SUPPLEMENTARY DATA

Supplementary data are available: Table **S1** contains the parameters of Eq. 1 for the reactions of compounds **1** – **33** with nucleophiles **34 – 40**; Table **S2** contains the parameters of the Brønsted and Hammett equations for the reactions of compounds **1** – **33** with nucleophiles **34 – 40**.

Table 1S: Substituent effects in leaving groups, nucleophiles and nonleaving groups on activation parameters in the reactions of compounds 1 - 33 with primary amines 35 – 37, 39, secondary cyclic amines 34, 40, and pyridines 38 in MeCN

Entry[a]	Reactants [b]	T_{exp} / K [b]	$\delta\Delta H^{\neq}$ / [c] kJ mol^{-1} σ^{-1}	$\delta\Delta S^{\neq}$ / [c] J mol^{-1} K^{-1} σ^{-1}	T_{exp} $\delta\Delta S^{\neq}$ / kJ mol^{-1} σ^{-1}	$\delta\Delta G^{\neq}$ / [c] kJ mol^{-1} σ^{-1}	$\delta\Delta H^{\neq}_{ext}$ / [d] kJ mol^{-1} σ^{-1}	$\delta\Delta H^{\neq}_{int}$ / [e] kJ mol^{-1} σ^{-1}	Ref. [f]
	Substituents R are varied	**on**	**leaving**	**groups**					
	Acyl-trasfer reactions								
4 [g]	$MeC(O)OC_6H_4R$ **6j,s** + 4-$MeC_6H_4CH_2NH_2$ **36c**	298	-8.79	-10.33	-3.08	-5.70	-3.31	-5.48	[46]
5 [g]	$MeC(O)OC_6H_4R$ **6j,s** + 4-$ClC_6H_4CH_2NH_2$ **36j**	298	-10.85	-5.17	-154	-9.31	-1.65	-9.19	[46]
6	$EtOC(O)SC_6H_4R$ **7c,k** + 4-$MeOC_6H_4CH_2NH_2$ **36b**	308	-19.85	-31.35	-9.65	-10.2	-10.03	-9.82	[44]
7	$EtOC(O)SC_6H_4R$ **7c,k** + 4-$ClC_6H_4CH_2NH_2$ **36j**	308	-2.10	20.92	6.44	-8.55	6.69	-8.79	[44]
8	$EtC(O)SC_6H_4R$ **8c,m** + 4-$MeOC_6H_4CH_2NH_2$ **36b**	308	-0.70	37.94	11.69	-12.39	12.14	-12.84	[47]
9	$PhNHC(O)SC_6H_4R$ **9c,k** + 4-$MeOC_6H_4CH_2NH_2$ **36b**	303	-3.77	27.8	8.42	-12.20	8.90	-12.67	[45]
10	$PhNHC(O)SC_6H_4R$ **9c,k** + 4-$ClC_6H_4CH_2NH_2$ **36j**	303	11.50	73.22	22.18	-10.70	23.43	-11.93	[45]
11	*cyclo*-$C_3H_5C(O)OC_6H_4R$ **10t,u** + 4-$MeC_6H_4CH_2NH_2$ **36c**	318	6.55	70.70	22.48	-15.94	-	-	[48]
12	*cyclo*-$C_3H_5C(O)OC_6H_4R$ **10t,u** + 3-$ClC_6H_4CH_2NH_2$ **36m**	318	-3.59	53.03	16.86	-20.45	-	-	[48]
13	*cyclo*-$C_4H_7C(O)OC_6H_4R$ **11t,u** + 4-$MeC_6H_4CH_2NH_2$ **36c**	318	-0.59	47.15	14.99	-15.59	-	-	[49]
14	*cyclo*-$C_4H_7C(O)OC_6H_4R$ **11t,u** + 3-$ClC_6H_4CH_2NH_2$ **36m**	318	-2.96	47.14	14.99	-17.96	-	-	[49]
15	$PhCH_2C(S)SC_6H_4R$ **12c,k** + 4-$MeOC_6H_4NH_2$ **37b**	308	1.05	52.30	16.11	-15.05	-	-	[50]
16	$PhCH_2C(S)SC_6H_4R$ **12c,k** + 4-$ClC_6H_4NH_2$ **37m**	308	-7.30	31.37	9.66	-16.95	-	-	[50]

(Table 1S). Continued.

17	$MeC(O)SC_6H_4R$ **13c,k** + 4-$MeOC_6H_4CH_2NH_2$ **36b**	308	-1.02	94.15	29.0	-30.02	-	-	[51]
18	$MeC(O)SC_6H_4R$ **13c,k** + 4-$ClC_6H_4CH_2NH_2$ **36j**	308	2.10	104.60	32.22	-30.10	-	-	[51]
19	$PhCH_2C(O)SC_6H_4R$ **14c,k** + 4-$MeOC_6H_4CH_2NH_2$ **36b**	318	7.32	52.30	16.63	-9.31	16.74	-9.42	[52]
20	$PhCH_2C(O)SC_6H_4R$ **14c,k** + 3-$ClC_6H_4CH_2NH_2$ **36m**	318	13.60	83.67	26.61	-13.0	26.77	-13.17	[52]
	Substituents R are varied Acyl-transfer reactions	**on**	**nucleophiles**						
27	$R'C_5H_4N$ **38f,g** + $PhC(O)OC_6H_3(NO_2)_2$-2,4 **19**	303	57.87	106.47	32.26	25.61	39.39	18.48	[36,64]
28 [g]	$MeC(O)OC_6H_4Cl$-4 **6j** + $R'C_6H_4CH_2NH_2$ **36c,j**	298	-1.05	-20.92	-6.23	5.20	-	-	[46]
29 [g]	$MeC(O)OC_6H_4CN$-4 **6s** + $R'C_6H_4CH_2NH_2$ **36c,j**	298	-5.22	-10.47	-3.12	-2.12	-	-	[46]
30	$PhNHC(O)SC_6H_4Me$-4 **9c** + $R'C_6H_4CH_2NH_2$ **36b,j**	303	-7.06	-48.4	-14.66	7.62	-17.91	10.85	[45]
31	$PhNHC(O)SC_6H_4Br$-4 **9k** + $R'C_6H_4CH_2NH_2$ **36b,j**	303	5.16	-12.06	-4.46	8.82	-3.65	9.62	[45]
32	*cyclo*-$C_3H_5C(O)OC_6H_4CN$-3 **10t** + $R'C_6H_4CH_2NH_2$ **36c,m**	318	7.91	-15.50	-4.93	12.83	-5.73	13.64	[48]
33	*cyclo*-$C_3H_5C(O)OC_6H_4NO_2$ -4 **10u** + $R'C_6H_4CH_2NH_2$ **36c,m**	318	-5.42	-38.74	-12.32	6.91	-14.33	8.91	[48]
34	*cyclo*-$C_4H_7C(O)OC_6H_4CN$-3 **11t** + $R'C_6H_4CH_2NH_2$ **36c,m**	318	7.76	-15.48	-4.92	12.68	-5.73	13.49	[49]
35	*cyclo*-$C_4H_7C(O)OC_6H_4NO_2$-4 **11u** + $R'C_6H_4CH_2NH_2$ **36c,m**	318	4.65	-15.5	-4.77	9.57	-5.73	10.38	[49]
36	$MeC(O)SC_6H_4Me$-4 **13c** + $R'C_6H_4CH_2NH_2$ **36b,j**	308	5.86	-8.36	-2.57	8.42	-3.09	8.95	[51]
37	$MeC(O)SC_6H_4Br$-4 **13k** + $R'C_6H_4CH_2NH_2$ **36b,j**	308	8.36	0	0	8.36	0	8.36	[51]
38	$PhCH_2C(O)SC_6H_4Me$-4 **14c** + $R'C_6H_4CH_2NH_2$ **36b,m**	318	-3.26	-39.22	-12.47	9.21	-14/51	11.25	[52]
39	$PhCH_2C(O)SC_6H_4Br$-4 **14k** + $R'C_6H_4CH_2NH_2$ **36b,m**	318	0.66	-19.61	-6.23	6.89	-7.25	7.92	[52]

(Table 1S). Continued.

	Ad_N reactions								
45	$R'C_6H_4CH_2NH_2$ **36b,j** + 4-$NO_2C_6H_4CH$ = $CHNO_2$ **29**	298	0.84	-25.1	-7.48	8.38	-9.29	10.13	[40]
46	$R'C_6H_4CH_2NH_2$ **36b,j** + 4-BrC_6H_4CH= C(CN)-$C_6H_4NO_2$ **30k**	298	5.86	-8.38	-2.50	8.36	-3.10	8.96	[41]
47	$R'C_6H_4CH_2NH_2$ **36b,j** + 4-$MeOC_6H_4CH$=C(CN)-$C_6H_4NO_2$-4 **30b**	298	-0.84	-25.1	-7.48	6.64	-9.29	8.45	[41]
	Substituents R are varied Acyl-transfer reactions	**on**	**nonleaving**	**groups**					
52	$RC_6H_4C(O)CH_2Br$ **20b,u** + 3-CNC_5H_4N **38t**	318	-4.89	-5.57	-1.77	-3.12	-	-	[53]
	Ad_N reactions								
59	RC_6H_4CH=C(Ph)NO_2 **31b,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	298	0.84	25.1	7.48	-6.38	7.78	-6.94	[41]
60	RC_6H_4CH=C(Ph)NO_2 **31b,k** **+** 4-$ClC_6H_4CH_2NH_2$ **36j**	298	-1.66	16.72	4.81	-6.38	4.98	-6.64	[41]
61	RC_6H_4CH=$CHNO_2$ **27c,u** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	288	1.76	39.64	11.42	-10.13	12.29	-10.53	[40]
62	RC_6H_4CH=C(CN)-$C_6H_4NO_2$-4 **30b,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	298	-1.68	16.74	4.99	-6.58	5.19	-6.87	[41]
63	RC_6H_4CH=C(CN)-$C_6H_4NO_2$-4 **30b,k** **+** 4-$ClC_6H_4CH_2NH_2$ **36j**	298	5.02	33.46	9.97	-4.78	10.37	-5.35	[41]
64	RC_6H_4CH=$C(COOEt)_2$ **32b,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	293	2.52	33.48	9.81	-7.30	10.38	-7.85	[42]
65	RC_6H_4CH=C(COOEt)$COCH_3$ **33b,j** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	288	3.34	33.48	9.64	-6.30	10.38	-7.04	[43]

[a] The entry numbers are identical with that in Table 1. [b] The middle temperature of experiments; temperature range in which the reaction rate constants were determined is twenty; number of the reaction rate constants at different temperatures is three. [c] The $\delta\Delta H^{\neq}$, $\delta\Delta S^{\neq}$, $\delta\Delta G^{\neq}$ reaction constants are estimated using two reactions in the correlation equations $\Delta H^{\neq} = \delta\Delta H^{\neq}\sigma + \Delta H^{\neq}_0$, $\Delta S^{\neq} = \delta\Delta S^{\neq}\sigma + \Delta S^{\neq}_0$, $\Delta G^{\neq} = \delta\Delta G^{\neq}\sigma + \Delta G^{\neq}_0$, respectively; σ^- and σ constants [65] were used in these correlations for entries 4 – 20 and 28 – 39, 45 – 47, 59 – 65, respectively. [d] Values are calculated by the equation $\delta\Delta H^{\neq}_{ext} = T_{comp}\,\delta\Delta S^{\neq}$, where T_{comp} = 320 K (entries 4 – 10, 19, 20), 370 K (entries 27, 30 – 39, 45 – 47), and 310 K (entries 59 – 65) are taken from Table 1. [e] $\delta\Delta H^{\neq}_{int} = \delta\Delta H^{\neq} - \delta\Delta H^{\neq}_{ext}$. [f] The references relate to the values of reactants, T_{exp}, activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ determined by the Eyring equation. [g] In DMSO.

Table 2S: Values of the Brønsted slopes β_R and $\beta_{R'}$, the Hammett reaction constants ρ_R and $\rho_{R'}$, cross-interaction constants $\rho_{RR'}$, and the associated mechanisms (concerted or stepwise) as the RDS (k_c or k_2) for the reactions of compounds 6 - 14, 19, 20, 27 - 33 with primary amines 35 – 37, 39, secondary cyclic amines 34, 40, and pyridines 38 in MeCN

Entry[a]	Reactants	β_R or $\beta_{R'}$	ρ_R or $\rho_{R'}$	$\rho_{RR'}$	Rate constant of the RDS	Ref.
	Substituents R are varied Acyl-trasfer reactions	**on leaving**	**groups**			
4 [b]	$MeC(O)OC_6H_4R$ **6j,s,t,u** + 4-$MeC_6H_4CH_2NH_2$ **36c**	-0.76	1.61	0.62	k_2	[46]
5 [b]	$MeC(O)OC_6H_4R$ **6j,s,t,u** + 4-$ClC_6H_4CH_2NH_2$ **36j**	-0.88	1.85	0.62	k_2	[46]

(Table 2S). Continued.

6	$EtOC(O)SC_6H_4R$ **7c,h,j,k** + $4\text{-}MeOC_6H_4CH_2NH_2$ **36b**	-0.66	1.63	-0.47	k_c	[44]
7	$EtOC(O)SC_6H_4R$ **7c,h,j,k** + $4\text{-}ClC_6H_4CH_2NH_2$ **36j**	-0.55	1.37	-0.47	k_c	[44]
8	$EtC(O)SC_6H_4R$ **8c,h,j,m** + $4\text{-}MeOC_6H_4CH_2NH_2$ **36b**	-0.90	2.12	2.36	k_2	[47]
9	$PhNHC(O)SC_6H_4R$ **9c,h,j,k** + $4\text{-}MeOC_6H_4CH_2NH_2$ **36b**	-0.55	2.07	-0.63	k_c	[45]
10	$PhNHC(O)SC_6H_4R$ **9c,h,j,k** + $4\text{-}ClC_6H_4CH_2NH_2$ **36j**	-0.46	1.74	-0.63	k_c	[45]
11	*cyclo*-$C_3H_5C(O)OC_6H_4R$ **10s,t,u,v** + $4\text{-}MeC_6H_4CH_2NH_2$ **36c**	-1.10	2.41	1.06	k_2	[48]
12	*cyclo*-$C_3H_5C(O)OC_6H_4R$ **10s,t,u,v** + $3\text{-}ClC_6H_4CH_2NH_2$ **36m**	-1.35	2.97	1.06	k_2	[48]
13	*cyclo*-$C_4H_7C(O)OC_6H_4R$ **11s,t,u,v** + $4\text{-}MeC_6H_4CH_2NH_2$ **36c**	-1.20	2.41	1.02	k_2	[49]
14	*cyclo*-$C_4H_7C(O)OC_6H_4R$ **11s,t,u,v** + $3\text{-}ClC_6H_4CH_2NH_2$ **36m**	-1.47	3.04	1.02	k_2	[49]
15	$PhCH_2C(S)SC_6H_4R$ **12c,h,j,k** + $4\text{-}MeOC_6H_4NH_2$ **37b**	-0.98	2.43	1.41	k_2	[50]
16	$PhCH_2C(S)SC_6H_4R$ **12c,h,j,k** + $4\text{-}ClC_6H_4NH_2$ **37m**	-1.33	3.31	1.41	k_2	[50]
17	$MeC(O)SC_6H_4R$ **13c,h,j,k** + $4\text{-}MeOC_6H_4CH_2NH_2$ **36b**	-2.10	5.00	0.90	k_2	[51]
18	$MeC(O)SC_6H_4R$ **13c,h,j,k** + $4\text{-}ClC_6H_4CH_2NH_2$ **36j**	-2.30	5.42	0.90	k_2	[51]
19	$PhCH_2C(O)SC_6H_4R$ **14c,h,j,k** + $4\text{-}MeOC_6H_4CH_2NH_2$ **36b**	-1.47	1.42	0.92	k_2	[52]
20	$PhCH_2C(O)SC_6H_4R$ **14c,h,j,k** + $3\text{-}ClC_6H_4CH_2NH_2$ **36m**	-1.72	1.79	0.92	k_2	[52]
	Substituents R are varied on nucleophiles Acyl-transfer reactions					
27	$R'C_5H_4N$ **38f,g** + $PhC(O)OC_6H_3(NO_2)_2\text{-}2,4$ **19**	0.90	-5.26	-	k_2	[64]
28 [b]	$MeC(O)OC_6H_4Cl\text{-}4$ **6j** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j**	1.04	-1.05	0.62	k_2	[46]

(Table 2S). Continued.

29 [b]	$MeC(O)OC_6H_4CN$-4 **6s** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j**	0.52	-0.56	0.62	k_2	[46]
30	$PhNHC(O)SC_6H_4Me$-4 **9c** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	1.28	-1.30	-0.63	k_c	[45]
31	$PhNHC(O)SC_6H_4Br$-4 **9k** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	1.51	-1.54	-0.63	k_c	[45]
32	*cyclo*-$C_3H_5C(O)OC_6H_4CN$-3 **10t** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	2.09	-2.10	1.06	k_2	[48]
33	*cyclo*-$C_3H_5C(O)OC_6H_4NO_2$ -4 **10u** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	1.33	-1.36	1.06	k_2	[48]
34	*cyclo*-$C_4H_7C(O)OC_6H_4CN$-3 **11t** + $R'C_6H_4CH_2NH_2$ **36b,c,f,h,i,j,m**	2.07	-2.08	1.02	k_2	[49]
35	*cyclo*-$C_4H_7C(O)OC_6H_4NO_2$-4 **11u** + $R'C_6H_4CH_2NH_2$ **36b,c,f,h,i,j,m**	1.48	-1.36	1.02	k_2	[49]
36	$MeC(O)SC_6H_4Me$-4 **13c** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	1.64	-1.65	0.90	k_2	[51]
37	$MeC(O)SC_6H_4Br$-4 **13k** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m**	1.28	-1.25	0.90	k_2	[51]
38	$PhCH_2C(O)SC_6H_4Me$-4 **14c** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m,q**	1.59	-1.54	0.92	k_2	[52]
39	$PhCH_2C(O)SC_6H_4Br$-4 **14k** + $R'C_6H_4CH_2NH_2$ **36b,c,h,j,m,q**	1.48	-1.44	0.92	k_2	[52]
	Ad_N reactions					
45	$R'C_6H_4CH_2NH_2$ **36b,c,h,j** + 4-$NO_2C_6H_4CH = CHNO_2$ **29**	1.59	-1.55	-0.41	k_c	[40]
46	$R'C_6H_4CH_2NH_2$ **36b,c,h,j** + 4-BrC_6H_4CH= C(CN)-$C_6H_4NO_2$ **30k**	1.24	-1.30	-0.67	k_c	[41]
47	$R'C_6H_4CH_2NH_2$ **36b,c,h,j** + 4-$MeOC_6H_4CH$=C(CN)-$C_6H_4NO_2$-4 **30b**	0.90	-0.95	-0.67	k_c	[41]
	Substituents R are varied	**on**	**nonleaving**	**groups**		
	Acyl-transfer reactions					
52	$RC_6H_4C(O)CH_2Br$ **20b,u** + 3-CNC_5H_4N **38t**	0.65 – 0.80	0.54	1.36	k_2	[53]
	Ad_N reactions					
59	RC_6H_4CH=C(Ph)NO_2 **31b,c,h,j,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	-	1.46	-0.52	k_c	[41]

(Table 2S). Continued.

60	$RC_6H_4CH=C(Ph)NO_2$ **31b,c,h,j,k** **+** 4-$ClC_6H_4CH_2NH_2$ **36j**	-	1.19	-0.52	k_c	[41]
61	$RC_6H_4CH=CHNO_2$ **27c,h,j,u** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	-	1.82	-0.41	k_c	[40]
62	$RC_6H_4CH=C(CN)$-$C_6H_4NO_2$-4 **30b,c,h,j,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	-	1.19	-0.67	k_c	[41]
63	$RC_6H_4CH=C(CN)$-$C_6H_4NO_2$-4 **30b,c,h,j,k** **+** 4-$ClC_6H_4CH_2NH_2$ **36j**	-	0.84	-0.67	k_c	[41]
64	$RC_6H_4CH=C(COOEt)_2$ **32b,c,h,j,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	-	1.24	-0.45	k_c	[42]
65	$RC_6H_4CH=C(COOEt)COCH_3$ **33b,c,h,j,k** **+** 4-$MeOC_6H_4CH_2NH_2$ **36b**	-	1.03	-0.38	k_c	[43]

[a] The entry numbers are identical with that in Table **1**. [b] In DMSO.