Table S1 Parameters of equations $\Delta H^{\neq} = \delta\Delta H^{\neq}\sigma + \Delta H^{\neq}_0$, $\Delta S^{\neq} = \delta\Delta S^{\neq}\sigma + \Delta S^{\neq}_0$, and $\Delta G^{\neq} = \delta\Delta G^{\neq}\sigma + \Delta G^{\neq}_0$ for the reactions of compounds **1** - **20** with nucleophiles **21**– **37**

Entry	Reactants	N [a]	$\delta\Delta H^{\neq}$/ kJ mol^{-1} σ^{-1} [b,c]	$\Delta H^{\neq}_0$/ kJ mol^{-1}	r (s)	$\delta\Delta S^{\neq}$/ J mol^{-1} K^{-1} σ^{-1} [b,c]	$\Delta S^{\neq}_0$/ J mol^{-1} K^{-1}	r (s)	$\delta\Delta G^{\neq}$/ kJ mol^{-1} σ^{-1} [b,c]	$\Delta G^{\neq}_0$/ kJ mol^{-1}	r (s)	Ref.
	S_N2 reactions											
1	$RC_6H_4NHC(O)$-CH_2Cl **1a,b,d,e,h,p,q,s,y** + $PhNMe_2$ **21**	9	34.9 ± 2.3	82.7 ± 1.0	0.984 (2.80)	-69.0 ± 4.1	-131.2 ± 1.7	0.988 (4.9)	-4.5	-34.9	-	68
2	$RC_6H_4CH_2Br$ **2b,e,g,j,q** + $PhNH_2$ **22**	5	-2.0	32.4	-	-17.3 ± 0.9 [d]	-187.1 ± 0.4	0.999 (0.49)	3.3 ± 0.3	90.0 ± 0.1	0.987 (0.23)	23
3	$RC_6H_4CH_2Cl$ **3b,e,g,j,q** + $PhNH_2$ **22**	5	0	38.0	-	-9.6 ± 0.7	-201.3 ± 0.3	0.993 (0.49)	3.1 ± 0.2	102.0± 0.1	0.994 (0.15)	23
4	$RC_6H_4CH_2Br$ **2b,e,q** + C_5H_5N **23**	3	17.5 ± 0.9	54.0 ± 0.4	0.999 (0.62)	50.2 ± 2.5	-137.2 ± 1.2	0.999 (1.82)	2.5 ± 0.1	94.9 ± 0.1	0.999 (0.08)	26
5	$RC_6H_4CH_2Br$ **2b,e,q** + C_5H_5N **23**	3	9.5 ± 0.8	46.8 ± 0.4	0.996 (0.58)	25.8 ± 4.4	-143.1 ± 2.0	0.986 (3.15)	1.8 ± 0.5	89.4 ± 0.2	0.965 (0.35)	26
6	$RC_6H_4CH_2Cl$ **3b,e,q** + C_5H_5N **23**	3	31.2 ± 3.5	76.7 ± 1.6	0.994 (2.5)	89.3 ± 6.5	-87.6 ± 3.0	0.997 (4.7)	4.6 ± 1.5	102.8 ± 0.7	0.949 (1.1)	26
7	$RC_6H_4CH_2Cl$ **3b,e,q** + C_5H_5N **23**	3	19.4 ± 1.2	57.0 ± 0.5	0.998 (0.86)	56.8 ± 9.7	-152.3 ± 4.4	0.986 (6.9)	2.5	102.4	-	26
8	$RC_6H_4CH_2Cl$ **3a,b,e,g,q** + PhS^-Li^+ **29**	5	-11.6	68.3	-	-22.2 ± 6.5 [e]	-47.1 ± 12.0	0.916 (10.0)	-5.1 ± 0.5 [e]	82.1 ± 7.1	0.944 (0.72)	16
9	$RC_6H_4CH(Me)Br$ **4b,e,h,q,y** + LiBr **30**	5	14.1 ± 4.1	60.4 ± 1.6	0.892 (3.4)	55.6 ± 10.2	-88.4 ± 4.0	0.953 (8.4)	-2.7	87.2	-	27
10	$RC_6H_4CH_2Br$ **2a,b,d,e,g,n,q**	7	12.6 ± 1.4 [f]	44.3 ± 0.3	0.976 (0.84)	36.8	-220.7	-	1.9 ± 0.6 [e]	108.3 ± 0.2	0.962 (0.94)	28

	+ C_5H_5N **23**											
11	$RC_6H_4CH_2Br$ **2a,b,d,e,g,n,q** + C_5H_5N **23**	7	7.3 ± 0.3 [g]	49.8 ± 0.1	0.998 (0.15)	13.1	-193.8	-	3.5 ± 0.5 [h]	106.0 ± 0.2	0.954 (0.43)	28
	S_NAr reactions											
12	RC_6H_4F **5 e,p,q** + MeONa **31**	3	-54.5 ± 2.0	154.4 ± 1.7	0.999 (1.79)	-34.3	13.7	-	-41.7 ± 2.6	149.3 ± 2.2	0.998 (2.31)	42,45, 69-75
13	RC_6H_4Cl **6g,j,m,q, r,t** + MeONa **31**	6	-44.60 ± 0.02	152.60 ± 0.04	0.999 (0.02)	-12.40 ± 0.04	-36.80 ± 0.03	0.999 (0.04)	-39.90 ± 0.03	166.30 ± 0.03	0.999 (0.03)	45,76 -78
14	1,2-$Cl_2C_6H_3R$ **7e,j, q** + MeONa **31**	3	-39.80 ± 0.01	138.00 ± 0.01	0.999 (0.01)	-7.30 ± 0.01	-39.10 ± 0.01	0.999 (0.01)	-37.1 ± 0.01	152.6 ± 0.01	0.999 (0.01)	45,79, 80
15	1-Cl-2-$CF_3C_6H_3R$ **8e,m,r,q** + MeONa **31**	4	-27.90 ± 0.02	122.90 ± 0.01	0.999 (0.02)	15.10 ± 0.05	-52.70 ± 0.04	0.999 (0.05)	-33.80 ± 0.04	143.60 ± 0.03	0.999 (0.03)	45,81, 82
16	RC_6F_5 **9e,f,g,m,q,r** + MeONa **31**	6	-27.50 ± 0.03	85.80 ± 0.02	0.999 (0.04)	18.30 ± 0.03	-59.60 ± 0.02	0.999 (0.03)	-33.40 ± 0.05	105.10 ± 0.03	0.999 (0.06)	45,83 -85
17	RC_6F_5 **9e,f,g,s** + $C_5H_{10}NH$ **24**	4	-13.4 ± 1.8	47.6 ± 0.8	0.981 (1.30)	54.2	-202.5	-	-30.9 ± 3.4	113.0 ± 1.7	0.982 (2.69)	45,86, 87
18	1-F-3-R-5-$NO_2C_6H_3$ **10e,i,j,k,p,r,u,v** + MeONa **31**	8	-24.20 ± 0.06	108.40 ± 0.03	0.999 (0.03)	36.70 ± 0.06	-35.20 ± 0.03	0.999 (0.04)	-37.90 ± 0.07	121.50 ± 0.03	0.999 (0.04)	45,72, 88
19	RC_6H_4Cl **6r,q,t,w** + NH_3 **25**	4	-43.4 ± 0.04	141.70 ± 0.05	0.999 (0.02)	31.00 ± 0.04	-190.00 ± 0.04	0.999 (0.02)	-58.10 ± 0.08	231.60 ± 0.08	0.999 (0.04)	45,89
20	1-Cl-2-$NO_2C_6H_3R$ **11e,r,q,t,x** + NH_3 **25**	5	-30.60 ± 0.03	77.20 ± 0.03	0.999 (0.04)	-22.60 ± 0.02	-174.40 ± 0.02	0.999 (0.02)	-21.00 ± 0.02	151.00 ± 0.02	0.999 (0.02)	45,90, 91
21	1-Cl-2-$NO_2C_6H_3R$ **11e,g,h,j,k,m,n,o,q** + $C_5H_{10}NH$ **24**	9	-23.60 ± 0.03	59.80 ± 0.02	0.999 (0.04)	-3.80 ± 0.03	-161.70 ± 0.02	0.999 (0.04)	-22.20 ± 0.04	120.20 ± 0.02	0.999 (0.05)	45,92
22	1-I-2-$NO_2C_6H_3R$ **12e,o,q,z** + NaN_3 **32**	4	-20.20 ± 0.05	106.50 ± 0.05	0.999 (0.05)	-5.20 ± 0.03	-40.20 ± 0.03	0.999 (0.03)	-18.50 ± 0.07	119.50 ± 0.07	0.999 (0.07)	45,75, 93
23	1-Cl-2-$NO_2C_6H_3R$ **11e,q,r,u,x** + $C_5H_{10}NH$ **24**	5	-20.90 ± 0.04	74.40 ± 0.04	0.999 (0.04)	5.3 ± 0.1	-129.5 ± 0.1	0.999 (0.12)	-22.90 ± 0.06	122.70 ± 0.06	0.999 (0.07)	45,94 -97
24	1-F-2-$NO_2C_6H_3R$ **13e,l,q** + MeONa **31**	3	-19.10 ± 0.02	73.90 ± 0.01	0.999 (0.02)	13.7 ± 0.01	-72.50 ± 0.01	0.999 (0.01)	-23.50 ± 0.03	97.30 ± 0.02	0.999 (0.03)	45,72, 75,98

25	1-Cl-2-$NO_2C_6H_3R$ **11e,n,q** + MeSNa **33**	3	-15.70 ± 0.04	75.70 ± 0.04	0.999 (0.04)	12.80 ± 0.02	-101.6 ± 0.02	0.999 (0.02)	-19.80 ± 0.07	108.50 ± 0.06	0.999 (0.63)	45,79
26	1-Cl-2-$NO_2C_6H_3R$ 11e,f,g,h,m,o,q,s,t, x,z + MeONa 31	11	-16.00 ± 0.02	98.80 ± 0.02	0.999 (0.04)	19.20 ± 0.02	-43.30 ± 0.02	0.999 (0.04)	-22.20 ± 0.03	112.80 ± 0.02	0.999 (0.05)	45,72, 76-78,90, 91, 100-104
	Acyl-transfer reactions											
27	$RC_6H_4C(O)OC_6H_4NO_2$-4 **14a,b,e,h,k,m** + PhSH·K_2CO_3 **34**	6	-108.5 ± 7.0	-5.3 ± 2.2 [i]	0.992 (5.0)	-332.0 ± 26.8	-20.0 ± 8.5 [i]	0.987 (19.2)	-9.2	0 [i]	-	105
28	$RC_6H_4C(O)OC_6H_4NO_2$-4 **14a,b,e,h,j, p,q** + 4-$ClC_6H_4OH·K_2CO_3$ **35**	7	-76.4 ± 4.9	-9.8 ± 2.3 [i]	0.990 (5.07)	-192.0 ± 15.8	-30.9 ± 7.5 [i]	0.983 (16.5)	-16.4	0 [i]	-	106
29	$RC_6H_4C(O)OC_6H_4NO_2$-4 **14b,e,g,o,q** + Imidazole **26**	5	-5.6 ± 0.8	39.8 ± 0.4	0.972 (0.64)	3.9	-148	-	-6.8 ± 0.3	84.4 ± 0.3	0.996 (0.27)	107
30	$RC_6H_4C(O)OC_6H_3(NO_2)_2$-2,4 **15b,e,g,o,q** + Na_2HPO_4 **36**	5	-10.2 ± 1.0	67.7 ± 0.5	0.986 (0.84)	10.2	-93.2	-	-13.4 ± 0.5 (0.998)	95.0 ± 0.2	0.998 (0.41)	108
31	$RC_6H_4C(O)OC_6H_3(NO_2)_2$-2,4 **15b,e,g,o,q** + Imidazole **26**	5	-2.9	37.2	-	23.7 ± 4.2	-123.6 ± 2.6	0.956 (3.71)	-10.0 ± 0.2	74.9 ± 0.1	0.999 (0.19)	107
32	$RC_6H_4C(O)OEt$ **16b,c,d,e,p,q** + OH^- **37**	7 [j]	-11.9 ± 0.4	58.9 ± 0.2	0.997 (0.50)	5.4	-96.6	-	-13.5 ± 0.3	87.0 ± 0.3	0.998 (0.41)	109
33	$RC_6H_4C(O)OEt$ **16a,b,c,e,g,h,q** + OH^- **37**	7	-15.9 ± 0.4	71.0 ± 0.2	0.998 (0.43)	-4.5	-67.3	-	-14.5 ± 0.3	92.0 ± 0.3	0.999 (0.33)	110
34	$RC_6H_4C(O)OEt$ **16a,b,c,e,h,q** + OH^- **37**	6	-6.2 ± 0.7	72.5 ± 0.3	0.975 (0.59)	21.2	-66.1	-	-12.5 ± 0.4	91.5 ± 0.1	0.998 (0.31)	46

35	$RC_6H_4C(O)Cl$ **17b,e,h,q** + H_2O **27**	4	-25.8 ± 3.5	46.5 ± 1.5	0.983 (2.5)	-48.0 ± 10.0	-177.2 ± 4.1	0.959 (7.2)	-11.5	99.6	-	111
36	$RC_6H_4C(O)Cl$ **17b,e,f,g,h,q** + EtOH **28**	6	-20.2 ± 1.7	59.5 ± 0.6	0.986 (1.23)	-37.2	-126.4	-	-9.6 ± 0.4	93.9 ± 0.2	0.996 (0.37)	112
37	$RC_6H_4C(O)Cl$ **17b,e,f,g,h,q** + EtOH **28**	6	-15.4 ± 1.2	61.5 ± 0.5	0.989 (0.94)	-22.0	-98.7	-	-8.8 ± 0.1	90.9 ± 0.3	0.988 (0.56)	46
38	$RC_6H_4C(O)Cl$ **17b,e,g,q** + $PhNH_2$ **22**	4	-8.2 ± 0.4	28.6 ± 0.2	0/998 (0.26)	3.0	-172.1	-	-9.1 ± 2.0	81.0 ± 0.8	0.954 (1.46)	113
39	$RC_6H_4C(O)NH_2$ **18b,e,g,o** + OH^- **37**	4	-12.9 ± 1.2	74.3 ± 0.5	0.991 (0.89)	-14.1	-112.0	-	-8.0 ± 0.4	114.3 ± 0.2	0.997 (0.29)	114
40	$RC_6H_4C(O)Z$ [k] **19b,e,g,q** + OH^- **37**	4	27.4	32.5	-	119.9 ± 22.6	-165.8 ± 9.4	0.966 (16.2)	-8.3 ± 0.3	82.0 ± 0.1	0.999 (0.19)	47,115, 116
41	$RC_6H_4C(O)Z$ [k] **19b,e,g,q** + H_2O **27**	4	9.4	36.5	-	58.9 ± 13.8	-175.2 ± 6.6	0.973 (9.3)	-8.1 ± 0.1	97.5 ± 0.1	0.999 (0.09)	47,115, 116
42	$RC_6H_4C(O)Z$ [k] **19b,e,g,o,q** + H_2O **27**	5	-10.8 ± 0.3	41.6 ± 0.1	0.999 (0.23)	-10.9	-158	-	-7.4 ± 0.3	88.4 ± 0.2	0.997 (0.28)	47,117
43	$[RC_6H_4C(O)]_2O$ **20a,b,e,g,p,q,o** + H_2O **27**	7 [j]	-16.6 ± 0.7 [l]	34.2 ± 1.5	0.980 (1.6)	-19.8 [l]	-77.3	-	-10.0 ± 0.2 [l]	67.8 ± 0.1	0.999 (0.17)	118

[a] Number of compounds. [b] σ constants[13] were used in the correlations; standard errors of the $\delta\Delta H^{\neq}$, $\delta\Delta S^{\neq}$ and $\delta\Delta G^{\neq}$ reaction constants are estimated to be less than 8%, 11% and 5%, respectively. [c] Values given without correlation coefficient are calculated by the equation $\delta\Delta G^{\neq} = \delta\Delta H^{\neq} - T\,\delta\Delta S^{\neq}$. [d] Value is calculated for compounds **2e,j,q**. [e] Value is calculated by the Yukawa – Tsuno equation.[119] [f] Value is calculated for compounds **2a,b,d,e,g,n**. [g] Value is calculated for compounds **2a,b,e,,g,n**. [h] Value is calculated for compounds **2b,d,e,g,n,q**. [i] The differences in the activation parameters $\Delta\Delta H_0^{\neq} = \Delta H_0^{\neq}(R) - \Delta H_0^{\neq}(H)$, $\Delta\Delta S_0^{\neq} = \Delta S_0^{\neq}(R) - \Delta S_0^{\neq}(H)$, and $\Delta\Delta G_0^{\neq} = \Delta G_0^{\neq}(R) - \Delta G_0^{\neq}(H)$, respectively. [j] The substituent R = 3-NH_2 is added.[13] [k] Z is Imidazolyl. [l] Value is halved due to the two carbonyl groups are available for attack in compound **20**.[118]