Supporting Information

A Kinetic Study on Michael-Type Reactions of β-Nitrostyrenes with Cyclic Secondary Amines in Acetonitrile: Transition-State Structures and Reaction Mechanism Deduced from Negative Enthalpy of Activation and Analyses of LFERs

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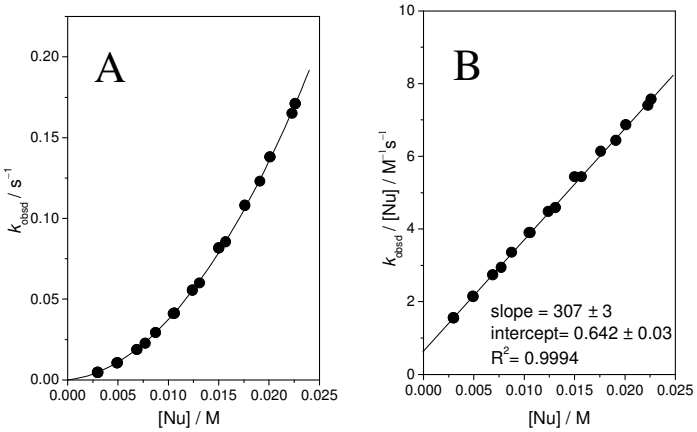
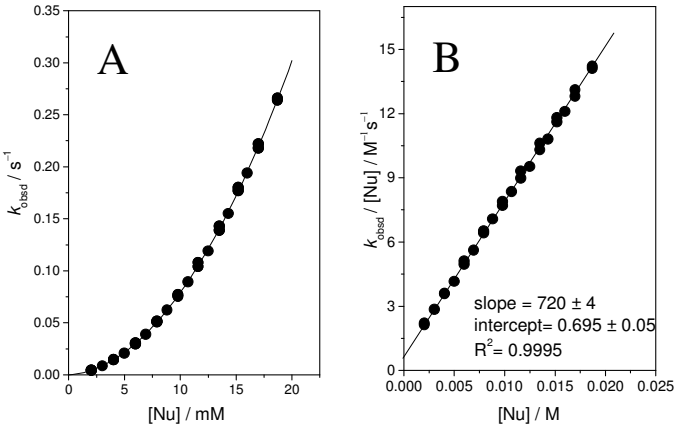


Figure S1. Plots of k_{obsd} vs [NH] (A) and k_{obsd}/[NH] vs [NH] (B) for the reaction of β-nitrostyrene **1g** with 3-methylpiperidine in MeCN at 25.0 ± 0.1 °C.



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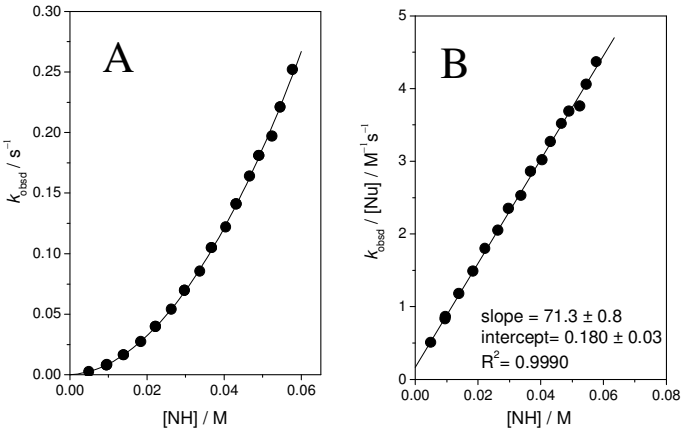

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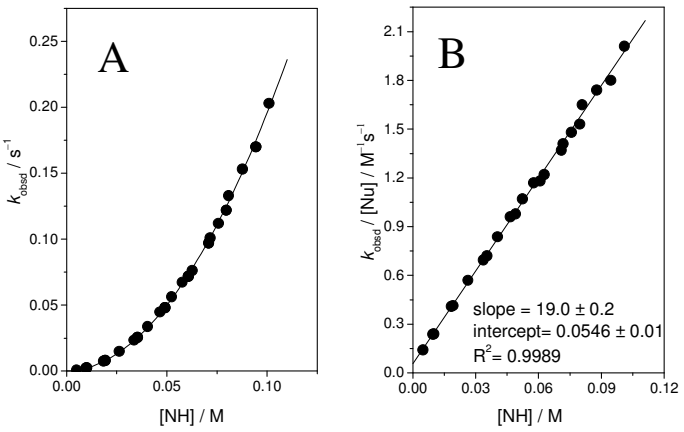
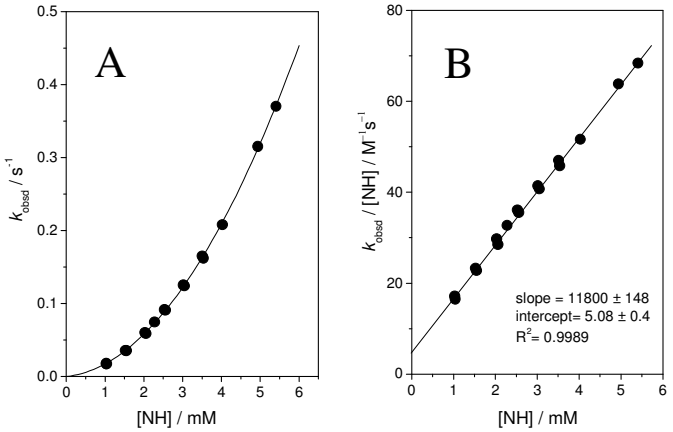


Figure S4. Plots of k_{obsd} vs [NH] (A) and k_{obsd}/[NH] vs [NH] (B) for the reaction of β-nitrostyrene **1g** with morpholine in MeCN at 25.0 ± 0.1 °C.



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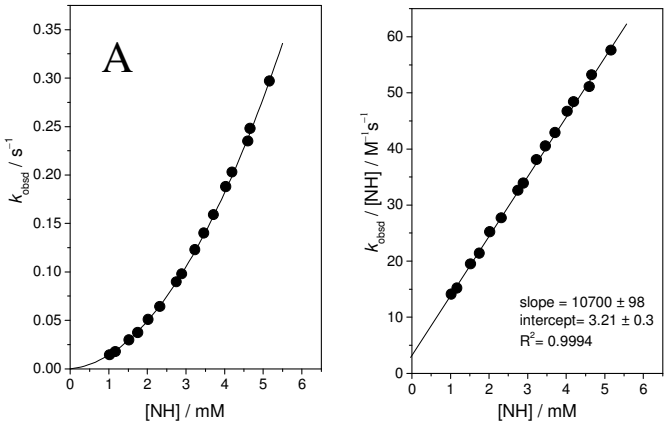

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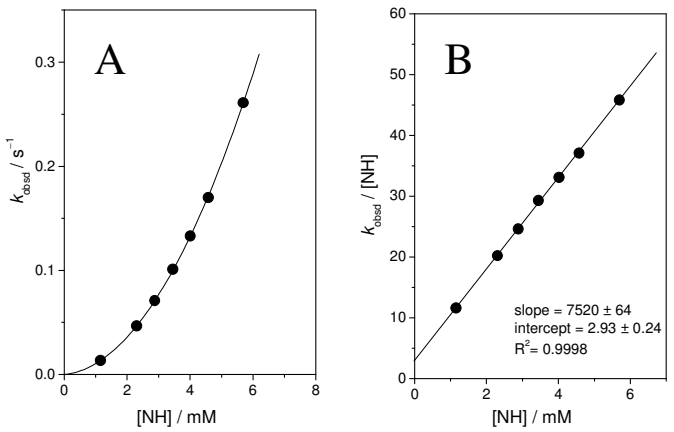

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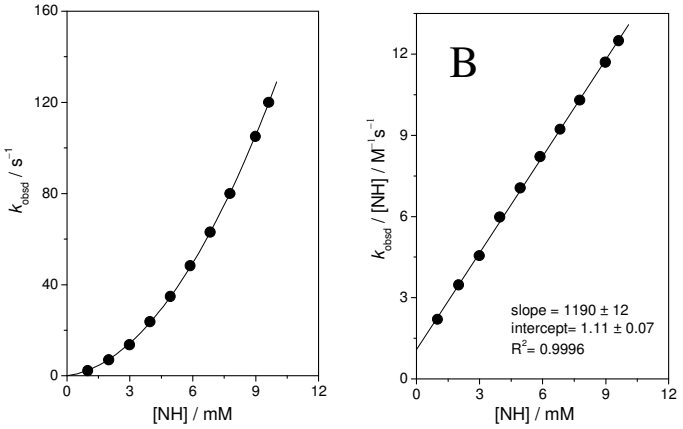

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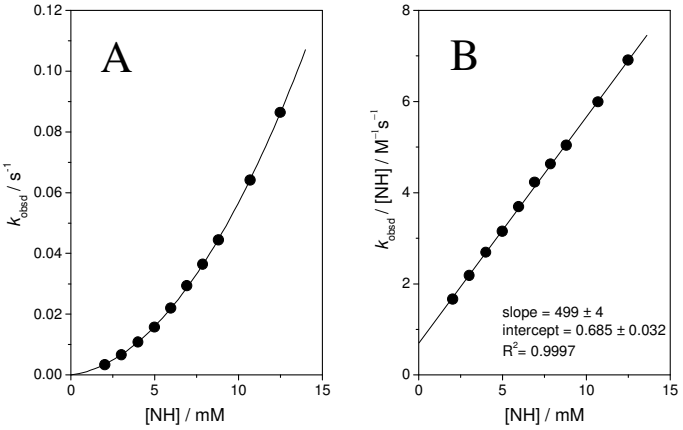

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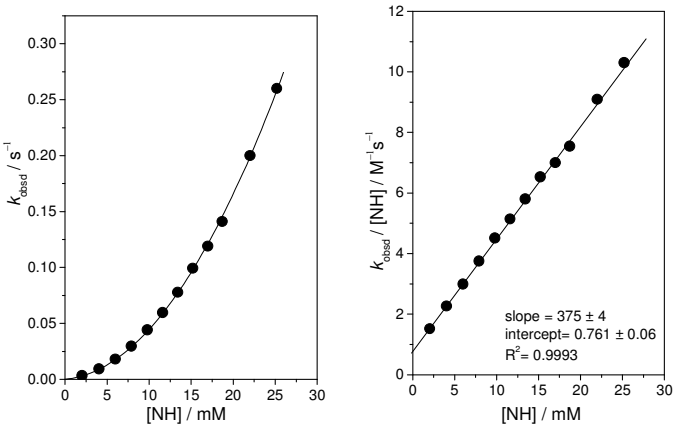

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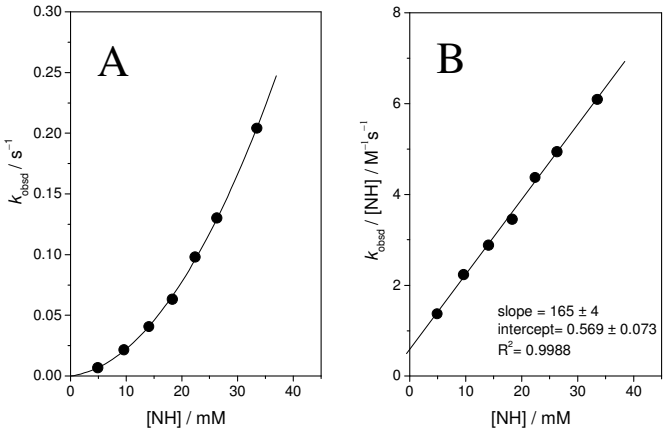

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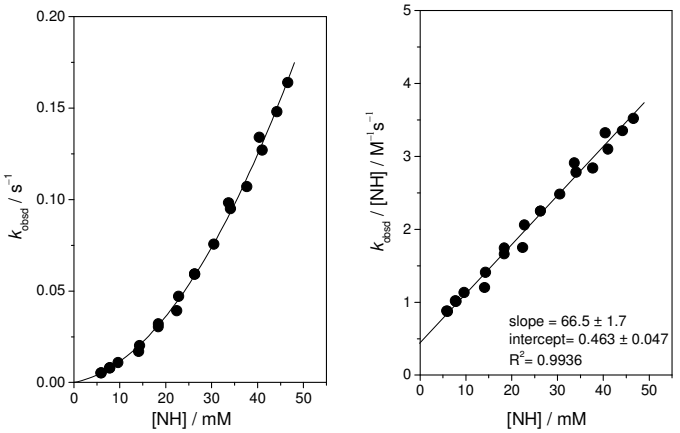

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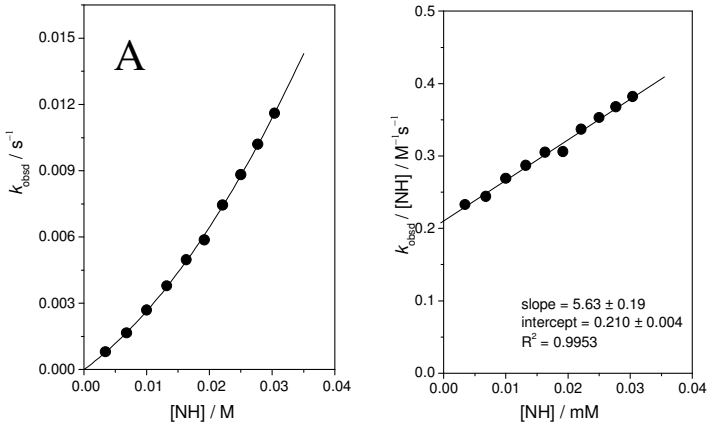

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Table S1. Kinetic data for the reaction of β-nitrostyrene **1g** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^3 k_{obsd}$/s^{-1}
2.00	3.07
3.95	9.35
5.87	18.5
7.75	30.8
9.60	46.6
11.4	64.5
12.8	79.8
14.1	94.0
15.9	119
17.4	141

Table S2. Kinetic data for the reaction of β-nitrostyrene **1g** with 3-methylpiperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}	[NH]/mM	k_{obsd}/s^{-1}
2.97	0.00463	12.4	0.0555
3.00	0.00464	13.1	0.0601
4.89	0.0105	15.0	0.0816
4.95	0.0106	15.7	0.0854
6.87	0.0188	17.6	0.108
7.72	0.0227	19.1	0.123
8.74	0.0294	20.1	0.138
10.5	0.0410	22.3	0.165
10.6	0.0413	22.6	0.171

Table S3. Kinetic data for the reaction of β-nitrostyrene **1g** with piperazine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}	[NH]/mM	k_{obsd}/s^{-1}	[NH]/mM	k_{obsd}/s^{-1}
2.04	0.00434	7.91	0.0515	13.5	0.143
2.04	0.00448	7.91	0.0508	13.5	0.139
3.02	0.00862	8.81	0.0623	14.3	0.155
4.03	0.0145	9.79	0.0771	15.2	0.180
4.03	0.0144	9.79	0.0754	15.2	0.177
4.99	0.0207	10.7	0.0893	16.0	0.194
5.99	0.0297	11.6	0.108	17.0	0.222
5.99	0.0306	11.6	0.104	17.0	0.218
6.92	0.0388	12.5	0.119	18.7	0.266
				18.7	0.264

Table S4. Kinetic data for the reaction of β-nitrostyrene **1g** with 1-(2-hydroxyethyl)piperazine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}	[NH]/mM	k_{obsd}/s^{-1}
4.93	0.00251	36.7	0.105
9.51	0.00793	40.4	0.122
9.62	0.00832	43.1	0.141
13.9	0.0164	46.6	0.164
18.4	0.0274	49.0	0.181
22.2	0.0399	52.4	0.197
26.3	0.0540	54.5	0.221
29.7	0.0698	57.7	0.252
33.7	0.0854		

Table S5. Kinetic data for the reaction of β-nitrostyrene **1g** with morpholine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}	[NH]/mM	k_{obsd}/s^{-1}
4.93	0.000697	57.7	0.0673
9.62	0.00228	60.8	0.0718
10.1	0.00242	62.7	0.0762
18.4	0.00752	70.9	0.097
19.3	0.00799	71.7	0.101
26.3	0.0150	75.8	0.112
33.7	0.0234	79.7	0.122
35.4	0.0255	80.8	0.133
40.4	0.0338	87.8	0.153
46.6	0.0448	94.5	0.170
49.1	0.0480	101	0.203
52.4	0.0563		

Table S6. Kinetic data for the reaction of 4-nitro-β-nitrostyrene **1a** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$	[NH]/mM	$10^2 k_{obsd}/s^{-1}$
1.03	1.76	3.02	12.5
1.04	1.72	3.05	12.4
1.53	3.57	3.51	16.5
1.55	3.53	3.54	16.2
2.03	6.02	4.03	20.8
2.06	5.87	4.94	31.5
2.28	7.45	5.41	37.0
2.53	9.14		
2.56	9.08		

Table S7. Kinetic data for the reaction of 3-nitro-β-nitrostyrenes **1b** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
1.02	1.44
1.17	1.78
1.52	2.97
1.75	3.74
2.02	5.10
2.32	6.42
2.75	8.97
2.89	9.80
3.23	12.3
3.46	14.0
3.71	15.9
4.03	18.8
4.19	20.3
4.60	23.5
4.66	24.8
5.16	29.7

Table S8. Kinetic data for the reaction of 4-cyano-β-nitrostyrenes **1c** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
1.16	1.34
2.31	4.66
2.89	7.11
3.45	10.1
4.02	13.3
4.58	17.0
5.70	26.1

Table S9. Kinetic data for the reaction of 4-chloro-β-nitrostyrenes **1d** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
1.00	0.220
2.00	0.693
2.99	1.36
3.96	2.37
4.93	3.48
5.88	4.83
6.83	6.30
7.77	7.99
8.99	10.5
9.62	12.0

Table S10. Kinetic data for the reaction of 3-methoxy-β-nitrostyrenes **1e** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
2.03	0.336
3.02	0.659
4.01	1.08
4.99	1.57
5.96	2.20
6.92	2.93
7.87	3.64
8.81	4.44
10.7	6.41
12.5	8.64

Table S11. Kinetic data for the reaction of 3-hydroxy-β-nitrostyrenes **1f** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
2.04	0.310
4.03	0.912
5.99	1.79
7.90	2.96
9.79	4.42
11.6	5.96
13.4	7.77
15.2	9.93
17.0	11.9
18.7	14.1
22.0	20.0
25.2	26.0

Table S12. Kinetic data for the reaction of 4-methyl-β-nitrostyrenes **1h** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^2 k_{obsd}/s^{-1}$
4.93	0.675
9.62	2.15
14.1	4.06
18.3	6.32
22.4	9.78
26.3	13.0
33.5	20.4

Table S13. Kinetic data for the reaction of 4-methoxy-β-nitrostyrene **1i** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^3 k_{obsd}/s^{-1}$	[NH]/mM	$10^3 k_{obsd}/s^{-1}$
5.88	5.17	26.3	59.1
5.97	5.22	26.3	59.3
7.77	7.89	30.5	75.6
7.88	7.99	33.7	98.2
9.62	10.9	34.1	94.9
14.1	16.9	37.7	107
14.3	20.2	40.4	134
18.4	30.5	41.0	127
18.4	32.0	44.2	148
22.4	39.2	46.6	164
22.8	47.0		

Table S14. Kinetic data for the reaction of 4-dimethylamino-β-nitrostyrenes **1j** with piperidine in MeCN at 25.0 ± 0.1 °C.

[NH]/mM	$10^3 k_{obsd}/s^{-1}$
3.44	0.802
6.79	1.66
10.0	2.69
13.2	3.79
16.3	4.97
19.2	5.87
22.1	7.44
25.0	8.82
27.7	10.2
30.4	11.6

Table S15. Kinetic data for the reaction of β-nitrostyrene **1g** with piperidine in MeCN at 15.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}
1.60	0.00215
3.18	0.00677
4.73	0.0146
7.01	0.0311
9.24	0.0519
11.4	0.0779
14.3	0.118
17.0	0.166
20.0	0.230

Table S16. Kinetic data for the reaction of β-nitrostyrene **1g** with piperidine in MeCN at 20.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}
1.60	0.00215
3.18	0.00676
4.73	0.0137
7.01	0.0279
9.24	0.0476
11.4	0.0702
14.3	0.108
17.0	0.151
20.0	0.207

Table S17. Kinetic data for the reaction of β-nitrostyrene **1g** with piperidine in MeCN at 30.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}
1.60	0.00246
3.18	0.00642
4.73	0.0126
6.26	0.0207
7.76	0.0299
9.24	0.0409
10.7	0.0537
12.8	0.0753
15.8	0.110
18.3	0.146

Table S18. Kinetic data for the reaction of β-nitrostyrene **1g** with piperidine in MeCN at 35.0 ± 0.1 °C.

[NH]/mM	k_{obsd}/s^{-1}
1.60	0.00248
3.18	0.00655
4.73	0.0123
7.01	0.0239
9.24	0.0386
11.4	0.0562
14.3	0.0833
17.0	0.114
20.0	0.153