

Electronic supplementary information

Nonlinear Hammett plots in pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates: Change in rate-determining step versus resonance contribution

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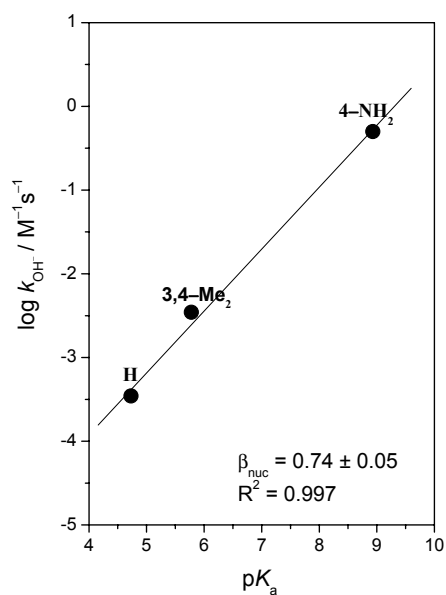


Figure S1. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-dimethylaminobenzoate (**1a**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

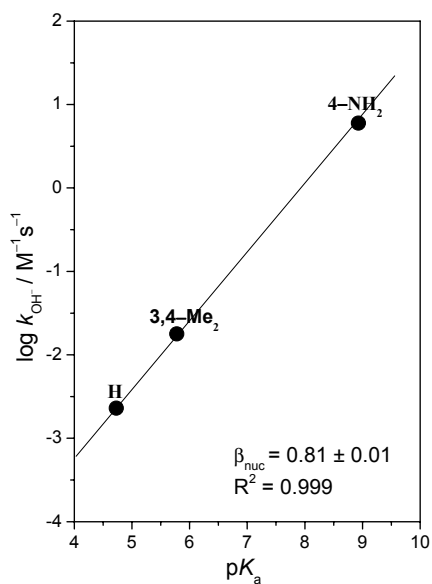


Figure S2. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-methoxybenzoate (**1b**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

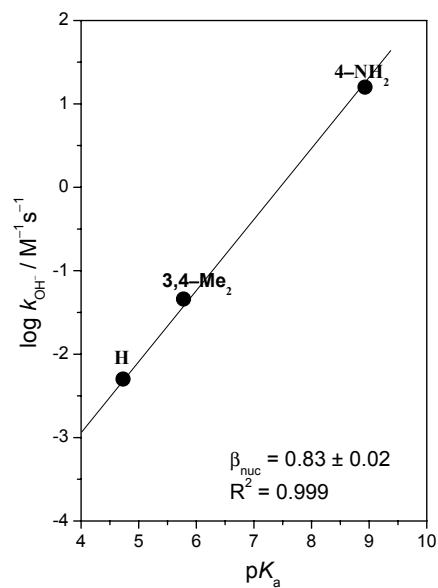


Figure S3. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-methylbenzoate (**1c**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

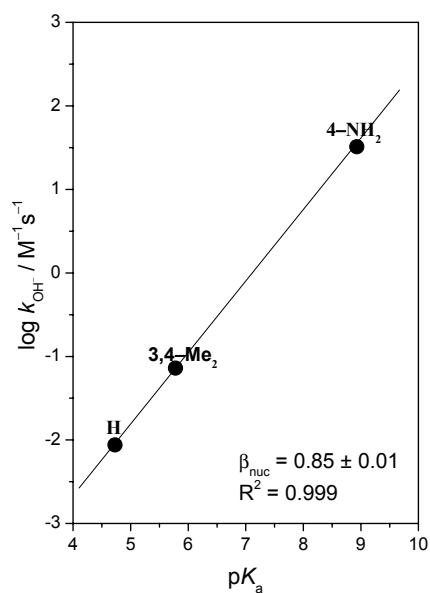


Figure S4. Brønsted-type plot for the reactions of 2,4-dinitrophenyl benzoate (**1d**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

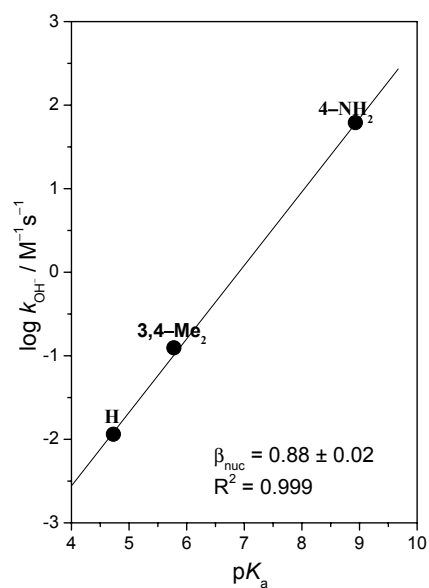


Figure S5. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-chlorobenzoate (**1e**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

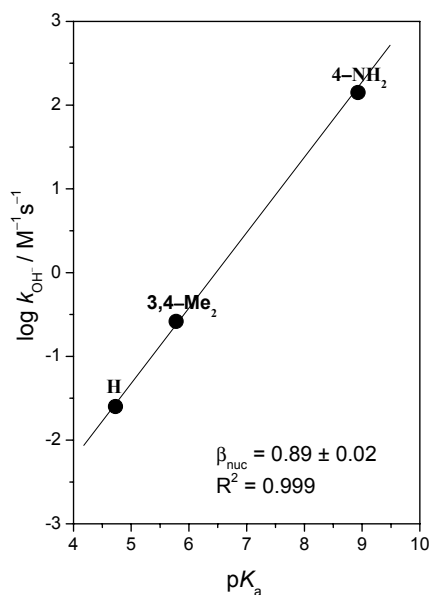


Figure S6. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 3-chlorobenzoate (**1f**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

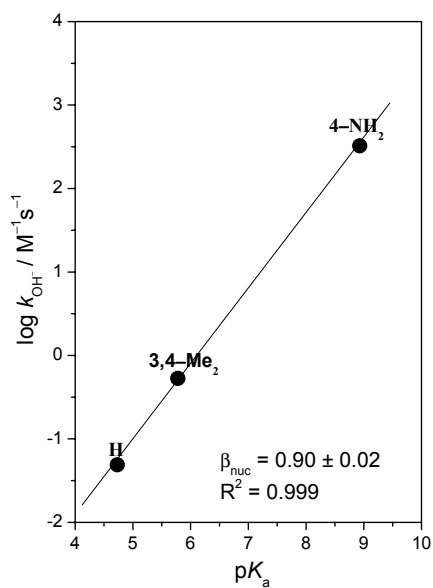


Figure S7. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-cyanobenzoate (**1g**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

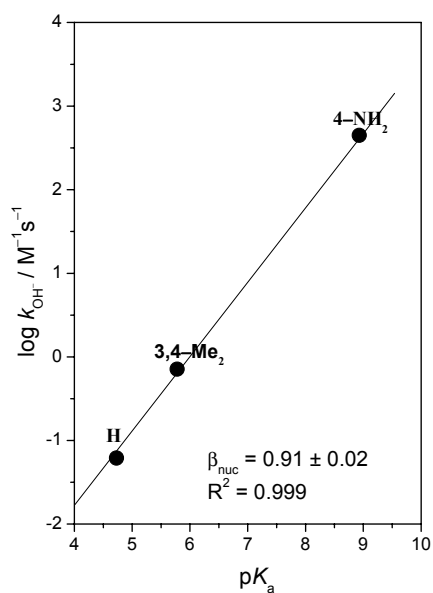


Figure S8. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-nitrobenzoate (**1h**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

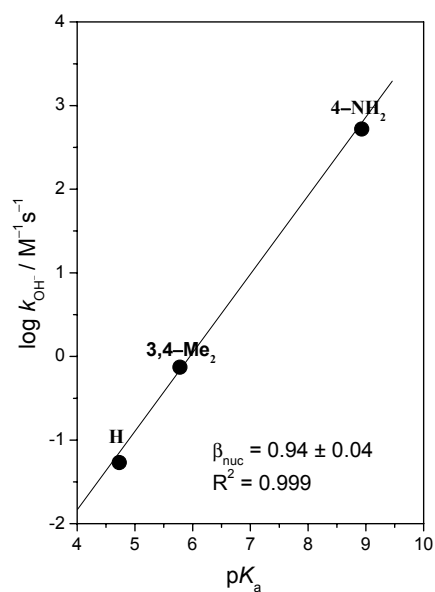


Figure S9. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 4-chloro-3-nitrobenzoate (**1i**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

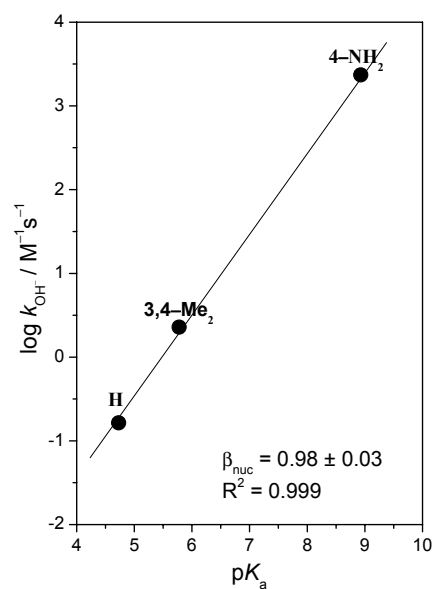


Figure S10. Brønsted-type plot for the reactions of 2,4-dinitrophenyl 3,5-dinitrobenzoate (**1j**) with Z-substituted pyridines (Z = H, 3,4-Me₂, and 4-NH₂) in 80 mol % H₂O / 20 mol % DMSO at 25.0 ± 0.1 °C.

Table S1. Kinetic data for reaction of 2,4-dinitrophenyl 4-dimethylaminobenzoate (**1a**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
18.8	9.54
34.5	17.0
47.8	23.4
59.1	29.6
69.0	34.5

$$k_{\text{OH}^-} = 0.499 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S2. Kinetic data for reaction of 2,4-dinitrophenyl 4-methoxybenzoate (**1b**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
4.04	24.0
7.92	46.5
11.7	69.7
15.3	91.5
18.7	111

$$k_{\text{OH}^-} = 5.97 \pm 0.04 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S3. Kinetic data for reaction of 2,4-dinitrophenyl 4-methylbenzoate (**1c**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
1.63	24.2
3.24	49.7
4.83	75.1
6.39	100
7.92	123

$$k_{\text{OH}^-} = 15.8 \pm 0.10 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S4. Kinetic data for reaction of 2,4-dinitrophenyl benzoate (**1d**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^4 [4-aminopyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
11.9	3.65
15.8	5.09
19.7	6.29
23.6	7.28
27.5	9.14
31.4	9.75

$$k_{\text{OH}^-} = 32.0 \pm 1.63 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9948$$

Table S5. Kinetic data for reaction of 2,4-dinitrophenyl 4-chlorobenzoate (**1e**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^4 [4-aminopyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
7.40	4.12
14.7	8.51
21.9	13.5
29.1	17.7
31.4	18.8

$$k_{\text{OH}^-} = 62.0 \pm 1.36 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9992$$

Table S6. Kinetic data for reaction of of 2,4-dinitrophenyl 3-chlorobenzoate (**1f**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^4 [4-aminopyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
3.60	4.48
5.70	7.66
7.10	9.50
10.6	15.0
14.1	19.2

$$k_{\text{OH}^-} = 142 \pm 4.00 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9988$$

Table S7. Kinetic data for reaction of of 2,4-dinitrophenyl 4-cyanobenzoate (**1g**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^4 [4-aminopyridine] / M	$k_{\text{obsd}} / \text{s}^{-1}$
20.0	0.61
40.0	1.22
60.0	1.90
80.0	2.52
100	3.17

$$k_{\text{OH}^-} = 321 \pm 2.51 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S8. Kinetic data for reaction of of 2,4-dinitrophenyl 4-nitrobenzoate (**1h**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$k_{\text{obsd}} / \text{s}^{-1}$
1.97	0.83
3.93	1.70
5.90	2.56
7.86	3.47
9.83	4.32

$$k_{\text{OH}^-} = 446 \pm 3.00 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S9. Kinetic data for reaction of of 2,4-dinitrophenyl 4-chloro,3-nitrobenzoate (**1i**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$k_{\text{obsd}} / \text{s}^{-1}$
1.97	1.07
3.93	2.16
5.90	3.12
7.86	4.17
9.83	5.17

$$k_{\text{OH}^-} = 520 \pm 5.00 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S10. Kinetic data for reaction of of 2,4-dinitrophenyl 3,5-dinitrobenzoate (**1j**) with 4-aminopyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [4-aminopyridine] / M	$k_{\text{obsd}} / \text{s}^{-1}$
1.97	4.06
3.93	8.51
5.90	13.1
7.86	17.6
9.83	22.5

$$k_{\text{OH}^-} = 2340 \pm 20.0 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S11. Kinetic data for reaction of of 2,4-dinitrophenyl 4-dimethylaminobenzoate (**1a**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^4 k_{\text{obsd}} / \text{s}^{-1}$
43.4	1.00
58.9	1.37
71.7	1.67
91.6	2.13
103	2.34

$$k_{\text{OH}^-} = 0.00227 \pm 0.00005 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9993$$

Table S12. Kinetic data for reaction of of 2,4-dinitrophenyl 4-methoxybenzoate (**1b**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
8.58	1.65
10.3	1.92
12.0	2.22
15.4	2.87
18.9	3.45

$$k_{\text{OH}^-} = 0.0177 \pm 0.0003 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9995$$

Table S13. Kinetic data for reaction of of 2,4-dinitrophenyl 4-methylbenzoate (**1c**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
43.4	2.28
58.9	2.96
71.7	3.59
82.4	4.08
103	4.96

$$k_{\text{OH}^-} = 0.0453 \pm 0.0007 \text{ M}^{-1} \text{ s}^{-1}$$
$$R^2 = 0.9996$$

Table S14. Kinetic data for reaction of of 2,4-dinitrophenyl benzoate (**1d**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
9.20	8.31
11.7	10.3
15.1	12.6
17.7	14.6
21.0	16.9

$$k_{\text{OH}^-} = 0.0725 \pm 0.0009 \text{ M}^{-1} \text{ s}^{-1}$$
$$R^2 = 0.9997$$

Table S15. Kinetic data for reaction of of 2,4-dinitrophenyl 4-chlorobenzoate (**1e**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
43.6	5.94
72.0	9.65
82.8	10.8
104	13.4
124	16.0

$$k_{\text{OH}^-} = 0.124 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$$
$$R^2 = 0.9997$$

Table S16. Kinetic data for reaction of of 2,4-dinitrophenyl 3-chlorobenzoate (**1f**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
18.7	4.98
34.3	8.65
47.5	12.2
58.9	15.4
68.7	17.9

$$k_{\text{OH}^-} = 0.261 \pm 0.005 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9994$$

Table S17. Kinetic data for reaction of of 2,4-dinitrophenyl 4-cyanobenzoate (**1g**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
19.0	1.04
34.9	1.95
48.3	2.64
59.8	3.25
69.8	3.74

$$k_{\text{OH}^-} = 0.531 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S18. Kinetic data for reaction of of 2,4-dinitrophenyl 4-nitrobenzoate (**1h**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
9.81	7.33
18.7	13.6
26.9	19.1
34.3	24.8
41.2	29.7

$$k_{\text{OH}^-} = 0.713 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S19. Kinetic data for reaction of of 2,4-dinitrophenyl 4-chloro,3-nitrobenzoate (**1i**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
19.0	1.40
34.9	2.64
48.3	3.65
59.8	4.44
69.8	5.19

$$k_{\text{OH}^-} = 0.743 \pm 0.008 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S20. Kinetic data for reaction of of 2,4-dinitrophenyl 3,5-dinitrobenzoate (**1j**) with 3,4-dimethylpyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [3,4-dimethylpyridine] / M	$10^2 k_{\text{obsd}} / \text{s}^{-1}$
8.05	1.85
15.5	3.61
19.0	4.42
22.4	5.14
25.7	5.87

$$k_{\text{OH}^-} = 2.28 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9997$$

Table S21. Kinetic data for reaction of of 2,4-dinitrophenyl 4-dimethylaminobenzoate (**1a**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^5 k_{\text{obsd}} / \text{s}^{-1}$
11.3	3.96
12.9	4.53
14.5	5.06
16.1	5.63
17.1	5.98

$$k_{\text{OH}^-} = (3.47 \pm 0.02) \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S22. Kinetic data for reaction of of 2,4-dinitrophenyl 4-methoxybenzoate (**1b**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^4 k_{\text{obsd}} / \text{s}^{-1}$
11.3	2.20
12.9	2.51
14.5	2.85
16.1	3.32
17.1	3.50

$$k_{\text{OH}^-} = 0.00231 \pm 0.0001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9970$$

Table S23. Kinetic data for reaction of of 2,4-dinitrophenyl 4-methylbenzoate (**1c**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^4 k_{\text{obsd}} / \text{s}^{-1}$
9.67	4.84
11.3	5.67
12.9	6.46
14.5	7.18
16.1	8.07

$$k_{\text{OH}^-} = 0.00496 \pm 0.00008 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9995$$

Table S24. Kinetic data for reaction of of 2,4-dinitrophenyl benzoate (**1d**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^4 k_{\text{obsd}} / \text{s}^{-1}$
9.82	9.15
13.1	11.9
14.7	13.2
16.4	14.8
17.3	15.6

$$k_{\text{OH}^-} = 0.00861 \pm 0.00001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S25. Kinetic data for reaction of of 2,4-dinitrophenyl 4-chlorobenzoate (**1e**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
11.3	1.49
12.9	1.68
14.5	1.85
16.1	2.04
17.0	2.14

$$k_{\text{OH}^-} = 0.0114 \pm 0.0001 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9998$$

Table S26. Kinetic data for reaction of of 2,4-dinitrophenyl 3-chlorobenzoate (**1f**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
47.6	1.08
75.4	1.75
109	2.58
151	3.62
177	4.27

$$k_{\text{OH}^-} = 0.0248 \pm 0.00004 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9999$$

Table S27. Kinetic data for reaction of of 2,4-dinitrophenyl 4-cyanobenzoate (**1g**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
65.4	3.28
73.6	3.65
83.3	4.15
89.9	4.43
105	5.20

$$k_{\text{OH}^-} = 0.0485 \pm 0.0007 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9996$$

Table S28. Kinetic data for reaction of of 2,4-dinitrophenyl 4-nitrobenzoate (**1h**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
6.46	3.67
7.36	4.24
8.33	4.79
8.99	5.36
10.6	6.23

$$k_{\text{OH}^-} = 0.0614 \pm 0.004 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9962$$

Table S29. Kinetic data for reaction of of 2,4-dinitrophenyl 4-chloro,3-nitrobenzoate (**1i**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^2 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
6.70	3.89
8.52	4.81
10.9	6.10
13.4	7.56
15.1	8.37
16.7	9.43
17.7	9.79
19.2	10.5
20.9	11.4

$$k_{\text{OH}^-} = 0.0534 \pm 0.0007 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9993$$

Table S30. Kinetic data for reaction of of 2,4-dinitrophenyl 3,5-dinitrobenzoate (**1j**) with pyridine in 80 mol % H₂O/20 mol % DMSO at 25.0 ± 0.1 °C.

10^3 [pyridine] / M	$10^3 k_{\text{obsd}} / \text{s}^{-1}$
56.4	8.96
65.4	10.2
73.6	11.6
83.3	13.1
89.9	14.5

$$k_{\text{OH}^-} = 0.164 \pm 0.006 \text{ M}^{-1}\text{s}^{-1}$$
$$R^2 = 0.9979$$