

Supporting Information

Mechanistic Assessment of S_NAr Displacement of Halides from 1-Halo-2,4-dinitrobenzenes by Selected Primary and Secondary Amines: Brønsted and Mayr Analyses

Ik-Hwan Um,* Li-Ra Im, Ji-Sun Kang, Samantha S. Bursey[†] and Julian M. Dust*[†]
Department of Chemistry and Division of Nano Sciences, Ewha Womans University, Seoul 120-
750, Korea
E-mail: ihum@ewha.ac.kr, Tel: 82-2-3277-2349, Fax: 82-2-3277-2844

[†]Departments of Chemistry and Environmental Science, Grenfell Campus-Memorial University
of Newfoundland, Corner Brook, Newfoundland and Labrador A2H 6P9, Canada
E-mail: jdust@grenfell.mun.ca, Tel: 1-709-637-6200 ext. 6330, Fax: 1-709-639-8125

Table of Contents

Figures S1 and S2. Plots of k_{obsd} vs $[\text{RR}'\text{NH}]$ (A) and $k_{\text{obsd}}/[\text{RR}'\text{NH}]$ vs $[\text{RR}'\text{NH}]$ (B) for the reactions of 1a with <i>N</i> -methylbenzylamine and diethanolamine in MeCN at 25.0 ± 0.1 °C. -----	S2.
Figure S3. Plots of $k_{\text{obsd}}/[\text{RR}'\text{NH}]$ vs $[\text{RR}'\text{NH}]$ (A) and $[\text{RR}'\text{NH}]/k_{\text{obsd}}$ vs $1/[\text{RR}'\text{NH}]$ (B) for the reaction of 1a with diethylamine in MeCN at 25.0 ± 0.1 °C. -----	S3.
Figures S4 – S6. Mayr plots of $\log k_1$ vs <i>N</i> for the reactions of 1b - 1d with amines in MeCN at 25.0 ± 0.1 °C. -----	S3 – S4.
Figure S7. Plot of the Mayr <i>E</i> value estimated for 1-X-2,4-dinitrobenzenes vs electronegativity of the halogen atoms.-----	S5.
Tables S1 – S10. Kinetic data for the reactions of 1-fluoro-2,4-dinitrobenzene 1a with amines in MeCN and H ₂ O at 25.0 ± 0.1 °C. -----	S5 – S9.
Tables S11 – S22. Kinetic data for the reactions of 1-chloro-2,4-dinitrobenzene 1b with amines in MeCN and H ₂ O at 25.0 ± 0.1 °C. -----	S10 – S14.
Tables S23 – S34. Kinetic data for the reactions of 1-bromo-2,4-dinitrobenzene 1c with amines in MeCN and H ₂ O at 25.0 ± 0.1 °C. -----	S14 – S18.
Tables S35 –S46. Kinetic data for the reactions of 1-iodo-2,4-dinitrobenzene 1d with amines in MeCN and H ₂ O at 25.0 ± 0.1 °C. -----	S17 – S22.

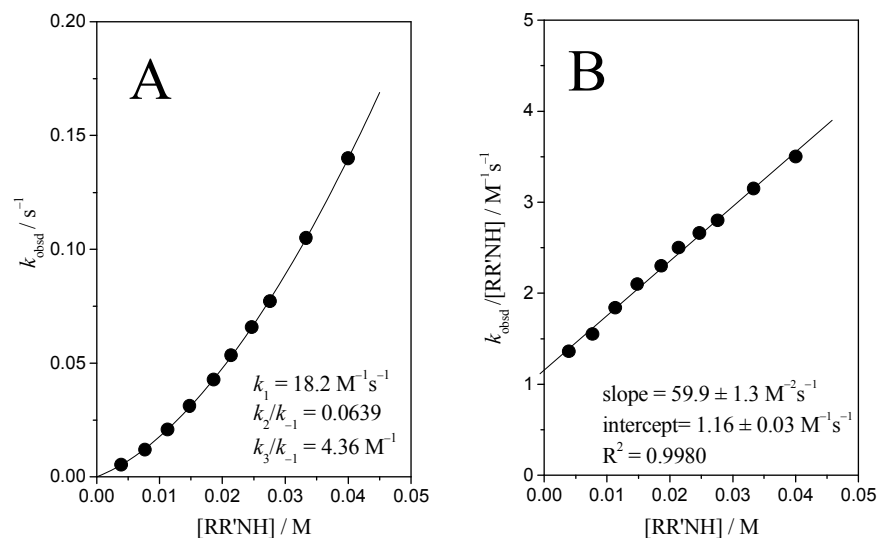


Figure S1. Plots of k_{obsd} vs $[\text{RR'NH}]$ (A) and $k_{\text{obsd}}/[\text{RR'NH}]$ vs $[\text{RR'NH}]$ (B) for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with *N*-methylbenzylamine in MeCN at 25.0 ± 0.1 °C.

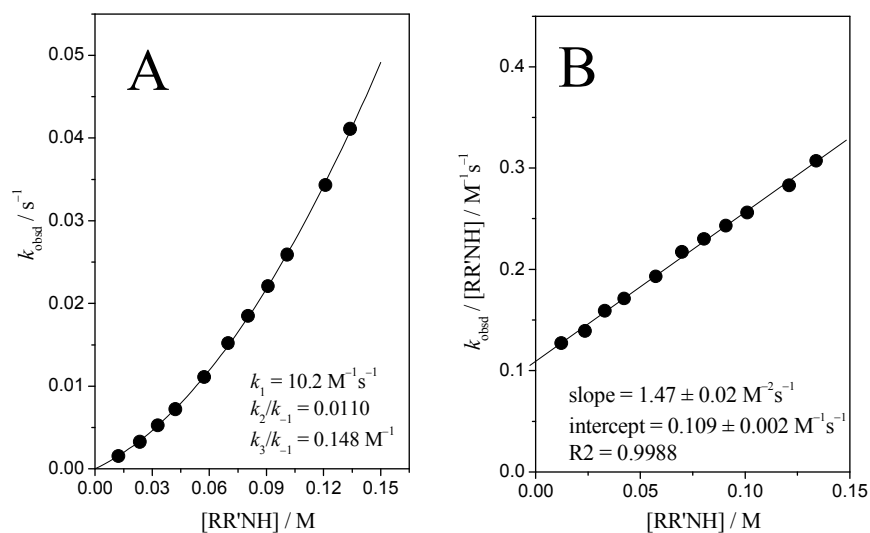


Figure S3. Plots of k_{obsd} vs $[\text{RR'NH}]$ (A) and $k_{\text{obsd}}/[\text{RR'NH}]$ vs $[\text{RR'NH}]$ (B) for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diethanolamine in MeCN at 25.0 ± 0.1 °C.

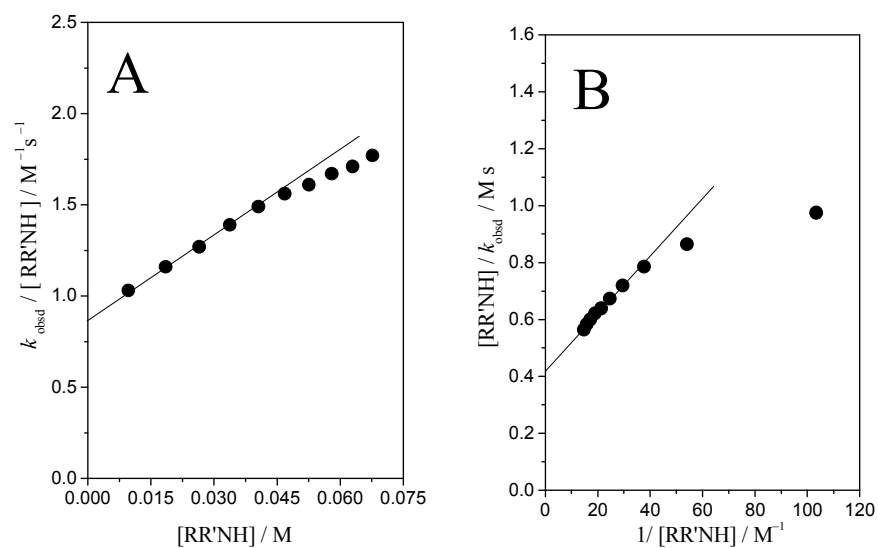


Figure S3. Plots of $k_{\text{obsd}}/[\text{RR'NH}]$ vs $[\text{RR'NH}]$ (A) and $[\text{RR'NH}]/k_{\text{obsd}}$ vs $1/[\text{RR'NH}]$ (B) for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diethylamine in MeCN at 25.0 ± 0.1 °C.

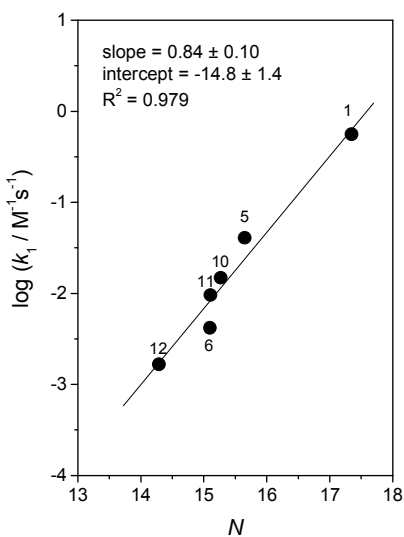


Figure S4. Mayr Plot of $\log k_1$ vs N for the reactions of 1-chloro-2,4-dinitrobenzene **1b** with amines in MeCN at 25.0 ± 0.1 °C.

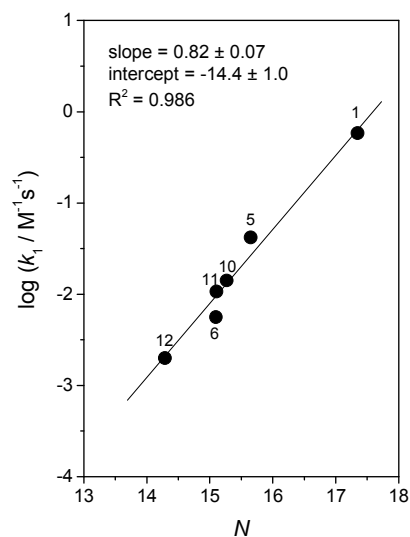


Figure S5. Mayr Plot of $\log k_1$ vs N for the reactions of 1-bromo-2,4-dinitrobenzene **1c** with amines in MeCN at 25.0 ± 0.1 °C.

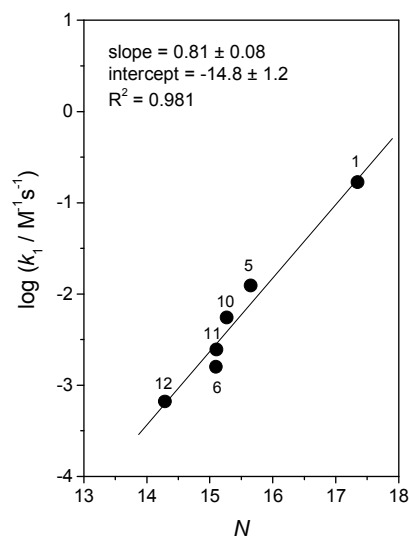


Figure S6. Mayr Plot of $\log k_1$ vs N for the reactions of 1-iodo-2,4-dinitrobenzene **1d** with amines in MeCN at 25.0 ± 0.1 °C.

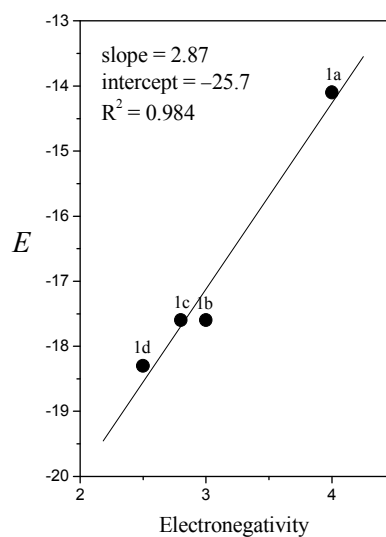


Figure S7. Plot of the Mayr E value estimated for 1-X-2,4-dinitrobenzenes vs electronegativity of the halogen atoms.

Table S1. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diethylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
9.67	0.00992
18.5	0.0214
26.5	0.0337
33.8	0.0470
40.6	0.0603
46.8	0.0732
52.6	0.0846
58.0	0.0966
63.0	0.108
67.7	0.120

Table S2. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with *N*-methylbenzylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
3.92	0.00533
7.69	0.0119
11.3	0.0208
14.8	0.0311
18.6	0.0428
21.4	0.0534
24.7	0.0658
27.6	0.0772
33.3	0.105
40.0	0.140

Table S3. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diallylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
24.5	0.000661
43.8	0.00167
59.4	0.00287
72.3	0.00406
83.2	0.00538
94.4	0.00684
104	0.00829
116	0.0101
125	0.0116
139	0.0140

Table S4. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diethanolamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
12.3	0.00156
23.6	0.00327
33.0	0.00526
42.3	0.00722
57.4	0.0111
69.9	0.0152
80.4	0.0185
90.9	0.0221
101	0.0259
121	0.0343
134	0.0411

Table S5. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with piperidine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
1.67	0.0140
3.32	0.0275
4.95	0.0406
6.54	0.0538
7.33	0.0602
8.12	0.0678
9.66	0.0790

$$k_1 = 8.20 \pm 0.07 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S6. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with diethylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
23.9	0.0113
42.7	0.0209
58.0	0.0280
70.6	0.0347
81.2	0.0397

$$k_1 = 0.496 \pm 0.005 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S7. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with *n*-butylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
1.60	0.0142
3.18	0.0278
4.73	0.0411
6.26	0.0545
7.77	0.0672

$$k_1 = 8.61 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S8. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with *n*-butylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
24.0	0.0101
42.9	0.0179
58.3	0.0245
71.0	0.0303
81.6	0.0349

$$k_1 = 0.432 \pm 0.005 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S9. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with *n*-propylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
2.95	0.0240
5.81	0.0473
9.50	0.0771
13.9	0.114
18.1	0.149
22.2	0.177

$$k_1 = 8.05 \pm 0.12 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9995$$

Table S10. Kinetic data for the reaction of 1-fluoro-2,4-dinitrobenzene **1a** with benzylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
3.98	0.00732
7.81	0.0145
15.0	0.0272
21.8	0.0400
28.0	0.0513
33.8	0.0621
40.6	0.0743

$$k_1 = 1.83 \pm 0.01 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S11. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with piperidine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
11.4	0.00620
21.5	0.0119
33.5	0.0180
40.2	0.0225
50.3	0.0277
64.0	0.0355
80.4	0.0448
101	0.0560

$$k_1 = 0.558 \pm 0.003 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S12. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with piperidine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
23.7	0.000910
42.3	0.00167
57.4	0.00232
69.9	0.00287
80.4	0.00336

$$k_1 = 0.0432 \pm 0.0006 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S13. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.3	0.0111
33.5	0.0199
46.4	0.0281
57.4	0.0347
67.0	0.0405

$$k_1 = 0.607 \pm 0.005 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S14. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with 1-(2-hydroxyethyl)piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.4	0.00202
33.7	0.00363
46.6	0.00498
57.7	0.00603
67.3	0.00693

$$k_1 = 0.101 \pm 0.002 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S15. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with 1-formylpiperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.5	0.00116
34.0	0.00211
47.1	0.00297
58.3	0.00372
68.0	0.00439

$$k_1 = 0.0653 \pm 0.0009 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S16. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with morpholine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.3	0.000808
33.5	0.00140
46.4	0.00193
57.4	0.00238
67.0	0.00282

$$k_1 = 0.0412 \pm 0.0006 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9996$$

Table S17. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with diethylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
40.6	0.000194
67.7	0.000318
102	0.000470
122	0.000538
135	0.000594
152	0.000657
162	0.000711

$$k_1 = 0.00417 \pm 0.00007 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9992$$

Table S18. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with diethylamine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
67.7	0.0000280
102	0.0000405
122	0.0000462
152	0.0000566
162	0.0000600

$$k_1 = 0.000336 \pm 0.000006 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9995$$

Table S19. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with *n*-butylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.4	0.000217
23.8	0.000281
33.7	0.000434
46.6	0.000623
57.7	0.000793

$$k_1 = 0.0148 \pm 0.0002 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S20. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with *n*-butylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
42.5	0.0000393
57.7	0.0000536
70.3	0.0000664
80.8	0.0000752
101	0.0000935

$$k_1 = 0.000927 \pm 0.000014 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S21. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with *n*-propylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
33.2	0.000313
61.9	0.000601
99.6	0.000947
120	0.00111
159	0.00152

$$k_1 = 0.00946 \pm 0.0002 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9993$$

Table S22. Kinetic data for the reaction of 1-chloro-2,4-dinitrobenzene **1b** with benzylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
67.0	0.000121
80.4	0.000142
101	0.000180
121	0.000212
134	0.000235
161	0.000277

$$k_1 = 0.00167 \pm 0.00002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9996$$

Table S23. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with piperidine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.5	0.0111
33.8	0.0202
46.8	0.0279
58.0	0.0346
67.7	0.0396

$$k_1 = 0.583 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9997$$

Table S24. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with piperidine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
23.7	0.00109
42.3	0.00194
57.4	0.00263
69.9	0.00328
80.4	0.00375

$$k_1 = 0.0472 \pm 0.0006 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9997$$

Table S25. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.4	0.0115
33.5	0.0216
46.4	0.0301
57.4	0.0383
67.0	0.0451

$$k_1 = 0.692 \pm 0.009 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S26. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with 1-(2-hydroxyethyl)piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.9	0.00233
34.7	0.00405
48.0	0.00536
59.4	0.00659
69.3	0.00766

$$k_1 = 0.105 \pm 0.001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S27. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with 1-formylpiperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
24.7	0.00176
44.2	0.00333
60.0	0.00453
73.0	0.00558
84.0	0.00637

$$k_1 = 0.0779 \pm 0.0007 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S28. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with morpholine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
24.2	0.00115
43.4	0.00197
58.9	0.00257
71.7	0.00313
82.4	0.00360

$$k_1 = 0.0418 \pm 0.0005 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9997$$

Table S29. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with diethylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
81.2	0.000451
102	0.000556
122	0.000670
135	0.000740
152	0.000847

$$k_1 = 0.00558 \pm 0.00012 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9992$$

Table S30. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with diethylamine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
68.3	0.0000324
82.0	0.0000392
103	0.0000478
123	0.0000569
137	0.0000631
154	0.0000720
164	0.0000767

$$k_1 = 0.000459 \pm 0.000006 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9994$$

Table S31. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with *n*-butylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.4	0.000226
33.7	0.000441
46.6	0.000632
57.7	0.000786
67.3	0.000919

$$k_1 = 0.0142 \pm 0.0001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S32. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with *n*-butylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
42.9	0.0000457
58.3	0.0000623
71.0	0.0000749
81.6	0.0000873
102	0.000110

$$k_1 = 0.00109 \pm 0.00001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S33. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with *n*-propylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
33.2	0.000348
61.9	0.000647
99.6	0.00103
120	0.00126
159	0.00169

$$k_1 = 0.0106 \pm 0.0001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S34. Kinetic data for the reaction of 1-bromo-2,4-dinitrobenzene **1c** with benzylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
67.3	0.000132
80.8	0.000160
101	0.000199
121	0.000237
135	0.000271
152	0.000304
162	0.000321

$$k_1 = 0.00201 \pm 0.00002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9996$$

Table S35. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with piperidine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.5	0.00305
33.8	0.00556
46.8	0.00767
58.0	0.00954
67.7	0.0113

$$k_1 = 0.167 \pm 0.002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9998$$

Table S36. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with piperidine in H_2O at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
9.57	0.000153
18.3	0.000302
26.2	0.000449
33.5	0.000575
40.2	0.000702

$$k_1 = 0.0179 \pm 0.0002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9998$$

Table S37. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.3	0.00322
33.5	0.00590
46.4	0.00830
57.4	0.0103
67.0	0.0120

$$k_1 = 0.181 \pm 0.001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S38. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with 1-(2-hydroxyethyl)piperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.9	0.000572
34.7	0.00109
48.0	0.00152
59.4	0.00185
69.3	0.00218

$$k_1 = 0.0317 \pm 0.0004 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S39. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with 1-formylpiperazine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
24.7	0.000519
35.0	0.000737
44.2	0.000919
60.0	0.00125
66.8	0.00141
73.0	0.00152
84.0	0.00177

$$k_1 = 0.0210 \pm 0.0002 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S40. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with morpholine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
34.3	0.000420
43.4	0.000533
58.9	0.000720
65.5	0.000802
71.7	0.000877
82.4	0.00101

$$k_1 = 0.0122 \pm 0.00003 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S41. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with diethylamine in MeCN at $25.0 \pm 0.1^\circ\text{C}$.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
67.7	0.000109
81.2	0.000127
102	0.000160
122	0.000192
135	0.000212
152	0.000241

$$k_1 = 0.00157 \pm 0.00002 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S42. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with diethylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
70.3	0.0000114
84.4	0.0000131
106	0.0000159
127	0.0000184
141	0.0000203
159	0.0000228
169	0.0000244

$$k_1 = 0.000130 \pm 0.000002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9993$$

Table S43. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with *n*-butylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
23.8	0.0000977
42.5	0.000207
57.7	0.000287
67.3	0.000341
70.3	0.000355

$$k_1 = 0.00553 \pm 0.00007 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9997$$

Table S44. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with *n*-butylamine in H₂O at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
18.4	0.00000905
23.8	0.0000116
42.5	0.0000200
57.7	0.0000273
70.3	0.0000323
80.8	0.0000372

$$k_1 = 0.000450 \pm 0.000005 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9997$$

Table S45. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with *n*-propylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
39.9	0.000116
66.5	0.000183
79.7	0.000218
99.6	0.000270
120	0.000316
133	0.000348
149	0.000385

$$k_1 = 0.00247 \pm 0.00003 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9996$$

Table S46. Kinetic data for the reaction of 1-iodo-2,4-dinitrobenzene **1d** with benzylamine in MeCN at 25.0 ± 0.1°C.

[amine]/mM	$k_{\text{obsd}}/\text{s}^{-1}$
39.9	0.0000265
66.5	0.0000441
79.7	0.0000524
99.6	0.0000657
120	0.0000795
133	0.0000878
149	0.0000984

$$k_1 = 0.000660 \pm 0.000002 \text{ M}^{-1}\text{s}^{-1}$$

$$R^2 = 0.9999$$