## Electronic Supplemetary Information

## Mechanistic pathways in aromatic nucleophilic substitution in conventional solvents and ionic liquids.

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Figure S1. Chromatogram of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S2. Chromatogram of piperidine (0.11 mol  $L^{-1}$ ) in water at pH=11.24 using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S3. Chromatogram of the 1-(2,4-dinitrophenylsulfonyl)piperidine  $(5.05 \times 10^{-5} \text{ mol } \text{L}^{-1})$  using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S4. Chromatogram of the 1-(2,4-dinitrophenyl)piperidine  $(5.00 \times 10^{-5} \text{ mol } \text{L}^{-1})$  using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S5. Chromatogram of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with piperidine (0.11 mol  $\text{L}^{-1}$ ) at 130 min. in water at pH=11.24, using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S6. Chromatogram of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with piperidine (0.11 mol  $\text{L}^{-1}$ ) at 150 min. of reaction in MeCN using a mobile phase of 50% MeOH/H<sub>2</sub>O, the flow rate was 0.5 mL min<sup>-1</sup> and UV-visible detection at 260 nm.



Figure S7. Chromatograms of 1-(2,4-dinitrophenyl)piperidine  $(5.00 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (cyan line); 1-(2,4-dinitrophenylsulfonyl)piperidine  $(5.05 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (magenta line); piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  pH=11.24 (green line) and the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  in water at pH=11.24 at 130 min. (blue line) using a mobile phase of 50% MeOH/H<sub>2</sub>O), the flow rate was 0.5 mL min<sup>-1</sup> and UV-vis detection at 260 nm.



Figure S8. Chromatograms of 1-(2,4-dinitrophenyl)piperidine  $(5.00 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (cyan line); 1-(2,4-dinitrophenylsulfonyl)piperidine  $(5.05 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (magenta line); piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  in water at pH=11.24 (dark green line) and the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  in water at pH=11.24 at different times: 130 min. (blue line), 35 min. (green line), 50 min. (pink line), 77 min. (olive line) and 102 min. (dark cian) using a mobile phase of 50% MeOH/H<sub>2</sub>O), the flow rate was 0.5 mL min<sup>-1</sup> and UV-vis detection at 260 nm.



Figure S9. Chromatograms of 1-(2,4-dinitrophenyl)piperidine  $(5.00 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (cyan line); 1-(2,4-dinitrophenylsulfonyl)piperidine  $(5.05 \times 10^{-5} \text{ mol } \text{L}^{-1})$  (magenta line); piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  in water at pH=11.24 (dark green line) and the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride  $(5.10 \times 10^{-5} \text{ mol } \text{L}^{-1})$  with piperidine  $(0.11 \text{ mol } \text{L}^{-1})$  in MeCN at different times: 150 min. (blue line), 15 min. (green line), 28 min. (pink line) and 130 min. (olive line) using a mobile phase of 50% MeOH/H<sub>2</sub>O), the flow rate was 0.5 mL min<sup>-1</sup> and UV-vis detection at 260 nm.



Figure S10. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine at three pH values, in aqueous solution, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S11. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperazine at three pH values, in aqueous solution, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S12. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with 1-(2-hydroxyethyl)piperazine at three pH values, in aqueous solution, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S13. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with morpholine at three pH values, in aqueous solution, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S14. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with 1-formylpiperazine at three pH values, in aqueous solution, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S15. Brønsted-type plot (statistically corrected) obtained in the reactions of secondary alicyclic amines with 2,4-dinitrobenzenesulfonyl chloride in aqueous solution, at 25.0 °C and an ionic strength of 0.2 M (KCl).



Figure S16. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in dimethylsulfoxide (DMSO) at 25.0 °C.



Figure S17. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethanol at 25.0 °C.



Figure S18. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 2-propanol at 25.0 °C.



Figure S19. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in butanol at 25.0 °C.



Figure S20. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in tert-butanol at 25.0 °C.



Figure S21. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in methanol at 25.0 °C.



Figure S22. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in formamide (FMA) at 25.0 °C.



Figure S23. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine at pH=10.82, in ethanol:water 50:50 mixture, at 25.0 °C and ionic strength 0.2M (KCl).



Figure S24. Plot of  $k_{obs}$  against free amine concentration [N<sub>F</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine at pH=10, in ethanol:water 90:10 mixture, at 25.0 °C.



Figure S25. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in ethylamonium nitrate (EAN) at 25.0 °C.



Figure S26. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>) at 25.0 °C.



Figure S27. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium thiocyanate (EMIMSCN) at 25.0 °C.



Figure S28. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) at 25.0 °C.



Figure S29. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) at 25.0 °C.



Figure S30. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate (MOEDEAFAP) at 25.0 °C.



Figure S31. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (EMIMFAP) at 25.0 °C.



Figure S32. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMIMFAP) at 25.0 °C.



Figure S33. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate (BMPLFAP) at 25.0 °C.



Figure S34. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium dicyanamide (BMIMDCN) at 25.0 °C.



Figure S35. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1-methylpyrrolidinium dicyanamide (BMPLDCN) at 25.0 °C.



Figure S36. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCN) at 25.0 °C.



Figure S37. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (BMIMNTF<sub>2</sub>) at 25.0 °C.



Figure S38. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMIMNTF<sub>2</sub>) at 25.0 °C.



Figure S39. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide (BMPLNTF<sub>2</sub>) at 25.0 °C.



Figure S40. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide (BM<sub>2</sub>IMNTF<sub>2</sub>) at 25.0 °C.



Figure S41. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in 1-hexyl 3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (HMIMNTF<sub>2</sub>) at 25.0 °C.



Figure S42. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetonitrile (MeCN) at 25.0 °C.



Figure S43. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetonitrile (MeCN) at 25.0 °C.



Figure S44. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in tetrahydrofuran (THF) at 25.0 °C.



Figure S45. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in tetrahydrofuran (THF) at 25.0 °C.



Figure S46. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at 25.0 °C.



Figure S47. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at 25.0 °C.



Figure S48. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in chloroform (CHCl<sub>3</sub>) at 25.0 °C.



Figure S49. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in chloroform (CHCl<sub>3</sub>) at 25.0 °C.



Figure S50. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in benzene (C<sub>6</sub>H<sub>6</sub>) at 25.0 °C.



Figure S51. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in benzene (C<sub>6</sub>H<sub>6</sub>) at 25.0 °C.



Figure S52. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in N,N-dimethylformamide (DMF) at 25.0 °C.



Figure S53. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in N,N-dimethylformamide (DMF) at 25.0 °C.



Figure S54. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1,4-dioxane at 25.0 °C.



Figure S55. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1,4-dioxane at 25.0 °C.



Figure S56. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetone at 25.0 °C.



Figure S57. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetone at 25.0 °C.



Figure S58. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in cyclohexane at 25.0 °C.



Figure S59. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in cyclohexane at 25.0 °C.



Figure S60. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in diethyl ether at 25.0 °C.



Figure S61. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in diethyl ether at 25.0 °C.



Figure S62. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethyl acetate at 25.0 °C.



Figure S63. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethyl acetate at 25.0 °C.



Figure S64. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in n-hexane at 25.0 °C.



Figure S65. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in n-hexane at 25.0 °C.



Figure S66. Plot of  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in n-heptane at 25.0 °C.



Figure S67. Plot of  $k_{obs}/[N_T]$  against total amine concentration  $[N_T]$  for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in n-heptane at 25.0 °C.



Figure S68. Comparison between  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in BMIMDCN, BMIMPF<sub>6</sub>, BMIMFAP, BMIMNTF<sub>2</sub> and BMIMBF<sub>4</sub> at 25.0 °C.



Figure S69. Comparison between  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in BMPLDCN, BMPLFAP and BMPLNTF<sub>2</sub> at 25.0 °C.



Figure S70. Comparison between  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in BMIMDCN, BMPLDCN and EMIMDCN at 25.0 °C.



Figure S71. Comparison between  $k_{obs}$  against total amine concentration [N<sub>T</sub>] for the reaction of 2,4dinitrobenzenesulfonyl chloride with piperidine in BMIMFAP, BMPLFAP, EMIMFAP and MOEDEAFAP at 25.0 °C.



Figure S72. Multiparametric regression of log  $k_N$  in terms of Hydrogen Bond Acidity ( $\alpha$ ), Hydrogen Bond Basicity ( $\beta$ ) and solvent polarity ( $\pi$ ) for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine for non catalyzed processes in COS of Table 3.



Figure S73. Multiparametric regression of log  $k_N$  in terms of Hydrogen Bond Acidity ( $\alpha$ ), Hydrogen Bond Basicity ( $\beta$ ) and solvent polarity ( $\pi$ ) for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in RTILs of Table 4.



	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} /{ m s}^{-1}$
1	2.73	2.27
2	6.82	6.20
3	10.9	10.6
4	15.0	15.0
5	19.1	19.7
6	23.2	23.7
7	27.3	29.0

Table S1. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=10.94.

Table S2. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=11.24.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs}  /  { m s}^{-1}$
1	2.56	3.99
2	6.40	10.0
3	10.2	15.6
4	14.1	22.6
5	17.9	28.7
6	21.7	33.8
7	25.6	39.7

Table S3. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=11.54.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$	
1	2.52	5.34	
2	6.29	12.5	
3	10.1	20.9	
4	13.8	28.6	
5	17.6	36.2	
6	21.4	45.5	
7	25.2	48.8	

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{ m s}^{-1}$
1	1.29	2.89
2	3.24	6.72
3	5.18	10.4
4	7.12	14.7
5	9.06	19.4
6	11.0	23.5
7	12.9	28.2

Table S4. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.64.

Table S5. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.94.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	1.20	3.88
2	3.00	8.96
3	4.80	15.0
4	6.60	20.5
5	8.40	26.1
6	10.2	31.6
7	12.0	36.1

Table S6. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=10.24.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$	
1	2.70	10.6	
2	6.76	24.2	
3	10.8	39.2	
4	14.9	53.0	
5	18.9	67.3	
6	23.0	82.2	
7	27.0	96.0	

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{\rm s}^{-1}$
1	2.33	1.63
2	4.86	2.66
3	5.83	3.46
4	6.68	3.76
5	8.50	4.74
6	9.32	5.50
7	12.1	6.49
8	12.8	7.24

Table S7. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1,2-hydroxyethyl piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.09.

Table S8. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1,2-hydroxyethyl piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.39.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs}  /  { m s}^{-1}$
1	1.09	1.26
2	2.72	2.61
3	4.35	3.38
4	5.98	5.22
5	7.60	6.50
6	9.23	7.69
7	10.9	9.08

Table S9. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1,2-hydroxyethyl piperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.69.

	$10^{2} [N]_{T}$	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	4.55	5.47
2	6.30	7.33
3	8.01	9.03
4	9.73	10.8
5	11.4	12.5

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{\rm s}^{-1}$
1	2.47	1.09
2	6.17	1.61
3	9.87	2.39
4	13.6	2.94
5	17.3	3.78
6	21.0	4.50
7	24.7	4.99

Table S10. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with morpholine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=8.48.

Table S11. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with morpholine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=8.78.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.53	1.21
2	6.31	2.02
3	10.1	2.98
4	13.9	3.79
5	17.7	4.76
6	21.5	5.70
7	25.3	7.00

Table S12. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with morpholine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=9.08.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs}  /  {\rm s}^{-1}$	
1	2.31	1.26	
2	5.78	2.57	
3	9.25	3.59	
4	12.7	4.75	
5	16.2	5.93	
6	19.7	6.48	
7	23.1	7.52	

	10 <sup>2</sup> [N] <sub>T</sub>	$10^{6} k_{\rm obs}  /  { m s}^{-1}$
1	2.07	3.56
2	17.6	6.91
3	20.1	9.06
4	24.5	9.63
5	28.8	10.6

Table S13. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1-formylpiperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=7.38.

Table S14. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1-formylpiperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=7.68.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^6 k_{\rm obs} / {\rm s}^{-1}$
1	1.98	3.11
2	4.96	5.54
3	7.94	6.40
4	10.9	6.79
5	13.9	8.62
6	16.9	9.84
7	19.8	10.9

Table S15. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with 1-formylpiperazine in aqueous solution at  $25^{\circ}C\pm0.1^{\circ}C$  and pH=7.98.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^6 k_{\rm obs} /{\rm s}^{-1}$
1	2.28	5.64
2	10.1	9.98
3	14.1	11.5
4	15.9	11.7
5	17.1	12.7
6	20.1	13.2

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Table S16. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in dimethylsulfoxide (DMSO) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S17. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethanol at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.98	4.29
2	7.45	6.27
3	11.9	9.40
4	16.4	12.3
5	20.9	15.7
6	25.3	19.7
7	29.8	23.4

Table S18. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 2-propanol at  $25^{\circ}C\pm0.1^{\circ}C$ .

	$10^{2} [N]_{T}$	$10^5 k_{\rm obs} /{\rm s}^{-1}$
1	2.42	8.45
2	4.03	10.2
3	7.24	11.1
4	10.4	14.2
5	14.4	15.9
6	16.7	17.9
7	19.8	19.9

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{ m s}^{-1}$
1	2.42	2.48
2	4.03	3.22
3	7.22	6.07
4	10.4	8.88
5	14.4	11.8
6	16.7	15.6
7	19.8	18.4

Table S19. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in butanol at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S20. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in tert-butanol at  $25^{\circ}C\pm0.1^{\circ}C$ .

	$10^{2} [N]_{T}$	$10^5 k_{\rm obs} /{ m s}^{-1}$
1	2.42	2.86
2	4.03	8.47
3	7.24	11.7
4	10.4	17.9
5	14.4	24.1
6	16.7	27.2

Table S21. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in methanol at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^{5}k_{\rm obs}$ / s <sup>-1</sup>
1	2.42	1.97
2	4.03	2.55
3	7.24	3.87
4	10.4	5.72
5	14.4	7.91
6	16.7	8.66
7	19.8	10.1

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{ m s}^{-1}$
1	2.51	10.1
2	6.28	29.7
3	10.1	48.1
4	12.8	70.3
5	17.6	87.2
6	21.4	113.0
7	25.1	134.0

Table S22. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in formamide (FMA) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S23. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine at pH=10.82, in ethanol:water 50:50 mixture, at 25.0 °C and ionic strength 0.2M (KCl).

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} /{ m s}^{-1}$
1	2.73	2.27
2	6.82	6.20
3	10.9	10.6
4	15.0	15.0
5	19.1	19.7
6	23.2	23.7
7	27.3	29.0

Table S24. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine at pH=10, in ethanol:water 90:10 mixture, at 25.0 °C.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} /{ m s}^{-1}$
1	2.73	0.301
2	6.82	0.830
3	10.9	1.37
4	15.0	1.96
5	19.1	2.47
6	23.2	3.21
7	27.3	4.10

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	6.27	0.397
2	12.5	1.04
3	18.8	1.68
4	25.1	2.11
5	31.4	2.75
6	37.6	3.36
7	44.3	3.64

Table S25. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethylamonium nitrate (EAN) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S26. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	7.90
2	5.06	11.8
3	13.2	24.8
4	18.2	36.3
5	21.2	44.0
6	25.3	53.6

Table S27. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium thiocyanate (EMIMSCN) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	40.7
2	5.06	48.1
3	9.11	65.7
4	13.2	75.9
5	18.2	95.9
6	25.3	151

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	37.4
2	5.06	47.4
3	9.11	54.8
4	13.2	65.5
5	18.2	95.0
6	21.2	123
7	25.3	131

Table S28. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S29. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	22.0
2	5.06	31.0
3	9.11	49.7
4	13.2	61.0
5	18.2	85.2
6	21.2	106
7	25.3	132

Table S30. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethyldimethyl-(2-methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate (MOEDEAFAP) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	4.77
2	5.06	7.66
3	9.11	12.0
4	13.2	18.4
5	18.2	27.4
6	21.2	32.3

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	8.53
2	5.06	12.3
3	9.11	13.3
4	13.2	21.4
5	18.2	28.6
6	21.2	40.0
7	25.3	47.8

Table S31. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (EMIMFAP) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S32. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMIMFAP) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	7.77
2	5.06	9.25
3	9.11	18.0
4	13.2	26.8
5	21.2	39.5
6	25.3	47.3

Table S33. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate (BMPLFAP) at 25°C±0.1°C.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	8.69
2	5.06	15.4
3	9.11	21.5
4	13.2	25.4
5	18.2	37.7
6	21.2	45.6
7	25.3	53.3

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} /{ m s}^{-1}$
1	3.04	7.78
2	5.06	10.9
3	9.11	21.0
4	13.2	32.8
5	18.2	41.7
6	21.2	50.1
7	25.3	59.8

Table S34. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium dicyanamide (BMIMDCN) at 25°C±0.1°C.

Table S35. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1methylpyrrolidinium dicyanamide (BMPLDCN) at 25°C±0.1°C.

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	5.06	9.00
2	9.11	14.9
3	13.2	31.7
4	18.2	43.9
5	21.2	52.8
6	25.3	69.3

Table S36. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCN) at 25°C±0.1°C.

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	58.6
2	5.06	83.9
3	9.11	109
4	13.2	132
5	18.2	169
6	21.2	182
7	25.3	226

	$10^{2} [N]_{T}$	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	19.2
2	5.06	20.1
3	9.11	34.8
4	13.2	43.5
5	18.2	48.6
6	21.2	66.7
7	25.3	77.5

Table S37. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide (BMIMNTf<sub>2</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S38. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMIMNTf<sub>2</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	5.06	17.2
2	9.11	31.7
3	13.2	51.0
4	18.2	63.4
5	21.2	71.1
6	25.3	91.2

Table S39. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-1methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide (BMPLNTf<sub>2</sub>) at 25°C±0.1°C.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	9.58
2	5.06	17.5
3	13.2	32.7
4	18.2	55.5
5	21.2	65.7
6	25.3	86.9

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1	3.04	14.6
2	5.06	21.7
3	9.11	30.3
4	13.2	36.9
5	18.2	52.8
6	25.3	74.7

Table S40. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide ( $BM_2IMNTf_2$ ) at 25°C±0.1°C.

Table S41. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (HMIMNTf<sub>2</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs}  /  {\rm s}^{-1}$
1	3.04	7.08
2	5.06	13.4
3	9.11	19.9
4	13.2	36.9
5	18.2	44.1
6	21.2	58.7
7	25.3	73.3

Table S42. Values of  $k_N$  and  $pK_a$  for the reactions of piperidine with 2,4-dinitrobenzenesulfonyl chloride in ethanol:water mixtures.

Ethanol:water mixture	$10^4 k_{\rm N}$ / M <sup>-1</sup> s <sup>-1</sup>	pKa
50:50	67.7	10.821
90:10	34.2	10.02

<sup>1</sup>E. A. Castro, M. Gazitúa, J. G. Santos, *J. Phys. Org. Chem.*, 2011, **24**, 466. <sup>2</sup>E. A. Castro, D. Millán, R. Aguallo, P. R. Campodónico, J. G. Santos, *Int. J. Chem. Kinet.* 2011, **43**, 687.

	$10^{2} [N]_{T}$	$10^4  k_{ m obs}  /  { m s}^{-1}$
1	2.48	2.12
2	6.19	7.54
3	9.91	15.2
4	13.6	24.6
5	17.3	36.4
6	21.1	49.7
7	24.8	64.3

Table S43. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetonitrile (MeCN) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S44. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in tetrahydrofurane (THF) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.52	3.76
2	6.29	10.9
3	10.0	25.5
4	13.8	45.0
5	17.6	70.9
6	21.4	104.0
7	24.8	145.0

Table S45. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in dichloromethane ( $CH_2Cl_2$ ) at 25°C±0.1°C.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs}  /  {\rm s}^{-1}$
1	2.49	7.96
2	6.22	29.1
3	9.95	74.3
4	13.7	140
5	17.4	223
6	21.1	318
7	24.9	421

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} /{\rm s}^{-1}$
1	2.78	4.77
2	6.96	10.1
3	11.1	20.0
4	15.3	34.5
5	19.5	53.4
6	23.7	78.1
7	27.8	110

Table S46. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in chloroform (CHCl<sub>3</sub>) at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S47. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in benzene  $(C_6H_6)$  at 25°C±0.1°C.

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs}  /  { m s}^{-1}$
1	2.95	1.17
2	7.37	3.73
3	11.8	8.92
4	16.2	16.1
5	20.6	24.7
6	25.1	36.2
7	29.5	49.8

Table S48. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in N,N-dimethylformamide (DMF) at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$	
1	2.89	2.83	
2	7.21	7.52	
3	11.5	13.6	
4	15.9	20.7	
5	20.2	29.4	
6	24.5	38.3	
7	28.9	47.7	

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.42	3.28
2	4.03	4.62
3	7.24	11.5
4	10.4	20.2
5	14.4	38.7
6	16.7	54.1
7	19.8	72.4

Table S49. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1,4-dioxane at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S50. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in acetone at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs}  /  {\rm s}^{-1}$
1	2.42	9.14
2	4.03	14.3
3	7.24	35.4
4	10.4	61.1
5	14.4	114
6	16.7	151
7	19.8	213

Table S51. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in cyclohexane at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	1.22	4.03
2	2.43	8.25
3	3.88	20.5
4	5.57	36.4
5	7.25	61.9
6	9.65	101.1
7	12.0	152.4
8	14.4	198.0

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.42	6.74
2	4.03	28.2
3	7.24	25.7
4	10.4	53.7
5	14.4	88.7
6	16.7	105
7	19.8	164

Table S52. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in diethyl ether at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S53. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in ethyl acetate at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^5 k_{\rm obs} / {\rm s}^{-1}$
1	2.42	2.07
2	4.03	2.24
3	7.24	3.69
4	10.4	4.34
5	14.4	7.89
6	16.7	10.3
7	19.8	13.8

10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs} / {\rm s}^{-1}$
1.21	0.146
2.43	0.466
3.88	0.907
4.03	1.51
5.57	2.67
7.23	4.69
7.26	3.81
9.56	6.93
10.4	10.0
12.0	10.6
14.4	17.3
14.4	14.3
16.7	21.6
	$\begin{array}{c} 10^2  [\mathrm{N}]_{\mathrm{T}} \\ 1.21 \\ 2.43 \\ 3.88 \\ 4.03 \\ 5.57 \\ 7.23 \\ 7.26 \\ 9.56 \\ 10.4 \\ 12.0 \\ 14.4 \\ 14.4 \\ 14.4 \\ 16.7 \end{array}$

Table S54. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in n-hexane at  $25^{\circ}C\pm0.1^{\circ}C$ .

Table S55. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in n-heptane at  $25^{\circ}C\pm0.1^{\circ}C$ .

	10 <sup>2</sup> [N] <sub>T</sub>	$10^4 k_{\rm obs}$ / s <sup>-1</sup>
1	1.01	0.185
2	1.21	0.152
3	2.02	0.344
4	2.43	0.716
5	3.88	1.68
6	4.03	1.39
7	5.57	2.90
8	7.24	6.56
9	7.26	4.16
10	10.4	12.4
11	14.4	22.3
12	16.7	28.3
13	19.8	38.1