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 **9 - 32** with nucleophiles **1**– **8**.

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	$RC_6H_4NMe_2$ **1b,c,f,h,i,j,s,t** + MeI **9**	8	16.4 ± 1.1	61.1 ± 0.2	0.987 (0.42)	7.0	-121.3	-	14.1 ± 0.6	100.9 ± 0.1	0.995 (0.22)	30,47, 49
2	$RC_6H_4NMe_2$ **1c,f,h,m,z** + MeI **9**	5	10.0 ± 0.6	48.8 ± 0.2	0.994 (0.44)	-14.2 ± 1.2	-152.3 ± 0.4	0.989 (0.88)	14.4 ± 0.3	96.5 ± 0.1	0.999 (0.22)	30,47, 50
3	$RC_6H_4NMe_2$ **1c,f,h,m,z,** + MeI **9**	5	9.8 ± 0.5 [d]	45.9 ± 0.2	0.997 (0.38)	-15.1 ± 1.4	-166.8 ± 0.5	0.991 (0.99)	14.6 ± 0.1	98.15 ± 0.03	0.999 (0.07)	30,47, 50
4	RC_5H_4N **2h,m,o,p,w** + MeI **9**	5	9.9 ± 1.7	53.7 ± 0.8	0.959 (1.0)	-10.7	-130.9	-	13.1 ± 1.3	92.7 ± 0.6	0.986 (0.74)	30,47, 51
5	$RC_6H_4NH_2$ **3b,c,e,h,j** + CH_2=CH-CH_2Br **10**	5	-20.9	42.9	-	-88.8 ± 13.3	-152.1 ± 2.4	0.968 (5.4)	6.0 ± 0.2	89.0 ±0.1	0.998 (0.1)	47,52
6	$RC_6H_4NH_2$ **3c,h,j,m** + $PhCH_2Br$ **11**	4	-1.9	29.0	-	-35.4 ± 3.2 [e]	-197.8 ± 0.9	0.995 (1.3)	9.0 ± 0.2	89.9 ± 0.1	0.999 (0.1)	47,53
7	$RC_6H_4NH_2$ **3b,c,h,j,m** + $PhCH_2Cl$ **12**	5	-0.6	40.0	-	-25.8 ± 0.5 [f]	-205.3 ± 0.1	0.999 (0.23)	7.9 ± 0.2	105.3 ± 0.1	0.999 (0.10)	47,53
8	$RC_6H_4NH_2$ **3c,f,h,j,k,m,n** + $PhCH_2Br$ **11**	7	8.0 ± 0.9 [g]	50.2 ± 0.3	0.981 (0.55)	7.9	-132.0	-	5.6 ± 1.0	90.2 ± 0.3	0.925 (0.67)	47,54
9	$RC_6H_4NH_2$ **3c,h,k,n,z** + $PhCH_2Br$ **11**	5	7.7 ± 2.0	45.8 ± 0.9	0.911 (1.5)	-0.3	-171.3	-	7.8 ± 1.8	97.7 ± 0.8	0.925 (1.4)	47,54

					S_NV	reactions						
10	$RC_6H_4S^-Na^+$ **4c,h,j,y** + $PhSO_2CH=CCl_2$ **13**	4	12.5 ± 4.6 [h]	58.5 ± 3.0	0.900 (5.2)	37.1 ± 13.8 [h]	-52.8 ± 8.9	0.900 (15.5)	1.7 ± 0.3 [h]	74.1 ± 0.2	0.973 (0.30)	55
					Ad_N	reactions						
11	$RC_6H_4CH_2NH_2$ **5b-f,h-m,v,z** + $PhCH=C(CN)_2$ **14**	13	21.8 ± 2.1	45.4 ± 0.6	0.982 (0.43)	48.8	-86.7	-	7.5 ± 0.3	70.8 ± 0.1	0.982 (0.44)	56
12	$RC_6H_4NH_2$ **3в-f,h,j,k,m,p,u-z** + (E)-$PhCH=CHNO_2$ **15**	15	16.0 ± 1.6	45.1 ± 0.7	0.940 (2.0)	18.1	-154.4	-	10.6 ± 0.6	91.1± 0.3	0.977 (0.78)	57
13	$RC_6H_4NH_2$ **3a-f,h,j,k** + $PhC\equiv C-C(O)Ph$ **16**	10	-3.4	157.4	-	-44.7 ± 6.2	-187.3 ± 2.3	0.930 (6.6)	10.6 ± 1.3	98.8 ± 0.5	0.947 (1.36)	58
14	$RC_6H_4SH\cdot Et_3N$ **6b,c,h,j,y** + hC≡C-C(O)Ph **16**	5	0	0	-	46.9 ± 1.5 [h]	-277.2 ± 0.9	0.998 (1.9)	-12.7 ± 0.5 [h]	75.5 ± 0.3	0.998 (0.6)	59
					S_NAr	reactions						
15	$RC_6H_4O^-Na^+$ **7b,c,f,h,j,k,v,y** + 2-Cl-5-$NO_2C_5H_3N$ **17**	8	34.5 ± 3.3	57.7 ± 1.2	0.974 (3.0)	77.1 ± 9.6	-124.7 ± 3.4	0.956 (8.8)	8.1 ± 0.4	100.5 ± 0.1	0.993 (0.36)	36,60
16	$RC_6H_4O^-Na^+$ **7b,c,f,h,j,k,v,y** + 2-Cl-3-$NO_2C_5H_3N$ **18**	8	34.3 ± 3.7	70.8 ± 1.3	0.966 (3.4)	85.0 ± 12.2	-98.9 ± 4.3	0.943 (11.2)	5.1 ± 0.6	104.7 ± 0.2	0.963 (0.54)	36,60
17	$RC_6H_4OH\cdot K_2CO_3$ **8c,g,h,j,k,y** + 1,3-$(NO_2)_2C_6H_4$ **19**	6	-77.2 ± 0.4 [h]	214.7 ± 0.1	0.999 (0.29)	-213.8 ± 0.3 [h]	203.7 ± 0.1	0.999 (0.21)	13.2 ± 0.3 [h]	128.5 ± 0.1	0.999 (0.30)	36,61, 62
18	$RC_6H_4OH\cdot K_2CO_3$ **8c,h,j,y** + 3-$NO_2C_6H_4F$	4	-86.3 ± 1.7 [h]	204.7 ± 0.6	0.999 (1.12)	-238.1 ± 2.7 [h]	175.2 ± 1.0	0.999 (1.78)	14.4 ± 0.7 [h]	130.6 ± 0.3	0.998 (0.43)	36,61, 62

	20											
19	$RC_6H_4OH \cdot K_2CO_3$ **8c,h,j,k,q,r,w,y** + 1,3-$(NO_2)_2$-5-$CF_3C_6H_3$	8	-63.7 ± 0.8 [h]	201.0 ± 0.5	0.999 (1.02)	-202.0 ± 2.1 [h]	214.6 ± 1.4	0.999 (2.63)	5.6 ± 0.3 [h]	127.4 ± 0.2	0.994 (0.32)	36,61, 62
	21											
20	$RC_6H_4OH \cdot K_2CO_3$ **8c,h,j,q,r,w,y** + 3-NO_2-5-CF_3-C_6H_3F	7	-123.3 ± 12.0 [h]	185.2 ± 8.5	0.977 (15.0)	-381.5 ± 36.1 [h]	167.8 ± 25.4	0.978 (45.1)	7.6 ± 0.5 [h]	127.6 ± 0.4	0.988 (0.66)	36,61, 62
	22											
21	$RC_6H_4NH_2$ + **3f,h,j,k,m,p** 2,4-$(NO_2)_2C_6H_3F$	6	21.0 ± 0.6 [h]	26.5 ± 0.1	0.998 (0.24)	-9.1	-197.9	-	23.7 ± 0.1 [h]	86.4 ± 0.1	0.999 (0.04)	36,63, 64
	23											
22	$RC_6H_4NH_2$ + **3f,h,j,k,m,p** 2,4-$(NO_2)_2C_6H_3Cl$	6	37.7 ± 0.1 [h]	46.4 ± 0.1	0.999 (0.03)	60.4 ± 0.1 [h]	-169.5 ± 0.1	0.999 (0.04)	18.4 ± 0.1 [h]	100.3 ± 0.1	0.999 (0.08)	9,36, 64
	24											
23	$RC_6H_4NH_2$ **3h,j,m** + 2,4,6-$(NO_2)_3C_6H_2Cl$	3	27.0 ± 8.2 [h]	33.4 ± 2.0	0.956 (2.2)	-2.0	-151.7	-	27.6 ± 2.4 [h]	78.6 ± 0.6	0.996 (0.62)	36,65
	25											
					Acyl-	transfer	reactions					
24	$RC_6H_4NH_2$ **3c,h,j,y,z** + PhCOCl	5	14.7 ± 1.5 [h]	28.6 ± 1.0	0.986 (1.9)	0	-166.1	-	14.7 ± 1.2 [h]	80.0 ± 0.8	0.992 (1.42)	35, 66,67
	26											
25	$RC_6H_4NH_2$ **3h,j,y,z** + PhCOCl	4	19.1 ± 0.5 [h]	22.9 ± 0.3	0.999 (0.45)	14.4	-181.8	-	14.8 ± 1.2 [h]	78.1 ± 0.9	0.994 (1.16)	35,67
	26											
26	$RC_6H_4NH_2$ **3h,m,z** + PhOCOCl	3	15.3 ± 4.0	20.5 ± 1.7	0.937 (2.1)	11.6	-154.7	-	11.8 ± 0.4	67.9 ± 0.2	0.999 (0.18)	35,68
	27											
27	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + PhCH=CHCOCl	6	17.1 ± 1.1	25.0 ± 0.4	0.992 (0.8)	-2.7	-177.2	-	17.9 ± 0.5	77.8 ± 0.2	0.998 (0.38)	69
	28											

28	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + 2-C_4H_3O-CH=CH-COCl **29**	6	16.2 ± 1.1	24.9 ± 0.4	0.990 (0.83)	-6.4	-178.5	-	18.1 ± 0.6	78.1 ± 0.2	0.998 (0.41)	69
29	$RC_6H_4NH_2$ **3c,f,j,h,m,z** + 2-C_4H_3S-CH=CH-COCl **30**	6	16.8 ± 0.8	25.8 ± 0.3	0.995 (0.61)	-2.3	-178.8	-	17.5 ± 0.4	78.5 ± 0.2	0.999 (0.32)	69
30	$RC_6H_4NH_2$ **3b,c,f,h,j,m,z** + 3-C_4H_3S-COCl **31**	7	17.5 ± 0.7	28.4 ± 0.2	0.995 (0.55)	-2.0	-173.8	-	18.1 ± 0.7	80.2 ± 0.2	0.996 (0.55)	70
31	$RC_6H_4OH \cdot K_2CO_3$ **8b,c,f** + $PhC(O)OC_6H_3$-$(NO_2)_2$-2,4 **32**	3	-0.25 ± 0.03	1.71 ± 0.01 [i]	0.993 (0.01)	-34.0 ± 1.2	3.09 ± 0.22 [i]	0.999 (1.15)	9.7	0 [i]	-	35,71
32	$RC_6H_4OH \cdot K_2CO_3$ **8j,p,z** + $PhC(O)OC_6H_3$-$(NO_2)_2$-2,4 **32**	3	-10.2 ± 0.3	1.06 ± 0.13 [i]	0.999 (0.10)	-40.1 ± 0.9	17.7 ± 0.4 [i]	0.999 (0.32)	1.5	0 [i]	-	35,71
33	$RC_6H_4OH \cdot K_2CO_3$ **8w,y,z** + $PhC(O)OC_6H_3$-$(NO_2)_2$-2,4 **32**	3	-7.0 ± 0.04	-1.25 ± 0.04 [i]	0.999 (0.02)	-45.5 ± 0.2	21.5 ± 0.2 [i]	0.999 (0.09)	6.3	0 [i]	-	35,71

[a] Number of compounds. [b] σ constants[12] 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 9%, 12% and 7%, 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 **1c,f,h,z**. [e] Value is calculated for compounds **3c,j,m.** [f] Value is calculated for compounds **3b,c,h,m**. [g] Value is calculated for compounds **3c,f,j,k,n**. [h] Value is calculated for compounds **3b,e,p**. [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.