

SUPPLEMENTARY MATERIALS

SUPPLEMENTARY TABLES

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Table S1. Kinetic data for the reaction of **3** with LiOEt in EtOH at 25.0°C.
(See Figure 1).

RUN ID	[LiOEt] (M)	k_{obs} (s ⁻¹)
BC4-3	0.00510	0.002373
BC4-4	0.0102	0.006767
BC4-5	0.0198	0.01633
BC4-6	0.0402	0.03649
BC4-7	0.0601	0.06061
BC4-10	0.0799	0.08307
BC4-8	0.0799	0.08538

Table S2. Kinetic data for the reaction of **3** with NaOEt in EtOH at 25.0°C.
(See Figure 1)

RUN ID	[NaOEt] (M)	k_{obs} (s ⁻¹)
BA1-13	0.00106	2.106x10 ⁻⁴
DPP5	0.00131	4.434x10 ⁻⁴
BA1-21	0.00199	4.554x10 ⁻⁴
DPP11	0.00218	5.669x10 ⁻⁴
DPP10	0.00305	9.432x10 ⁻⁴
DPP9	0.00524	2.307x10 ⁻³
DPP8	0.00698	3.667x10 ⁻³
BA1-25	0.00896	3.026x10 ⁻³
DPP7	0.00918	5.240x10 ⁻³
DPP6	0.01096	2.744x10 ⁻³
DPP1	0.0131	7.264x10 ⁻³
DPP3	0.0175	1.303x10 ⁻²
DPP4	0.0175	1.152x10 ⁻²
BA1-24	0.0200	9.877x10 ⁻³
BA1-23	0.0298	1.693x10 ⁻²
BA1-22	0.0396	2.441x10 ⁻²
BA1-20	0.0498	2.919x10 ⁻²
BA1-19	0.0596	3.709x10 ⁻²
BA1-18	0.0695	4.748x10 ⁻²
BA1-17	0.0793	6.350x10 ⁻²
BA1-16	0.0895	7.654x10 ⁻²
BA1-15	0.0980	8.569x10 ⁻²

Table S3. Kinetic data for the reaction of **3** with KOEt in EtOH at 25.0°C.
(See Figure 1).

RUN ID	[KOEt] (M)	k_{obs} (s ⁻¹)	k_{obs} average (s ⁻¹)	(std. dev.) (s ⁻¹)
BB2-8	0.00243	4.903x10 ⁻⁴		
BB2-2	0.00486	1.319x10 ⁻³	1.307x10 ⁻³	(0.012x10 ⁻³)
BB2-7	0.00486	1.295x10 ⁻³		
BB1-1	0.0097	3.439x10 ⁻³		
BB2-1	0.0121	6.219x10 ⁻³		
BB2-11	0.0199	7.992x10 ⁻³	8.269x10 ⁻³	(0.200x10 ⁻³)
BB2-9	0.0199	8.460x10 ⁻³		
BB2-10	0.0199	8.354x10 ⁻³		
BB2-12	0.0401	2.199x10 ⁻²	2.129x10 ⁻²	(0.005x10 ⁻²)
BB2-13	0.0401	2.094x10 ⁻²		
BB2-14	0.0401	2.189x10 ⁻²		
BB4-8	0.0607	3.553x10 ⁻²	3.514x10 ⁻²	(0.093x10 ⁻²)
BB4-1	0.0607	3.556x10 ⁻²		
BB4-2	0.0607	3.331x10 ⁻²		
BB2-16	0.0607	3.535x10 ⁻²		
BB4-7	0.0607	3.593x10 ⁻²		
BB2-17	0.0789	5.028x10 ⁻²	4.929x10 ⁻²	(0.099x10 ⁻²)
BB2-18	0.0789	4.829x10 ⁻²		
BB4-6	0.0803	4.711x10 ⁻²		
BB4-4	0.100	6.457x10 ⁻²	6.497x10 ⁻²	(0.306x10 ⁻²)
BB4-5	0.100	6.144x10 ⁻²		
BB2-6	0.100	6.890x10 ⁻²		

Table S4. Kinetic data for the reaction of **3** with CsOEt in EtOH at 25.0°C.
(See Figure 1).

Run ID	[CsOEt] (M)	k_{obs} (s ⁻¹)
BD4-1	0.00497	0.001058
BD4-2	0.00921	0.002102
BD4-3	0.0200	0.005343
BD4-4	0.0400	0.01206
BD4-5	0.0600	0.01930
BD4-6	0.0829	0.02815

Table S5. Kinetic data for the reaction of **3** with KOEt in the presence of 18-Crown-6 in EtOH at 25.0°C. (See Figure 2).

RUN ID	[KOEt] (M)	[18C6] (M)	[18C6] [KOEt]	k_{obs} (s ⁻¹)	$k_{\text{obs}}/[\text{MOEt}]$ (s ⁻¹ M ⁻¹)
BB4-7	0.0607	0.0000	0.000	0.03593	0.5918
BB4-8	0.0607	0.0000	0.000	0.03553	0.5852
BBA4-1	0.0607	0.0121	0.200	0.03382	0.5570
BBA4-2	0.0607	0.0243	0.400	0.02718	0.4477
BBA4-12	0.0607	0.0304	0.500	0.02336	0.3848
BBA4-3	0.0607	0.0364	0.600	0.02152	0.3545
BBA4-4	0.0607	0.0486	0.80	0.01051	0.1731
BBA4-8	0.0607	0.0607	1.00	0.007796	0.1284
BBA4-11	0.0607	0.0607	1.00	0.009312	0.1534
BBA4-6	0.0607	0.0607	1.00	0.008978	0.1479
BBA4-9	0.0607	0.122	2.00	0.008177	0.1347
BBA4-13	0.0607	0.182	3.00	0.008429	0.1388
BBA4-10	0.0607	0.182	3.00	0.008324	0.1371
BBA4-5	0.0152	0.078	5.14	0.001785	0.1176
BBA4-7	0.0152	0.0455	3.00	0.002019	0.1330

Average $k_{\text{obs}} / [\text{MOEt}]$ for ratios of [18-crown-6] / [KOEt] $\geq 1.0 = 0.1336 \pm 0.0104$ s⁻¹M⁻¹ corresponds to the constant rate observed after a 1:1 crown:metal ion ratio was achieved.

Table S6(a). Kinetic data for the reaction of **3** with LiOEt in the presence of LiCl in EtOH at 25.0°C. Run ID BCC5. (See Figure 3).

Ratio LiCl/LiOEt	k_{obs} (s ⁻¹)
0.00	3.01x10 ⁻³
1.47	4.12x10 ⁻³
3.30	4.94x10 ⁻³
6.60	5.85x10 ⁻³
9.90	6.10x10 ⁻³
19.8	7.13x10 ⁻³
30.1	7.36x10 ⁻³
49.9	7.66x10 ⁻³

Table S6(b). Kinetic data for the reaction of **3** with LiOEt in the presence of LiNO₃ in EtOH at 25.0°C. Run ID BCB5. (See Figure 3).

Ratio LiNO ₃ /LiOEt	k_{obs} (s ⁻¹)
0.00	2.99x10 ⁻³
9.50	6.13x10 ⁻³
19.3	6.93x10 ⁻³
28.1	7.04x10 ⁻³
38.7	6.65x10 ⁻³
63.7	6.86x10 ⁻³

Table S6(c). Kinetic data for the reaction of **3** with KOEt in the presence of KO(O)CCH₃ in EtOH at 25.0°C. Run ID BCE5. (See Figure 3).

Ratio KOOCCH ₃ /KOEt	k _{obs} (s ⁻¹)
0.00	1.31x10 ⁻³
3.36	2.01x10 ⁻³
3.36	1.97x10 ⁻³
4.70	2.05x10 ⁻³
6.71	1.97x10 ⁻³
10.1	2.52x10 ⁻³
20.1	2.92x10 ⁻³
30.2	3.23x10 ⁻³
50.4	3.63x10 ⁻³

Table S6(d). Kinetic data for the reaction of **3** with KOEt in the presence of KI in EtOH at 25.0°C. Run ID BCF5. (See Figure 3).

Ratio KI/KOEt	k _{obs} (s ⁻¹)
0.00	1.81x10 ⁻⁴
1.19	2.23x10 ⁻⁴
4.94	3.16x10 ⁻⁴
7.90	3.48x10 ⁻⁴
13.8	3.71x10 ⁻⁴
27.7	4.53x10 ⁻⁴
41.5	4.85x10 ⁻⁴

Table S7. Kinetic data for the reaction of **3** with KOEt in the presence and absence of 18-Crown-6 and with added Bu₄NCl in EtOH at 25.0°C. [KOEt]₀ = 0.0188 M.

Run ID	[18-C-6] (M)	$\frac{[18-C-6]}{[KOEt]}$ (ratio)	[Bu ₄ NCl] (M)	$\frac{[Bu_4NCl]}{[KOEt]}$ (ratio)	k _{obs} (s ⁻¹)	$\frac{k_{obs} (avg)}{k_{obs} \text{ for EtO-}}$ (ratio)
BBN6-5	0	0	0	0	7.295x10 ⁻³	
BBN6-5	0	0	0	0	7.264x10 ⁻³3.301
BBA6-6	2.282x10 ⁻²	1.21	0	0	2.186x10 ⁻³	
BBA6-7	2.536x10 ⁻²	1.35	0	0	2.225x10 ⁻³1.000
BBAD6-1	2.282x10 ⁻²	1.21	8.935x10 ⁻³	0.474	2.279x10 ⁻³1.033
BBAD6-2	2.282x10 ⁻²	1.21	2.223x10 ⁻²	1.187	2.295x10 ⁻³1.041

Table S8. Data for the ion pairing treatment of the reaction of KOEt with **3** in EtOH at 25°C. (See Figure 4).

Run ID	[KOEt] (M)	k_{obs} (s ⁻¹)	[EtO ⁻] (M)	$k_{\text{obs}}/[\text{EtO}^-]$ (M ⁻¹ s ⁻¹)
BB2-8	0.00243	4.90x10 ⁻⁴	2.051x10 ⁻³	2.391x10 ⁻¹
BB2-2,4,7	0.00486	1.19x10 ⁻³	3.655x10 ⁻³	3.252x10 ⁻¹
BB1-1	0.00972	3.44x10 ⁻³	6.226x10 ⁻³	5.524x10 ⁻¹
BB2-1	0.01214	6.22x10 ⁻³	7.317x10 ⁻³	8.499x10 ⁻¹
BB2-9,10,11	0.01992	8.27x10 ⁻³	1.032x10 ⁻²	8.009x10 ⁻¹
BB2-12,13,14	0.04007	2.16x10 ⁻²	1.626x10 ⁻²	1.329
BB4-1,2,7,8,2-16	0.06071	3.51x10 ⁻²	2.100x10 ⁻²	1.673
BB2-17,18	0.07892	4.93x10 ⁻²	2.457x10 ⁻²	2.006
BB4-6	0.08026	4.71x10 ⁻²	2.482x10 ⁻²	1.898
BB2-5,6 4-3,4,5	0.10017	6.63x10 ⁻²	2.827x10 ⁻²	2.347

$$R^2 = 1.000, \text{ slope} = 76.67 \pm 3.14$$

$$k_{\text{EtO}^-} = 0.0940 \pm 0.0915 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{\text{KOEt}} = 0.8519 \pm 0.0348 \text{ M}^{-1}\text{s}^{-1}$$

Table S9. Data for the ion pairing treatment of the reaction of KOEt with **3** in the presence of excess

Run ID	[KOEt] (M)	[18-crown-6] (M)	k_{obs} (s ⁻¹)	[18C6]/[EtO ⁻] (M ⁻¹ s ⁻¹)	$k_{\text{obs}}/[\text{EtO}^-]$ (M ⁻¹ s ⁻¹)
BBA6-5	0.00911	0.01268	0.000864	1.392	0.09483
BBA6-4	0.01821	0.02789	0.001790	1.531	0.09831
BBA6-3	0.03882	0.06948	0.003997	1.790	0.1030
BBA6-2	0.06071	0.09128	0.006599	1.504	0.1087
BBA5-1	0.07892	0.09990	0.008653	1.266	0.1096

$$R^2 = 0.962; \text{ slope} = 0.2172 \pm 0.0248$$

$$k_{\text{EtO}^-} = 0.0939 \pm 0.0014 \text{ M}^{-1}\text{s}^{-1}$$