduces the results obtained in the presence of [2.2.2] cryptand, DC-18-C-6 and 18-C-6 for the reaction of this substrate with KOEt (see footnotes in Table S3).