Supplementary Information

New examples of specific-base catalysis in mononuclear rearrangements of heterocycles found via a designed modification of the side-chain structure

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Table 5. Calculated or measured apparent rate constants (at 293 K) and activation parameters for the rearrangement of **3d** at various pS^+ in D/W (1:1, v:v).

pS^+[a]	3.90	4.90	5.80	6.85	7.50	7.85
$10^7(k_{A,R})_{\mathbf{3d}}$[b]	0.00333	0.0316	0.184	1.54	6.82	15.3
$\Delta H^{\#}$[c]	100	100	103	101	100	100
$\Delta S^{\#}$[d]	–84	–67	–46	–29	–21	–15
pS^+[e]	8.80	9.17	9.41	9.67	9.91	10.07
$10^5(k_{A,R})_{\mathbf{3d}}$[b]	1.24	2.79	4.48	7.45	12.3	17.5
$\Delta H^{\#}$[c]	82	80	81	82	82	82
$\Delta S^{\#}$[d]	–61	–57	–51	–45	–38	–35
pS^+[e]	10.25	10.52	10.74	10.95	11.17	11.37
$10^4(k_{A,R})_{\mathbf{3d}}$[b]	2.58	4.48	7.10	11.1	17.7	28.0
$\Delta H^{\#}$[c]	82	82	81	79	81	81
$\Delta S^{\#}$[d]	–35	–31	–28	–30	–21	–17
pS^+[e]	11.53	11.78	12.05	12.30	12.52	12.78
$10^3(k_{A,R})_{\mathbf{3d}}$[b]	3.88	6.58	11.9	20.9	32.7	58.9[f]
$\Delta H^{\#}$[c]	81	81	81	81	81	
$\Delta S^{\#}$[d]	–14	–10	–5	0	+3	
pS^+[e]	12.96	13.11	13.40	13.55	13.74	13.82
$10^2(k_{A,R})_{\mathbf{3d}}$[f]	8.32	11.6	21.6	28.7	44.0	51.7
pS^+[e]	14.07	14.20				
$(k_{A,R})_{\mathbf{3d}}$[f]	0.835	1.05				

[a]Citrate buffer; total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters at 293 K. The experimental rate constants were measured in the range 288–333 K and were reproducible within ±3%. [c]kJ mol^{-1}. At 313 K the maximum error is 3 kJ mol^{-1}. [d]J K^{-1} mol^{-1}. At 313 K the maximum error is 8 J K^{-1} mol^{-1}. [e]Borate buffer; total buffer concentration 0.0125 M. [f]s^{-1}, values directly measured at 293 K.

Table 6. Calculated or measured apparent rate constants (at 293.1 K) and activation parameters for the rearrangement of **3e** at various pS^+ in D/W (1:1, v:v).

pS^{+a}	4.25	4.95	5.63	6.14	6.80	7.29	7.73
$10^7(k_{A,R})_{\mathbf{3e}}{}^b$	0.0615	0.267	1.16	3.31	13.9	38.8	104
$\Delta H^{\#c}$	98	99	99	99	100	100	100
$\Delta S^{\#d}$	–68	–54	–42	–31	–18	–9	–1
pS^{+e}	8.18[a]	8.68	9.14	9.38	9.67	9.92	10.18
$10^5(k_{A,R})_{\mathbf{3e}}{}^b$	2.74	9.18	24.2	40.4	74.3	126	219
$\Delta H^{\#c}$	97	85	85	85	85	84	84
$\Delta S^{\#d}$	0	–34	–26	–22	–17	–13	–9
pS^{+e}	10.46	10.78	11.10	11.38	11.61		
$10^3(k_{A,R})_{\mathbf{3e}}{}^b$	3.94	7.82	15.3	27.9	45.5		
$\Delta H^{\#c}$	84	83	83	82	82		
$\Delta S^{\#d}$	–4	–1	+5	+6	+8		
pS^{+e}	11.71	11.95	12.20	12.30	12.42	12.73	12.95
$10^2(k_{A,R})_{\mathbf{3e}}{}^f$	6.05	9.10	14.1	17.9	23.0	42.0	62.0
pS^{+e}	13.10	13.25	13.45	13.62	13.77	13.99	14.18
$(k_{A,R})_{\mathbf{3e}}{}^f$	0.820	1.03	1.35	1.68	2.00	2.42	2.72
pS^{+e}	14.41						
$(k_{A,R})_{\mathbf{3e}}{}^f$	3.00						

[a]Citrate buffer; total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters at 293.1 K. The experimental rate constants were measured in the range 288.1–333.1 K and were reproducible within ±3%. [c]kJ mol^{-1}. At 313.1 K the maximum error is 3 kJ mol^{-1}. [d]J K^{-1} mol^{-1}. At 313.1 K the maximum error is 8 J K^{-1} mol^{-1}. [e]Borate buffer; total buffer concentration 0.0125 M. [f]s^{-1}, values directly measured at 293.1 K.

Table 7. Calculated or measured apparent rate constants (at 293.1 K) and activation parameters for the rearrangement of **3f** at various pS^+ in D/W (1:1, v:v).

pS^{+a}	4.50	4.93	5.54	5.97	6.57	7.22	7.50
$10^7(k_{A,R})_{\mathbf{3f}}{}^b$	0.0733	0.175	0.621	1.47	4.89	25.8	43.8
$\Delta H^{\#c}$	99	99	99	100	100	100	100
$\Delta S^{\#d}$	–63	–55	–44	–35	–24	–10	–6
pS^{+e}	8.30[a]	8.98	9.35	9.75	10.02	10.25	10.45
$10^5(k_{A,R})_{\mathbf{3f}}{}^b$	2.38	11.6	24.4	60.5	107	178	266
$\Delta H^{\#c}$	101	84	83	83	83	83	83
$\Delta S^{\#d}$	+12	–35	–29	–23	–19	–15	–13
pS^{+e}	10.66	10.88	11.06	11.35	11.55		
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	4.15	6.62	9.66	17.4	26.7		
$\Delta H^{\#c}$	82	82	82	83	82		
$\Delta S^{\#d}$	–9	–6	–3	+4	+5		
pS^{+e}	11.78	11.95	12.05	12.24	12.43	12.75	13.01
$10^2(k_{A,R})_{\mathbf{3f}}{}^f$	4.53	6.70	8.70	12.8	19.5	38.5	58.0
pS^{+e}	13.25	13.40	13.59	13.88	14.02	14.37	14.60
$(k_{A,R})_{\mathbf{3f}}{}^f$	0.840	1.12	1.45	1.86	2.02	2.30	2.44
pS^{+e}	14.80						
$(k_{A,R})_{\mathbf{3f}}{}^f$	2.50						

[a]Citrate buffer; total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters at 293.1 K. The experimental rate constants were measured in the range 288.1–333.1 K and were reproducible within ±3%. [c]kJ mol^{-1}. At 313.1 K the maximum error is 3 kJ mol^{-1}. [d]J K^{-1} mol^{-1}. At 313.1 K the maximum error is 8 J K^{-1} mol^{-1}. [e]Borate buffer; total buffer concentration 0.0125 M. [f]s^{-1}, values directly measured at 293.1 K.

Table 8. Calculated apparent rate constants (at 298.1 K) and activation parameters for the rearrangement of **3d** at various pS^+ and at different borate buffer concentrations in D/W (1:1, v:v).

pS^{+a}	9.91	10.07	10.25	10.52	10.74	10.95
$10^4(k_{A,R})_{\mathbf{3d}}{}^b$	2.21	3.10	4.60	7.98	12.6	19.6
pS^{+a}	11.17	11.37	11.53	11.78	12.05	12.30
$10^3(k_{A,R})_{\mathbf{3d}}{}^b$	3.14	4.98	6.90	11.7	21.1	37.2
pS^{+c}	9.79	10.10	10.29	10.53	10.79	10.97
$10^4(k_{A,R})_{\mathbf{3d}}{}^b$	1.76	3.25	4.95	8.41	14.6	20.9
$\Delta H^{\#d}$	87	85	85	85	84	83
$\Delta S^{\#e}$	–27	–25	–23	–21	–19	–18
pS^{+c}	11.22	11.50	11.92	12.40		
$10^4(k_{A,R})_{\mathbf{3d}}{}^b$	36.1	65.3	162	461		
$\Delta H^{\#d}$	82	82	82	82		
$\Delta S^{\#e}$	–18	–13	–4	+4		
pS^{+f}	9.77	9.95	10.23	10.47	10.67	10.89
$10^4(k_{A,R})_{\mathbf{3d}}{}^b$	1.67	2.45	4.50	7.40	11.2	17.1
$\Delta H^{\#d}$	85	87	85	86	85	85
$\Delta S^{\#e}$	–31	–24	–22	–16	–18	–11
pS^{+f}	11.05	11.24	11.64	12.16		
$10^4(k_{A,R})_{\mathbf{3d}}{}^b$	24.8	38.7	89.1	269		
$\Delta H^{\#d}$	86	85	83	82		
$\Delta S^{\#e}$	–7	–5	–6	–1		

[a]Total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters. The experimental rate constants were measured in the range 288.1–313.1 K and were reproducible within ±3%. [c]Total buffer concentration 0.0250 M. [d]kJ mol^{-1}. At 313.1 K the maximum error is 3 kJ mol^{-1}. [e]J K^{-1} mol^{-1}. At 313.1 K the maximum error is 8 J K^{-1} mol^{-1}. [f]Total buffer concentration 0.0500 M.

Table 9. Calculated apparent rate constants (at 298.1 K) and activation parameters for the rearrangement of **3e** at various pS^+ and at different borate buffer concentrations in D/W (1:1, v:v).

pS^{+}[a]	9.67	9.92	10.18	10.46	10.78	11.10
$10^3(k_{A,R})_{\mathbf{3e}}$[b]	1.35	2.30	3.97	7.16	14.1	27.6
pS^{+}[a]	11.38	11.61				
$10^3(k_{A,R})_{\mathbf{3e}}$[b]	49.9	81.1				
pS^{+}[c]	10.03	10.35	10.70	10.97	11.26	11.48
$10^3(k_{A,R})_{\mathbf{3e}}$[b]	2.88	5.66	11.6	21.1	38.1	59.7
$\Delta H^{\#}$[d]	83	83	84	82	82	82
$\Delta S^{\#}$[e]	–15	–9	0	–1	+3	+7
pS^{+}[f]	9.78	10.11	10.55	10.85	11.14	11.45
$10^3(k_{A,R})_{\mathbf{3e}}$[b]	1.73	3.41	8.73	16.3	30.8	57.3
$\Delta H^{\#}$[d]	84	83	83	82	82	82
$\Delta S^{\#}$[e]	–18	–15	–8	–3	+1	+8

[a]Total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters. The experimental rate constants were measured in the range 288.1–313.1 K and were reproducible within ±3%. [c]Total buffer concentration 0.0250 M. [d]kJ mol^{-1}. At 313.1 K the maximum error is 3 kJ mol^{-1}. [e]J K^{-1} mol^{-1}. At 313.1 K the maximum error is 8 J K^{-1} mol^{-1}. [f]Total buffer concentration 0.0500 M.

Table 10. Calculated apparent rate constants (at 298.1 K) and activation parameters for the rearrangement of **3f** at various pS^+ and at different borate buffer concentrations in D/W (1:1, v:v).

pS^{+a}	9.35	9.75	10.02	10.25	10.45	10.66
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	0.441	1.09	1.93	3.21	4.79	7.45
pS^{+a}	10.88	11.06	11.35	11.55		
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	11.9	17.3	31.2	47.8		
pS^{+c}	9.03	9.57	9.88	10.24	10.53	10.85
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	0.242	0.748	1.39	2.97	5.66	11.4
$\Delta H^{\#d}$	84	84	84	84	87	82
$\Delta S^{\#e}$	–34	–24	–19	–13	–6	–6
pS^{+c}	11.12	11.44				
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	19.5	38.8				
$\Delta H^{\#d}$	82	82				
$\Delta S^{\#e}$	–2	+4				
pS^{+f}	9.25	9.50	9.85	10.15	10.50	10.97
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	0.359	0.638	1.29	2.61	5.38	13.9
$\Delta H^{\#d}$	84	84	84	85	84	82
$\Delta S^{\#e}$	–29	–24	–19	–10	–7	–4
pS^{+f}	11.27	11.60				
$10^3(k_{A,R})_{\mathbf{3f}}{}^b$	26.1	56.1				
$\Delta H^{\#d}$	83	82				
$\Delta S^{\#e}$	+2	+8				

[a]Total buffer concentration 0.0125 M. [b]s^{-1}, values calculated by activation parameters. The experimental rate constants were measured in the range 288.1–313.1 K and were reproducible within ±3%. [c]Total buffer concentration 0.0250 M. [d]kJ mol^{-1}. At 313.1 K the maximum error is 3 kJ mol^{-1}. [e]J K^{-1} mol^{-1}. At 313.1 K the maximum error is 8 J K^{-1} mol^{-1}. [f]Total buffer concentration 0.0500 M.

Table 11. Apparent first order rate constants, $k_{A,R}$,[a] for the rearrangement of **3d–f** in toluene at 313.1 K in the presence of various amines.

(3d)[b]											
[BuA]	0.0397	0.0590	0.0790	0.119	0.159	0.199	0.248	0.298	0.397	0.496	
$10^4 k_{A,R}$	0.684	1.18	1.81	3.27	5.28	7.64	11.2	15.4	25.5	38.7	
[PIP]	0.0204	0.0408	0.0612	0.0816	0.102	0.122	0.153	0.184	0.204	0.255	0.296
$10^3 k_{A,R}$	0.570	1.15	1.80	2.25	2.80	3.35	4.25	5.07	5.64	7.10	8.22
[TEA]	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.00	
$10^4 k_{A,R}$	0.187	0.374	0.573	0.761	0.940	1.14	1.31	1.52	1.72	1.92	
(3e)[c]											
[BuA]	0.0397	0.0590	0.0790	0.119	0.159	0.199	0.248	0.298	0.397	0.496	
$10^3 k_{A,R}$	0.187	0.335	0.532	1.07	1.76	2.64	3.97	5.63	9.69	14.8	
[PIP]	0.0250	0.0400	0.0600	0.0800	0.100	0.120	0.150	0.180	0.200	0.250	
$10^3 k_{A,R}$	1.88	3.04	4.50	5.95	7.43	8.95	11.1	13.4	15.1	18.7	
[TEA]	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.00	
$10^4 k_{A,R}$	0.730	1.45	2.24	2.98	3.74	4.48	5.18	5.90	6.60	7.37	
(3f)[d]											
[BuA]	0.0397	0.0590	0.0790	0.119	0.159	0.199	0.248	0.298	0.397	0.496	
$10^4 k_{A,R}$	0.915	1.56	2.45	4.65	7.47	11.0	16.1	22.4	37.6	57.2	
[PIP]	0.00980	0.0196	0.0294	0.0392	0.0588	0.0784	0.0980	0.137	0.196		
$10^3 k_{A,R}$	0.343	0.708	1.06	1.42	2.05	2.78	3.50	4.83	6.94		
[TEA]	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.00	
$10^4 k_{A,R}$	0.326	0.647	1.00	1.33	1.67	1.98	2.31	2.63	2.95	3.29	

[a]The rate constants (s^{-1}) are accurate to within ±3%. [b][**3d**] 6.60 x 10^{-5} M; a λ 308 nm; log ε 4.22 ± 0.02. [c][**3e**] 5.65 x 10^{-5} M; a λ 324 nm; log ε 4.08 ± 0.02. [d][**3f**] 5.60 x 10^{-5} M; a λ 293 nm; log ε 4.22 ± 0.02.

Table 12. Apparent first order rate constants, $k_{A,R}$,[a] for the rearrangement of **3d–f** in toluene at 313.1 K in the presence of pairs of amines.

(3d)[b,]										
[BuA][c]	0.101	0.152	0.202	0.253	0.303	0.354	0.404	0.455	0.505	
$10^3 k_{A,R}$	0.395	0.680	1.02	1.40	1.90	2.44	3.03	3.75	4.50	
[TEA][d]	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	1.00
$10^3 k_{A,R}$	1.40	1.52	1.62	1.78	1.83	1.97	2.10	2.22	2.30	2.46
(3e)[e]										
[BuA][f]	0.0404	0.0606	0.0808	0.121	0.152	0.202	0.253	0.303	0.354	0.404
$10^3 k_{A,R}$	0.486	0.705	0.969	1.63	2.26	3.51	5.07	6.88	9.01	11.4
[TEA][g]	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	
$10^3 k_{A,R}$	4.42	4.79	5.15	5.53	5.88	6.25	6.60	6.98	7.38	
(3f)[h]										
[BuA][i]	0.0510	0.102	0.153	0.204	0.55	0.306	0.357	0.408	0.459	0.510
$10^3 k_{A,R}$	0.437	0.817	1.32	1.99	2.57	3.36	4.29	5.29	6.42	7.65
[TEA][j]	0.102	0.2304	0.306	0.408	0.510	0.612	0.714	0.816	0.918	1.02
$10^3 k_{A,R}$	2.06	2.26	2.44	2.60	2.81	3.03	3.20	3.40	3.59	3.75

[a]The rate constants (s^{-1}) are accurate to within ±3%. [b][**3d**] 6.60 x 10^{-5} M; a λ 308 nm; log ε 4.22 ± 0.02. [c][TEA] 0.250 M. [d][BuA] 0.270 M. [e][**3e**] 5.65 x 10^{-5} M; a λ 324 nm; log ε 4.08 ± 0.02. [f][TEA] 0.25 M. [g][BuA] 0.25 M. [h][**3f**] 5.60 x 10^{-5} M; a λ 293 nm; log ε 4.22 ± 0.02. [i][TEA] 0.50 M. [j][BuA] 0.27 M.