New Journal of Chemistry

Electronic Supplemetary Information

Nature of the nucleophile and solvent effect on a S_NAr reaction.

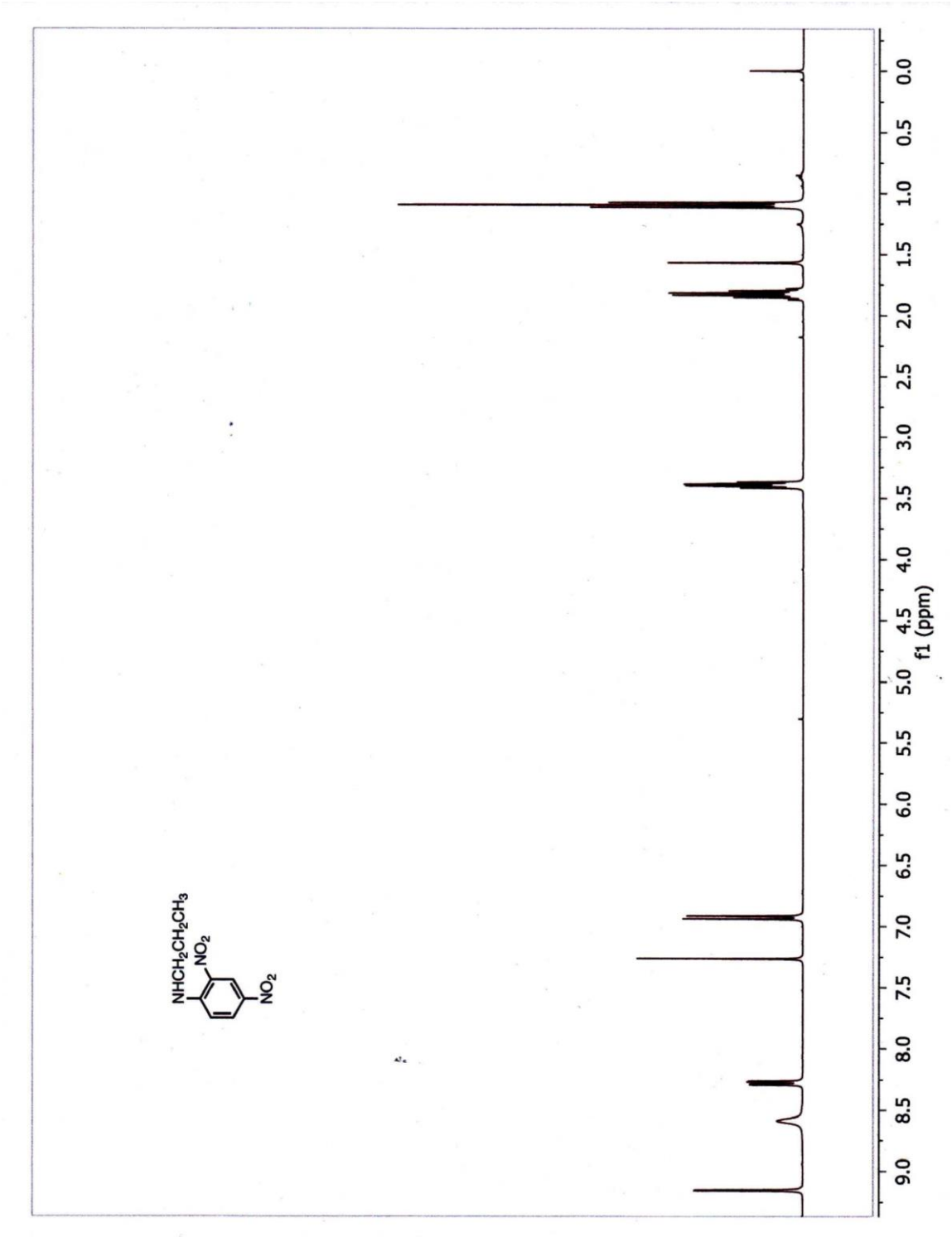
Marcela Gazitúa,[1] Ricardo Tapia,[2] Renato Contreras[3] and Paola R. Campodónico.[1]*

[1]Centro de Química Médica, Facultad de Medicina, Clínica Alemana Universidad del Desarrollo, Código Postal 7710162, Santiago, Chile. [2]Facultad de Química, Pontificia Universidad Católica de Chile, Código Postal 7820436, Santiago, Chile. [3]Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile.

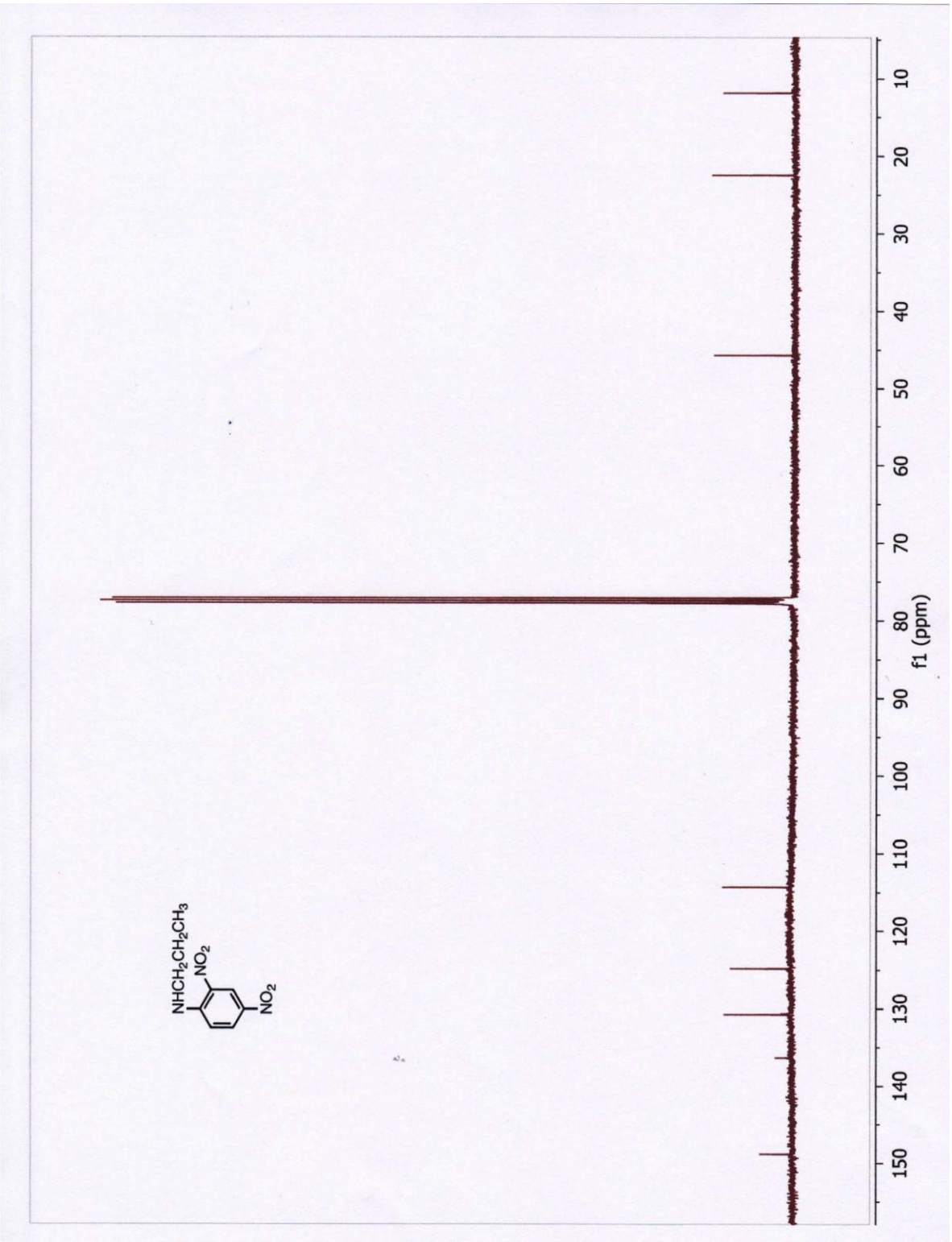
migazitu@uc.cl

Table of Contents

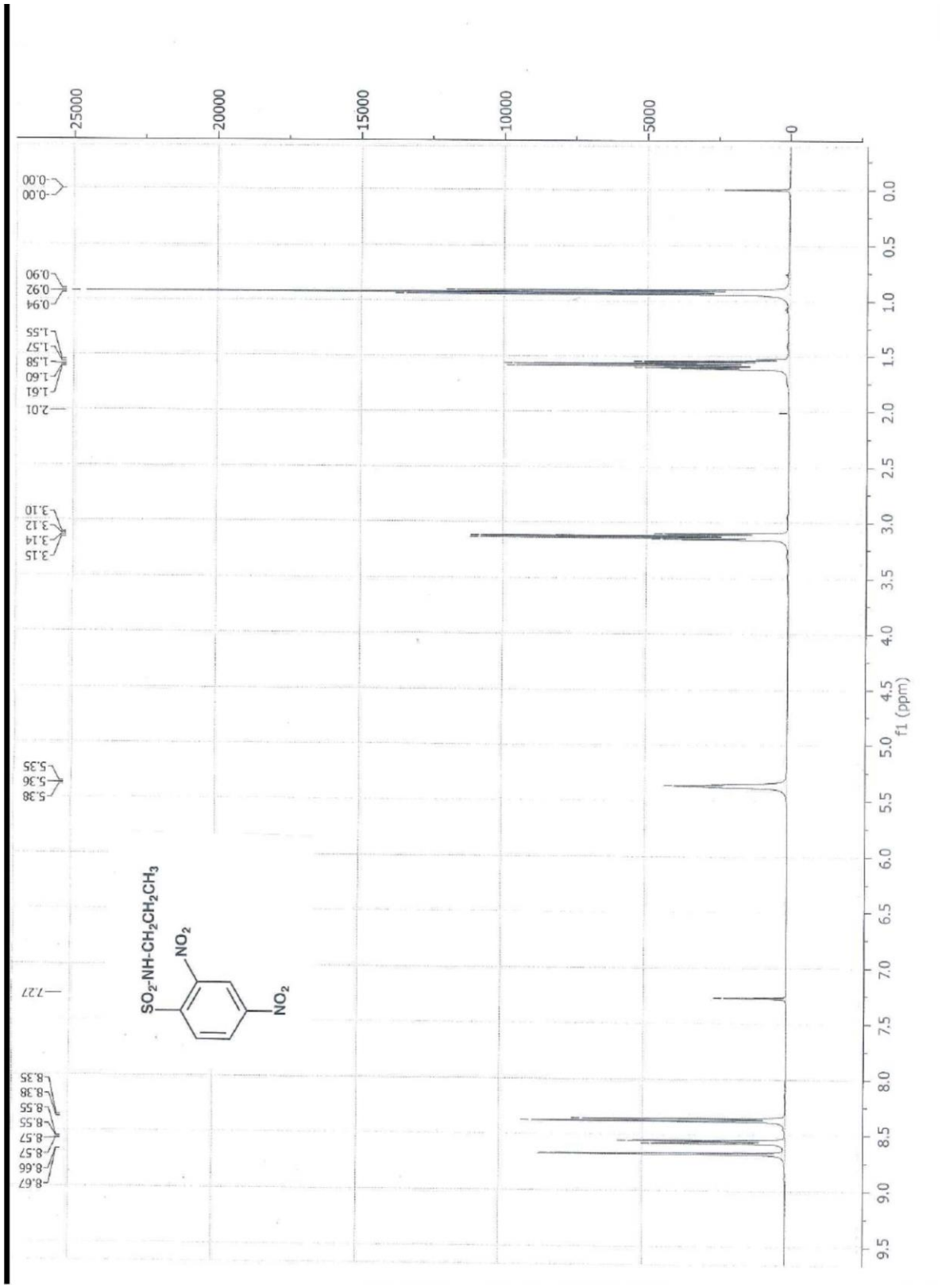
^{1}H NMR Spectra of 2,4-Dinitro-*N*-*n*-propylaniline.



^{1}C NMR Spectra of 2,4-Dinitro-*N*-*n*-propylaniline.



^{1}H NMR Spectra Spectra of 2,4-Dinitro-*N*-*n*-propylbenzenesulfonamide.



^{1}C NMR Spectra Spectra of 2,4-Dinitro-*N*-*n*-propylbenzenesulfonamide.

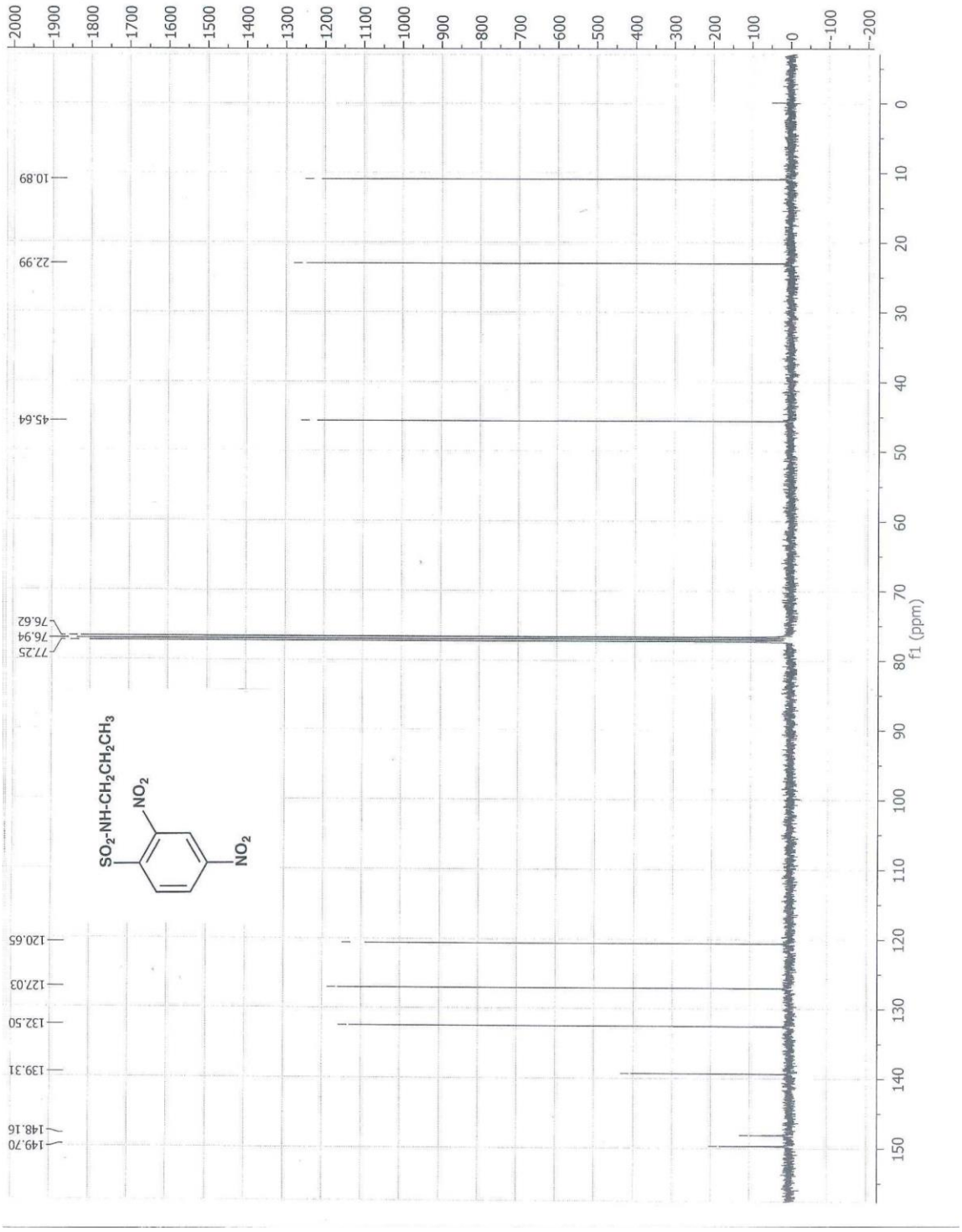


Figure S1. Chromatogram of 2,4-dinitrobenzenesulphonyl chloride (5.10×10^{-5} mol L^{-1}) using a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

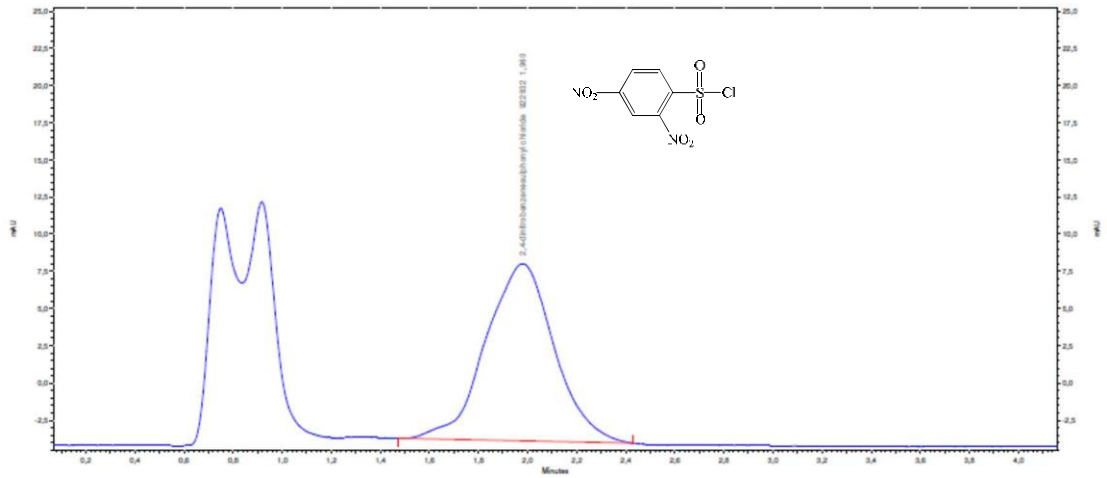


Figure S2. Chromatogram of propylamine (0.15 mol L^{-1}) in butanol a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

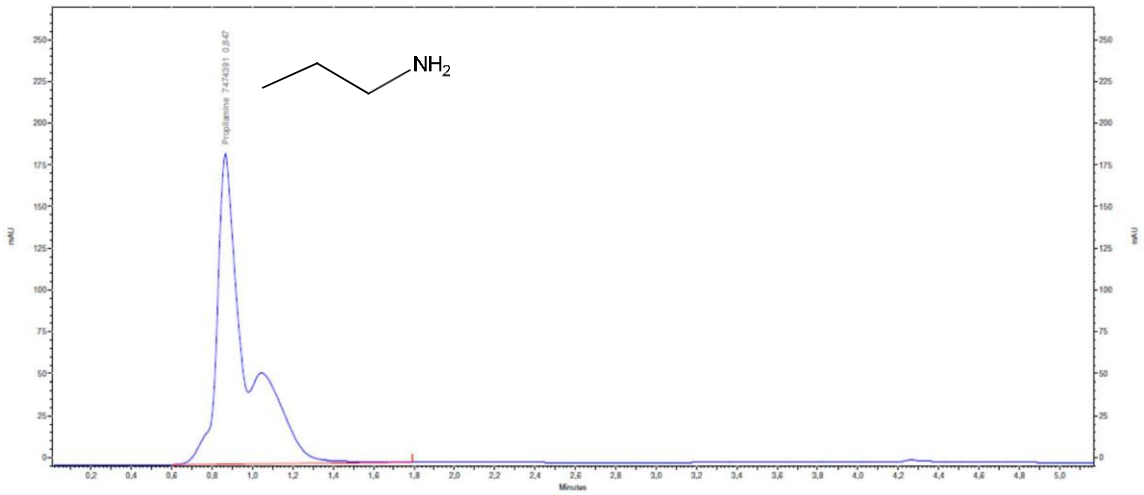


Figure S3. Chromatogram of the 2,4-Dinitro-*N*-*n*-propylaniline (5.05×10^{-5} mol L^{-1}) using a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

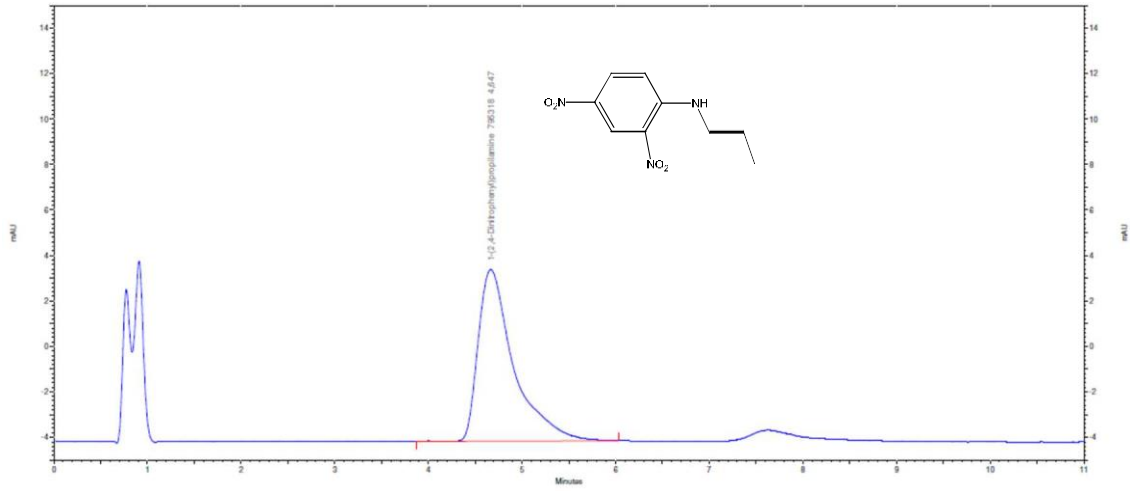


Figure S4. Chromatogram of the 2,4-Dinitro-*N*-*n*-propylbenzenesulfonamide (5.00×10^{-5} mol L^{-1}) using a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

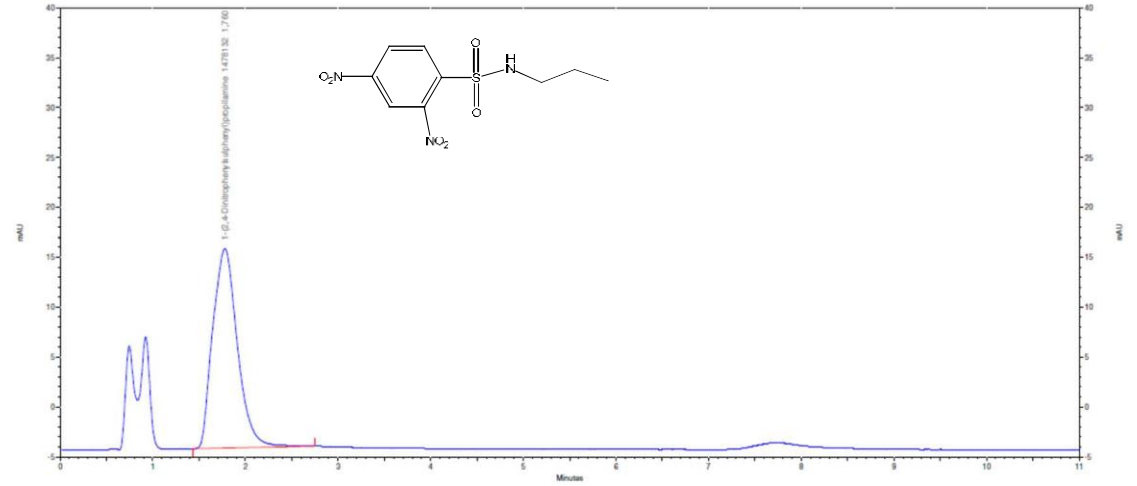


Figure S5. Chromatogram of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride (5.10×10^{-5} mol L^{-1}) with propylamine (0.14 mol L^{-1}) at 90 min. in butanol, using a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

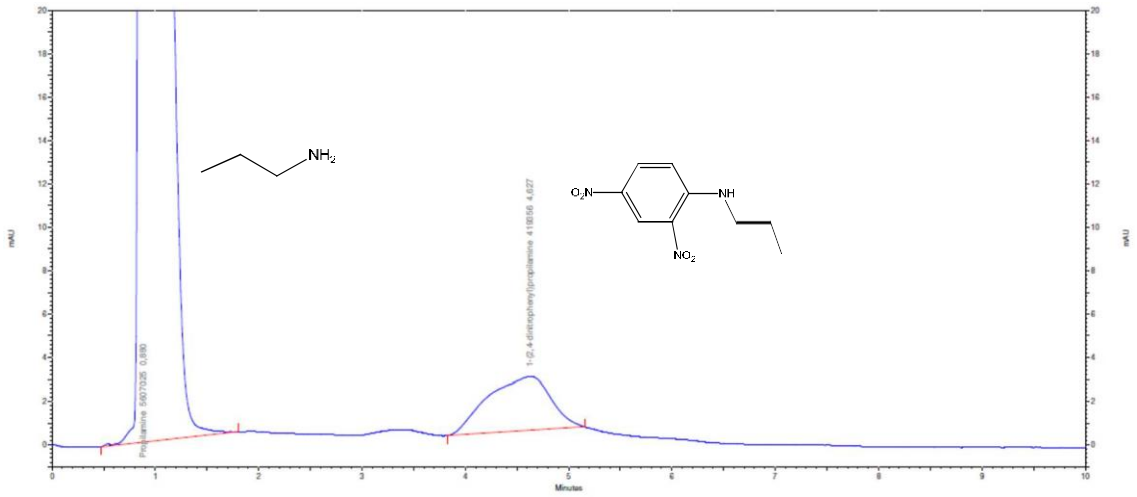


Figure S6. Chromatogram of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride (5.10×10^{-5} mol L^{-1}) with propylamine (0.14 mol L^{-1}) at 75 min. of reaction in acetonitrile using a mobile phase of 70% MeOH 30% H_2O, the flow rate was 1 mL min^{-1} and UV-visible detection at 260 nm.

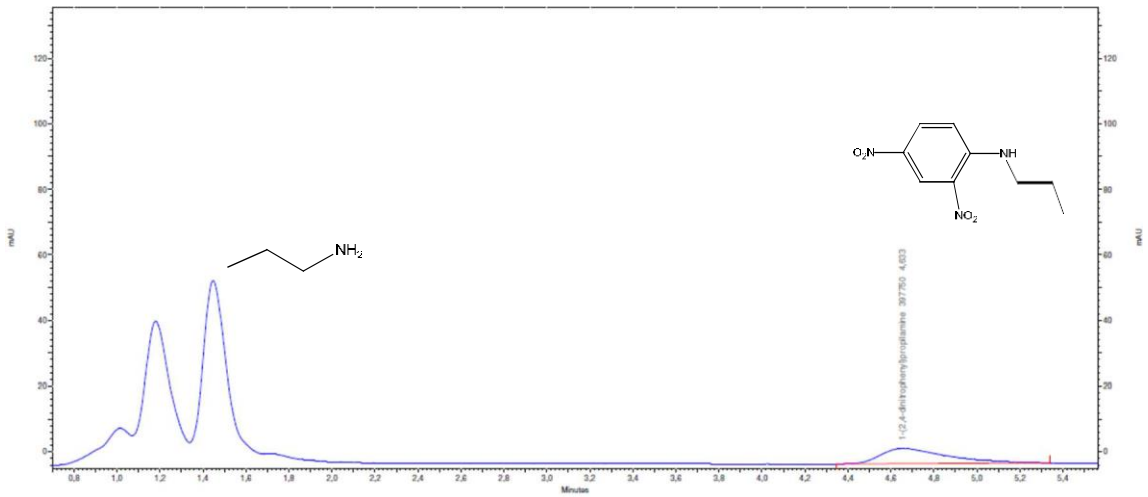


Figure S7. Chromatograms of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride (5.10×10^{-5} mol L^{-1}) with propylamine (0.14 mol L^{-1}) in butanol at different times: 30 min. (olive line), 95 min. (cyan line), 300 min. (magenta line) and 1140 min. (green line) using a mobile phase of 70% MeOH 30% H_2O), the flow rate was 1 mL min^{-1} and UV-vis detection at 260 nm.

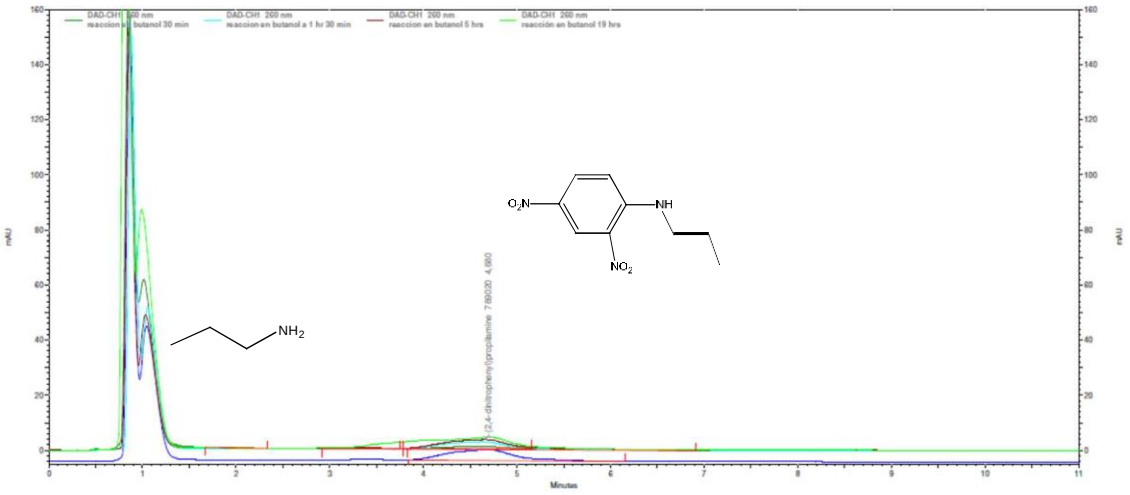


Figure S8. Chromatograms of the reaction mixture of 2,4-dinitrobenzenesulphonyl chloride (5.10×10^{-5} mol L^{-1}) with propylamine (0.14 mol L^{-1}) in acetonitrile at different times: 15 min. (olive line), 30 min. (cyan line), 45 min. (magenta line),60 min. (green line) and 75 min. (pink line) using a mobile phase of 70% MeOH 30% H_2O), the flow rate was 1 mL min^{-1} and UV-vis detection at 260 nm.

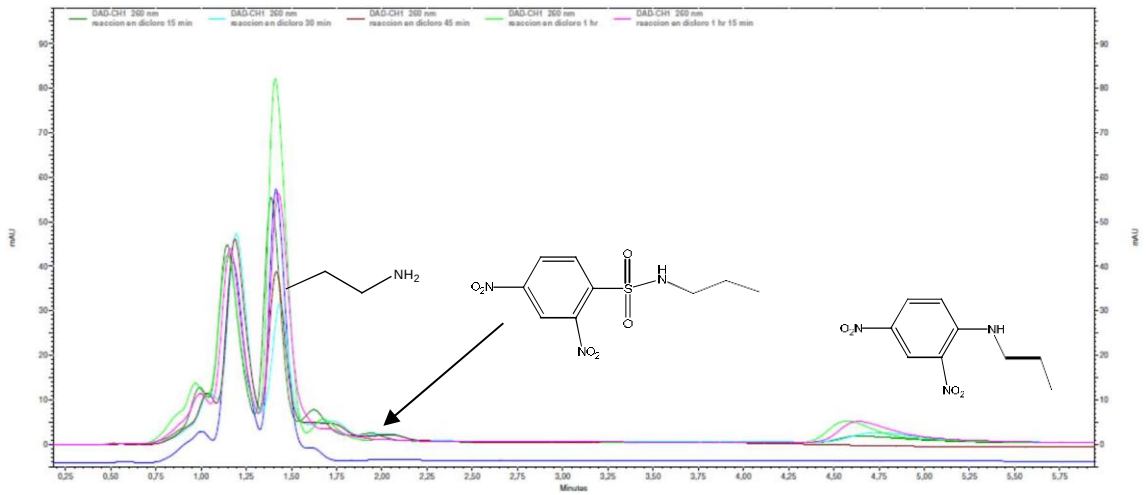


Figure S9. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in N,N-dimethylformamide (N,N-DMF) at 25.0 °C.

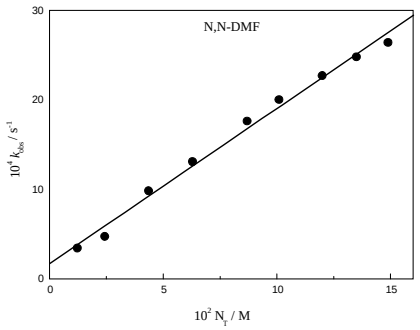


Figure S10. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in acetonitrile (MeCN) at 25.0 °C.

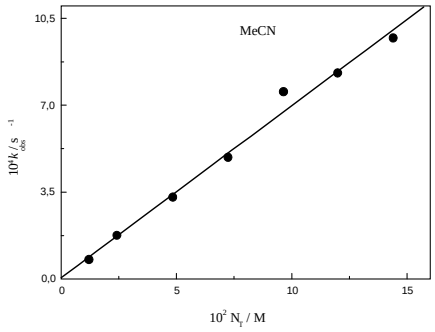


Figure S11. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in dimethylsulfoxide (DMSO) at 25.0 °C.

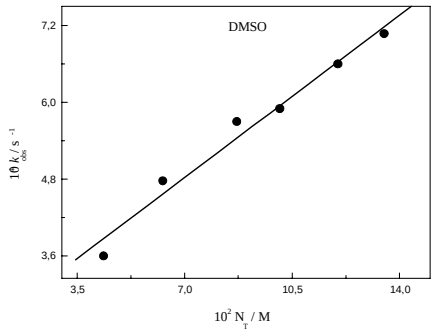


Figure S12. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in formamide (FMA) at 25.0 °C.

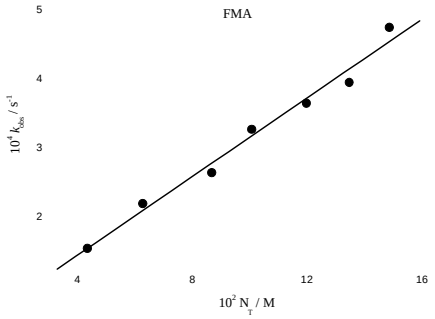


Figure S13. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in tert-butanol at 25.0 °C.

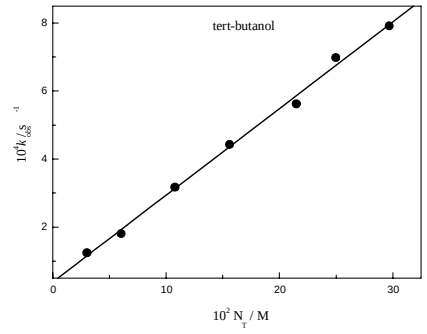


Figure S14. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 2-propanol at 25.0 °C.

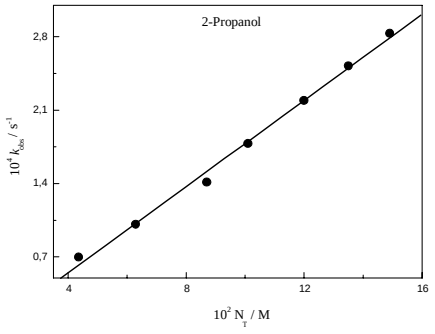


Figure S15. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in butanol at 25.0 °C.

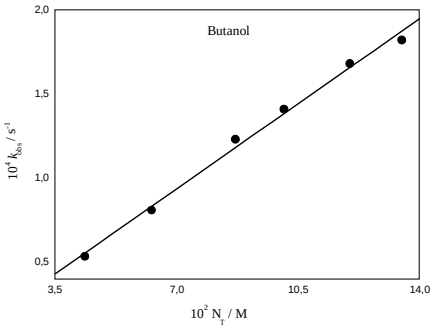


Figure S16. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in methanol at 25.0 °C.

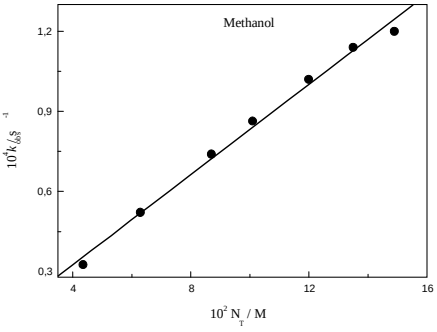


Figure S17. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethanol at 25.0 °C.

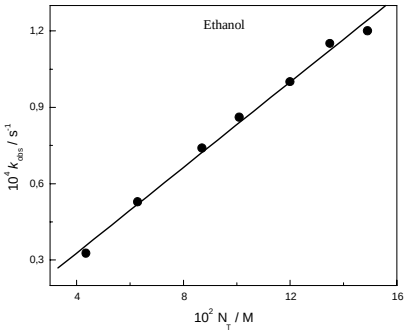


Figure S18. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in aqueous solution at 25.0 °C.

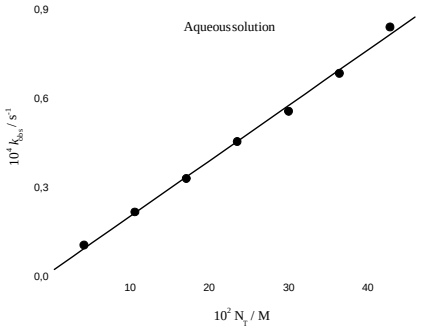


Figure S19. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethyl acetate at 25.0 °C.

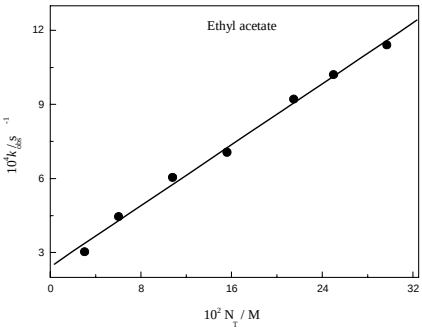


Figure S20. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) at 25.0 °C.

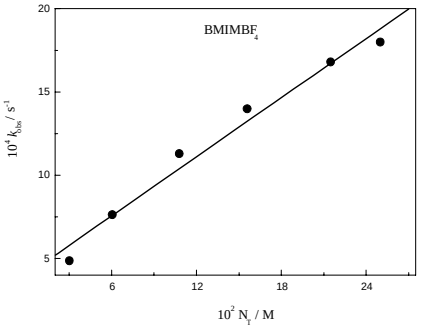


Figure S21. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($BMIMNTF_2$) at 25.0 °C.

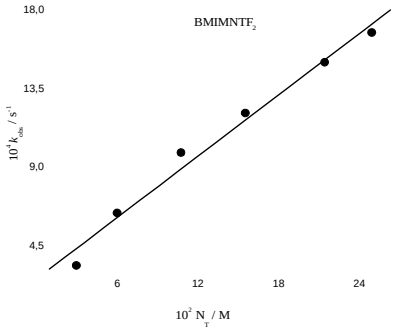


Figure S22. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium dicyanamide (BMIMDCN) at 25.0 °C.

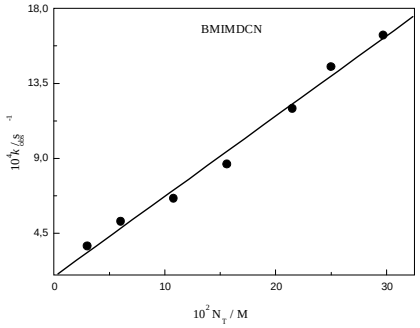


Figure S23. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMIMFAP) at 25.0 °C.

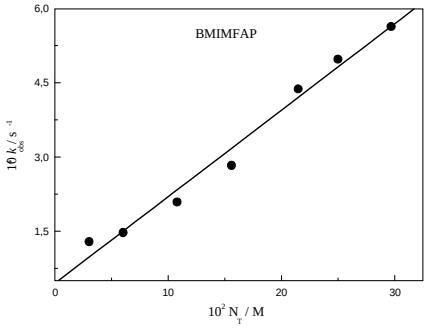


Figure S24. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) at 25.0 °C.

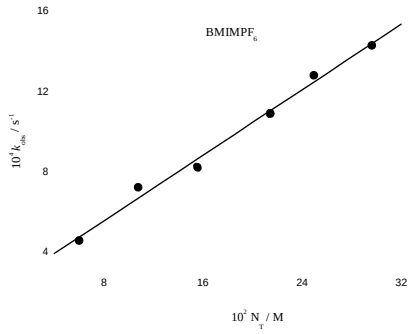


Figure S25. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide (BM_2IMNTF_2) at 25.0 °C.

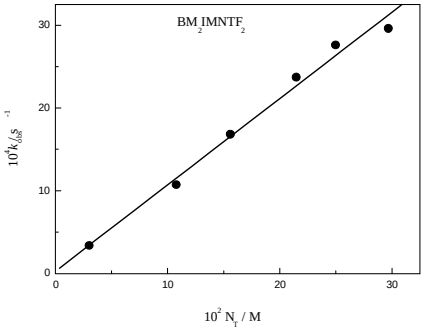


Figure S26. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-hexyl 3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($HMIMNTF_2$) at 25.0 °C.

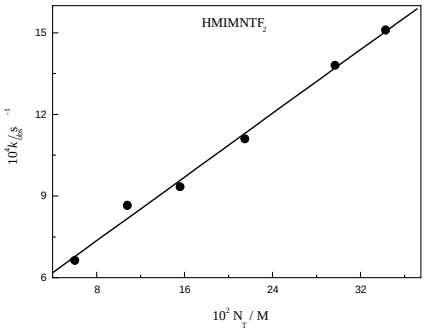


Figure S27. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethyl-dimethyl-propylammonium bis((trifluoromethyl)sulfonyl)imide ($NEMMPNTF_2$) at 25.0 °C.

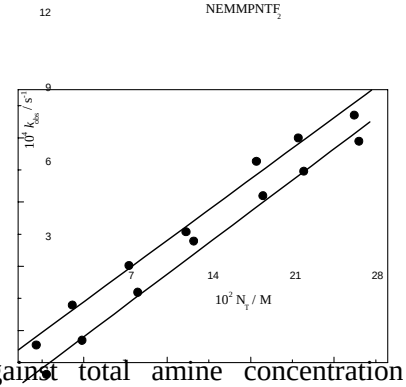


Figure S28. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-ethyl 3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($EMIMNTF_2$) at 25.0 °C.

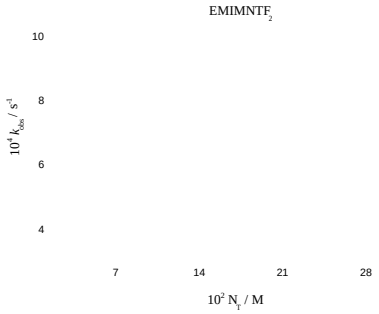


Figure S29. Plot of k_{obs} against total amine concentration $[N_T]$ for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-ethyl 3-methylimidazolium dicyanamide (EMIMDCN) at 25.0 °C.

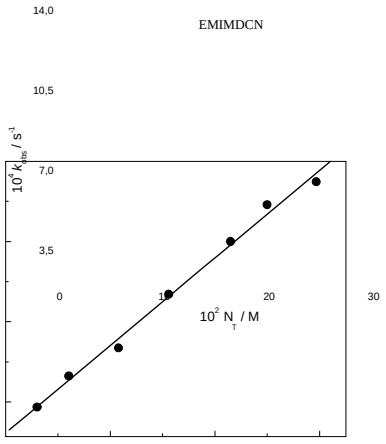


Figure S30. Comparison between k_{obs} against total amine concentration for the reaction of DNBSCl with propylamine in $BMIMNTF_2$; BM_2IMNTF_2 ; $HMIMNTF_2$; $NEMMPNTF_2$ and $EMIMNTF_2$.

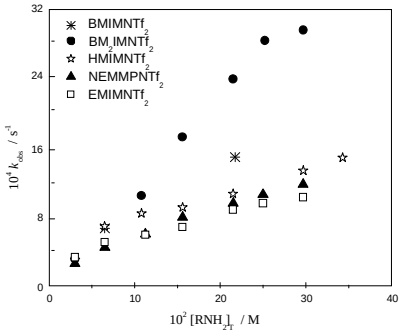


Figure S31. Comparison between k_{obs} against total amine concentration for the reaction of DNBSCl with propylamine in $BMIMBF_4$; $BMIMNTF_2$; BMIMDCN ; BMIMFAP and $BMIMPF_6$.

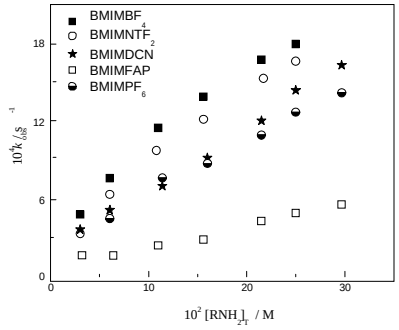


Table S1. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in N,N-dimethylformamide (N,N-DMF) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	1.22	3.44
2	2.43	4.73
3	4.36	9.84
4	6.29	13.1
5	8.70	17.6
6	10.1	20.0
7	12.0	22.7
8	13.5	24.8
9	14.9	26.4

Table S2. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in acetonitrile (MeCN) at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	1.22	0.786
2	2.43	1.76
3	4.85	3.30
4	7.25	4.90
5	9.65	7.54
6	12.0	8.30
7	14.4	9.71

Table S3. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in dimethylsulfoxide (DMSO) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	4.36	3.60
2	6.29	4.77
3	8.70	5.70
4	10.1	5.90
5	12.0	6.60
6	13.5	7.07

Table S4. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in formamide (FMA) at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	4.36	1.59
2	6.29	2.19
3	8.70	2.64
4	10.1	3.27
5	12.0	3.65
6	13.5	3.95
7	14.9	4.75

Table S5. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in tert-butanol at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	3.03	1.24
2	6.05	1.80
3	10.8	3.17
4	15.6	4.42
5	21.5	5.62
6	25.0	6.98
7	29.7	7.91

Table S6. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 2-propanol at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	4.36	0.696
2	6.29	1.01
3	8.70	1.41
4	10.1	1.78
5	12.0	2.19
6	13.5	2.52
7	14.9	2.83

Table S7. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in butanol at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	4.36	0.534
2	6.29	0.808
3	8.70	1.23
4	10.1	1.41
5	12.0	1.68
6	13.5	1.82

Table S8. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in methanol at 25°C±0.1°C.

	10^2 $[N]_T$	$10^5 k_{obs}$ / s^{-1}
1	4.36	0.326
2	6.29	0.522
3	8.70	0.740
4	10.1	0.864
5	12.0	1.02
6	13.5	1.14
7	14.9	1.2

Table S9. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethanol at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	4.36	0.326
2	6.29	0.528
3	8.70	0.740
4	10.1	0.860
5	12.0	1.00
6	13.5	1.15
7	14.9	1.20

Table S10. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in aqueous solution at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	4.29	0.106
2	10.7	0.218
3	17.2	0.331
4	23.6	0.456
5	30.1	0.558
6	36.5	0.687
7	42.9	0.843

Table S11. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethyl acetate at 25°C±0.1°C.

	10^2 $[N]_T$	10^5 k_{obs} / s^{-1}
1	3.03	3.03
2	6.05	4.46
3	10.8	6.04
4	15.6	7.06
5	21.5	9.21
6	25.0	10.2
7	29.7	11.4

Table S12. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	4.88
2	6.05	7.64
3	10.8	11.3
4	15.6	14.0
5	21.5	16.8
6	25.0	18.0

Table S13. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with piperidine in 1-buthyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide ($BMIMNTF_2$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	3.42
2	6.05	6.40
3	10.8	9.85
4	15.6	12.1
5	21.5	15.0
6	25.0	16.7

Table S14. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium dicyanamide (BMIMDCN) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	3.74
2	6.05	5.22
3	10.8	6.60
4	15.6	8.65
5	21.5	12.0
6	25.0	14.5
7	29.7	16.4

Table S15. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMIMFAP) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	1.29
2	6.05	1.47
3	10.8	2.09
4	15.6	2.83
5	21.5	4.38
6	25.0	4.98
7	29.7	5.64

Table S16. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	6.05	4.56
2	10.8	7.21
3	15.6	8.22
4	21.5	10.9
5	25.0	12.8
6	29.7	14.3

Table S17. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-buthyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)imide (BM_2IMNTF_2) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	3.36
2	6.05	-
3	10.8	10.7
4	15.6	16.8
5	21.5	23.7
6	25.0	27.6
	29.7	29.6

Table S18. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-hexyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($HMIMNTF_2$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	6.05	6.63
2	10.8	8.66
3	15.6	9.34
4	21.5	11.1
5	29.7	13.8
6	34.3	15.1

Table S19. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in ethyl-dimethyl-propylammonium bis((trifluoromethyl)sulfonyl)imide ($NEMMPNTF_2$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	2.81
2	6.05	4.18
3	10.8	6.12
4	15.6	8.18
5	21.5	10.0
6	25.0	11.0
7	29.7	12.2

Table S20. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ($EMIMNTF_2$) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	3.55
2	6.05	4.79
3	10.8	6.02
4	15.6	7.07
5	21.5	9.27
6	25.0	10.0
7	29.7	10.7

Table S21. Kinetic data for the reaction of 2,4-dinitrobenzenesulfonyl chloride with propylamine in 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCN) at 25°C±0.1°C.

	10^2 $[N]_T$	10^4 k_{obs} / s^{-1}
1	3.03	3.28
2	6.05	4.63
3	10.8	5.86
4	15.6	8.20
5	21.5	10.1
6	25.0	12.1
7	29.7	13.1