Supporting information of the article entitled: Nucleophilic Substitution in Ionizable Fischer Thiocarbene Complexes: Steric Effect of the Alkyl Substituent on the Heteroatom.

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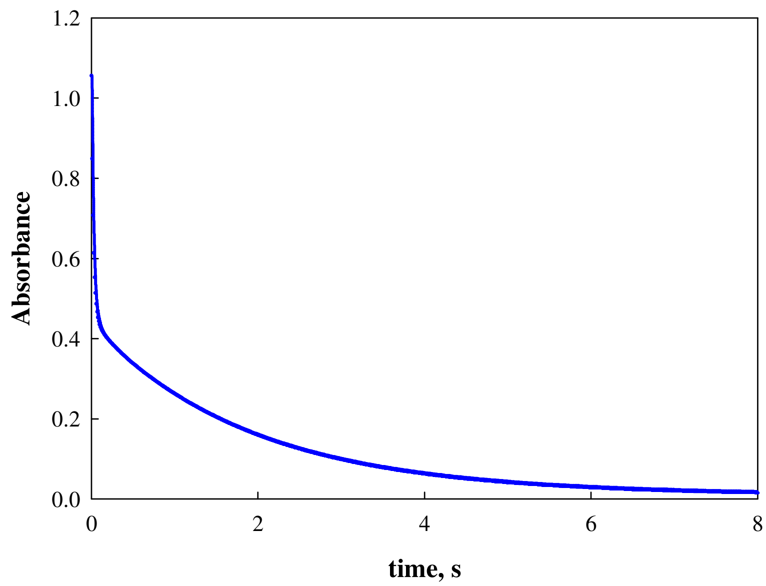

Figure S1. Kinetic trade (at λ = 335 nm) for the reaction of **4W-cHex** with morpholine in 50 % MeCN- 50% water at 25 °C. Conditions: [**4W-*c*Hex**] **=** 1.0×10^{-4}, $[\text{Morph}]_{\text{Total}} = 1.25 \times 10^{-2}$ M, pH = 8.70 and ionic strength = 0.1 M (KCl).

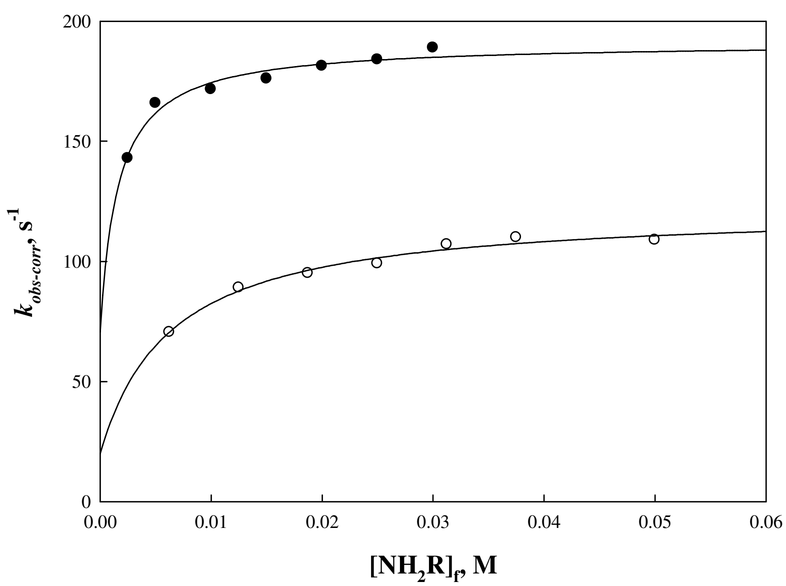

Figure S2 Plot of $k_{obs\text{-}corr}$ *vs.* $[RNH_2]_f$ for the reaction of **4Cr-*n*Bu** with: (●) benzylamine, pH = 9.12; (○) furfurylamine, pH = 8.58, ionic strength= 0.1 M (KCl), 25 °C.

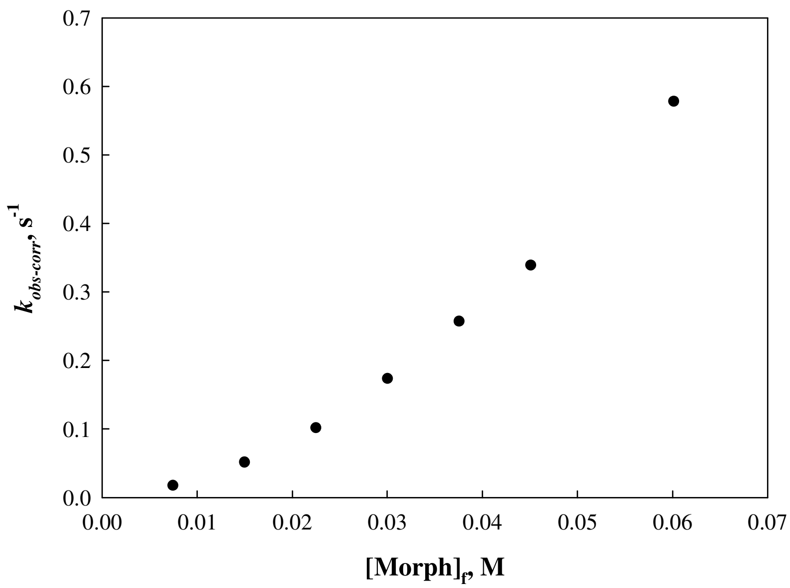

Figure S3. Plot of $k_{obs\text{-}corr}$ *vs.* [Morph]$_f$ for the reaction between morpholine and **4W-*i*Pr** in 50% MeCN – 50% Water. Conditions: [**4W-*i*Pr**] = 1.0 × 10^{-4} M, p*H* =8.88, ionic strength = 0.1 M (KCl) and T = 25° C.

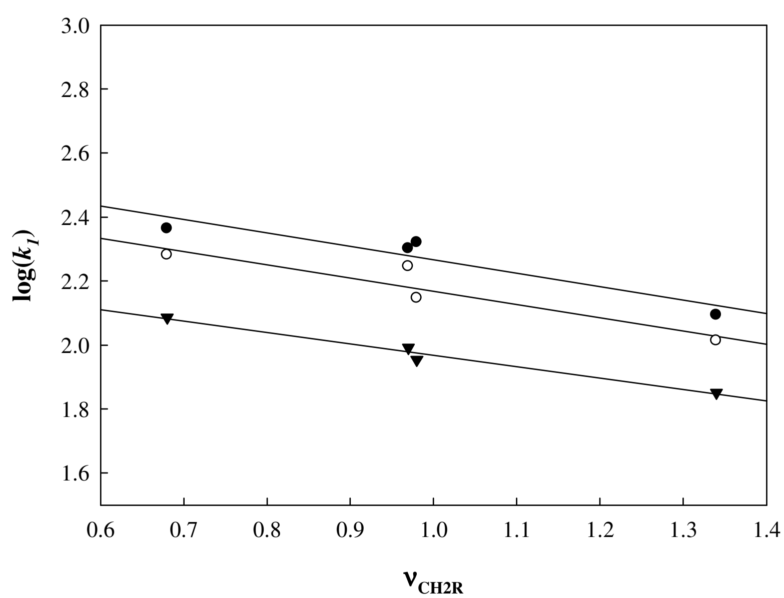

Figure S4. Plot of log(k_1) *vs.* ν_{CH2R} for the reaction of **4Cr-R** with (●) *n*-butylamine, (○) benzylamine and (▼) furfurylamine in 50 % MeCN – 50% water at 25 °C and Ionic strength = 0.1 M (KCl).

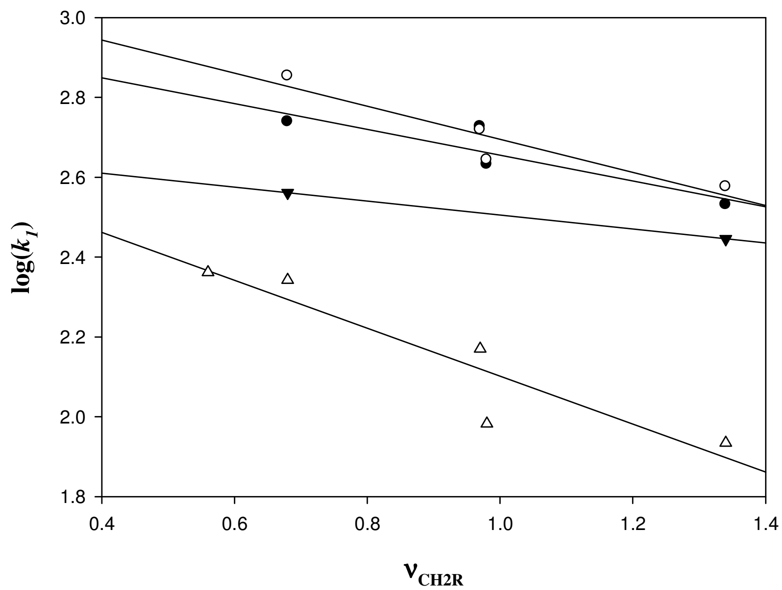

Figure S5. Plot of log(k_1) vs. ν_{CH2R} for the reaction of **4W-R** with (●) 2-methoxyethylamine, (○) benzylamine, (▼) furfurylamine and (Δ) glycin ethyl ester in 50 % MeCN – 50% water at 25 °C and ionic strength = 0.1 M (KCl).

Table S1. Summary of the ψ values of the nucleophilic attachment in the aminolysis reactions of **4M-R** Fischer carbene complexes in 50% MeCN-50% Water at 25 °C.[a]

	Reactant	Nucleophiles	ψ
1	$(CO)_5Cr{=}C(SR)CH_3$	*n*-butylamine	-0.42 ± 0.08
2	$(CO)_5Cr{=}C(SR)CH_3$	Benzylamine	-0.41 ± 0.08
3	$(CO)_5Cr{=}C(SR)CH_3$	Furfurylamine	-0.36 ± 0.03
4	$(CO)_5W{=}C(SR)CH_3$	*n*-butylamine	-0.11[b]
5	$(CO)_5W{=}C(SR)CH_3$	2-methoxyethylamine	-0.32 ± 0.08
6	$(CO)_5W{=}C(SR)CH_3$	Benzylamine	-0.42 ± 0.08
7	$(CO)_5W{=}C(SR)CH_3$	Furfurylamine	-0.17 ± 0.07
8	$(CO)_5W{=}C(SR)CH_3$	Glycin ethyl ester	-0.57 ± 0.05

[a] Ionic strength = 0.1 (KCl). [b] Two points.

Table S2. Reaction of **4W-*n*Bu** with Morpholine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Morph]_f$, M	k_{obs}, s^{-1} [b]	$k_{A\text{-}corr}$, M^{-1} s^{-1}
0.0250	0.0151	0.0987 ± 0.0005	18.49
0.0375	0.0226	0.1964 ± 0.0003	24.53
0.0500	0.0301	0.354 ± 0.001	33.15
0.0625	0.0376	0.563 ± 0.003	42.18
0.7500	0.0452	0.766 ± 0.003	47.83
0.1000	0.0602	1.234 ± 0.003	57.79

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 8.88. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S3. Reaction of **4W-*n*Bu** with Morpholine in 50% MeCN- 50% water at 25 °C varying the p*H*.[a]

p*H*	$[HO^-]$, M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
9.588	2.50 10^{-6}	0.126 ± 0.001	146.43
9.667	3.00 10^{-6}	0.1168 ± 0.0002	157.13
9.792	4.00 10^{-6}	0.1094 ± 0.0007	187.54
9.889	5.00 10^{-6}	0.0926 ± 0.0004	193.02
10.065	7.50 10^{-6}	0.0755 ± 0.0003	227.31
10.190	1.00 10^{-5}	0.0650 ± 0.0002	256.02
10.366	1.50 10^{-5}	0.0514 ± 0.0002	297.82
10.491	2.00 10^{-5}	0.0457 ± 0.0002	349.70
10.588	2.50 10^{-5}	0.03998 ± 0.00004	380.26
10.667	3.00 10^{-5}	0.0407 ± 0.0003	462.53
10.792	4.00 10^{-5}	0.0342 ± 0.0003	515.75
10.889	5.00 10^{-5}	0.0316 ± 0.0003	594.05
11.065	7.50 10^{-5}	0.0255 ± 0.0001	716.09
11.190	1.00 10^{-4}	0.0204 ± 0.0002	762.43

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0 × 10^{-4} M, [morph] = 0.01 M and [TEA] = 0.01M. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S4. Reaction of **4W-*n*Bu** with Morpholine in 50% MeCN- 50% water at 25 °C varying the concentration of the external TEA buffer.[a]

[TEA], M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
0.001	0.0243 ± 0.0001	353.67
0.002	0.025197 ± 0.000006	366.72
0.003	0.0263 ± 0.0001	382.78
0.004	0.0267 ± 0.0001	388.60
0.005	0.02673 ± 0.00005	389.04
0.007	0.02952 ± 0.00006	429.65
0.008	0.02964± 0.00009	431.39
0.009	0.02962 ± 0.00009	431.10
0.010	0.02918 ± 0.00005	424.70
0.015	0.03250 ± 0.00009	473.02
0.020	0.0341 ± 0.0002	496.31
0.025	0.03294 ± 0.00004	479.42
0.030	0.0354 ± 0.0002	515.23
0.040	0.0338 ± 0.0002	491.94
0.050	0.03469 ± 0.00005	504.89

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0 10^{-4} M, [Morph] = 0.01 M, p*H* = 10.78. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S5. Reaction of **4W-*n*Bu** with Glycinethylester in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.425 ± 0.001
0.0250	0.01250	1.092 ± 0.006
0.0375	0.01875	1.739 ± 0.009
0.0500	0.02500	2.524 ± 0.008
0.0625	0.03125	3.42 ± 0.01
0.0750	0.03750	4.59 ± 0.03
0.1000	0.05000	6.41 ± 0.05

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 7.43. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S6. Reaction of **4W-*n*Bu** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	1.42 ± 0.05
0.0250	0.01250	2.79 ± 0.01
0.0375	0.01875	4.14 ± 0.01
0.0500	0.02500	5.45 ± 0.02
0.0625	0.03125	6.56 ± 0.05
0.0750	0.03750	7.62 ± 0.02
0.1000	0.05000	9.80 ± 0.05

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0×10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S7. Reaction of **4W-*n*Bu** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.999 ± 0.002
0.0250	0.01250	2.51 ± 0.02
0.0375	0.01875	3.45 ± 0.04
0.0500	0.02500	4.55 ± 0.04
0.0625	0.03125	5.59 ± 0.06
0.0750	0.03750	6.55 ± 0.07
0.1000	0.05000	8.71 ± 0.07

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0×10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S8. Reaction of **4W-*n*Bu** with 2-Methoxyethylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.00625	$3.1250\ 10^{-3}$	0.268 ± 0.003
0.01250	$6.2500\ 10^{-3}$	0.490 ± 0.008
0.01875	$9.3750\ 10^{-3}$	0.98 ± 0.02
0.02500	0.0125	1.120 ± 0.009
0.03125	0.0156	1.35 ± 0.02
0.03750	0.0188	1.61 ± 0.02
0.05000	0.0250	2.00 ± 0.03

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 9.39. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S9. Reaction of **4W-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[\text{Morph}]_f$, M	k_{obs}, s^{-1}	$k_{A\ corr}$, $M^{-1}\ s^{-1}$
0.0250	0.0151	0.0512 ± 0.0004	7.48
0.0375	0.0226	0.116 ± 0.0008	11.30
0.0500	0.0301	0.202 ± 0.002	14.76
0.0625	0.0376	0.3150 ± 0.0003	18.41
0.7500	0.0452	0.421 ± 0.001	20.51
0.1000	0.0602	0.725 ± 0.002	26.49

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 8.88. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S10. Reaction of **4W-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C varying the p*H*.[a]

pH	$[HO^-]$, M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, $M^{-1}\ s^{-1}$
9.588	2.50 10^{-6}	0.1035 ± 0.0005	83.44
9.667	3.00 10^{-6}	0.09379 ± 0.00007	86.89
9.792	4.00 10^{-6}	0.0870 ± 0.0002	101.73
9.889	5.00 10^{-6}	0.0706 ± 0.0001	99.78
10.065	7.50 10^{-6}	0.0608 ± 0.0002	123.09
10.190	1.00 10^{-5}	0.04997 ± 0.00005	131.79
10.366	1.50 10^{-5}	0.0427 ± 0.0002	164.95
10.491	2.00 10^{-5}	0.0352 ± 0.0002	179.17
10.588	2.50 10^{-5}	0.0314 ± 0.00008	198.40
10.667	3.00 10^{-5}	0.0290 ± 0.0005	218.73
10.792	4.00 10^{-5}	0.02565 ± 0.0005	256.44
10.889	5.00 10^{-5}	0.023550 ± 0.00008	293.30
11.065	7.50 10^{-5}	0.01980 ± 0.0001	368.03
11.190	1.00 10^{-4}	0.016040 ± 0.00006	396.62

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0 × 10^{-4} M, [morph] = 0.01 M and [TEA] = 0.01M. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S11. Reaction of **4W-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C varying the concentration of the external TEA buffer.[a]

[TEA], M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
0.001	0.0224 ± 0.0004	216.16
0.002	0.0231 ± 0.0005	222.43
0.004	0.02300 ± 0.00003	221.56
0.005	0.02430 ± 0.00007	234.49
0.006	0.0248 ± 0.0001	239.32
0.007	0.02470 ± 0.00007	238.35
0.008	0.02520 ± 0.00005	243.18
0.009	0.02660 ± 0.00007	256.69
0.010	0.02660 ± 0.00005	256.98
0.015	0.02950 ± 0.00007	284.67
0.020	0.0319 ± 0.0002	307.83
0.025	0.0330 ± 0.0001	318.45
0.040	0.0368 ± 0.00006	355.12
0.050	0.03760 ± 0.00008	362.84
0.075	0.0371 ± 0.0003	358.01
0.100	0.03710 ± 0.00005	358.01

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0 × 10^{-4} M, [Morph] = 0.01 M, p*H* = 10.78 and [morph] = 0.01. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S12. Reaction of **4W-*c*Hex** with Glycinethylester in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.2997 ± 0.0004
0.0250	0.01250	0.769 ± 0.001
0.0375	0.01875	1.205 ± 0.003
0.0500	0.02500	1.860 ± 0.009
0.0625	0.03125	2.52 ± 0.02
0.0750	0.03750	3.29 ± 0.02
0.1000	0.05000	4.58 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 7.43. [b] Determined with a *stopped-flow* machine monitoring at 437 nm.

Table S13. Reaction of **4W-*c*Hex** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	1.045 ± 0.003
0.0250	0.01250	2.21 ± 0.02
0.0375	0.01875	3.43 ± 0.01
0.0500	0.02500	4.43 ± 0.01
0.0625	0.03125	5.52 ± 0.05
0.0750	0.03750	6.47 ± 0.05
0.1000	0.05000	8.51 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0×10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S14. Reaction of **4W-*c*Hex** with Methoxyethylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.00625	$3.1250\ 10^{-3}$	0.278 ± 0.006
0.01250	$6.2500\ 10^{-3}$	0.609 ± 0.005
0.01875	$9.3750\ 10^{-3}$	0.959 ± 0.005
0.02500	0.0125	1.36 ± 0.01
0.03125	0.0156	1.726 ± 0.009
0.03750	0.0188	2.011 ± 0.002
0.05000	0.0250	2.62 ± 0.04

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0×10^{-4} M, p*H* = 9.39. [b] Determined with a *stopped-flow* machine monitoring at 437 nm.

Table S15. Reaction of **4W-*c*Hex** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.124 ± 0.005
0.0250	0.01250	0.27 ± 0.02
0.0375	0.01875	0.434 ± 0.002
0.0500	0.02500	0.480 ± 0.009
0.0625	0.03125	0.5 ± 0.03
0.0750	0.03750	0.68 ± 0.04

0.1000	0.05000	1.04 ± 0.07

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 437 nm.

Table S16. Reaction of **4W-*i*Pr** with Morpholine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Morph]_f$, M	k_{obs} , s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
0.0125	0.0075	0.01650 ± 0.00006	5.37
0.0250	0.0151	0.0505 ± 0.0002	8.22
0.0375	0.0226	0.1006 ± 0.0003	10.91
0.0500	0.0301	0.1723 ± 0.0004	14.02
0.0625	0.0376	0.256 ± 0.001	16.66
0.7500	0.0452	0.338 ± 0.001	18.34
0.1000	0.0602	0.577 ± 0.004	23.47

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 10^{-4} M, pH = 8.88. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S17. Reaction of **4W-*i*Pr** with Morpholine in 50% MeCN- 50% water at 25 °C varying the p*H*.[a]

pH	$[HO^-]$, M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
9.588	2.50 10^{-6}	0.0694 ± 0.0002	65.68
9.667	3.00 10^{-6}	0.0634 ± 0.0003	69.19
9.792	4.00 10^{-6}	0.0583 ± 0.0002	80.68
9.889	5.00 10^{-6}	0.0491 ± 0.0001	82.37
10.065	7.50 10^{-6}	0.0412 ± 0.0001	99.42
10.190	1.00 10^{-5}	0.0354 ± 0.0001	111.51
10.366	1.50 10^{-5}	0.03128 ± 0.00001	144.62
10.491	2.00 10^{-5}	0.026000 ± 0.0001	158.58
10.588	2.50 10^{-5}	0.0253 ± 0.0002	191.67
10.667	3.00 10^{-5}	0.0213 ± 0.0002	192.72
10.792	4.00 10^{-5}	0.0182 ± 0.0002	218.39
10.889	5.00 10^{-5}	0.0171 ± 0.0002	255.70
11.065	7.50 10^{-5}	0.0143 ± 0.0002	319.27
11.190	1.00 10^{-4}	0.01199 ± 0.00002	356.20

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, [morph] = 0.01 M and [TEA] = 0.01M. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S18. Reaction of **4W-*i*Pr** with Morpholine in 50% MeCN- 50% water at 25 °C varying the concentration of the external TEA buffer.[a]

[TEA], M	k_{obs}, s^{-1}	$k_{A\text{-}corr}$, M^{-1} s^{-1}
0.001	0.01624 ± 0.00009	161.81
0.002	0.01670 ± 0.00005	160.33
0.003	0.01716 ± 0.00003	164.87
0.004	0.01616 ± 0.00007	169.41
0.005	0.01795 ± 0.00007	159.54
0.007	0.01815 ± 0.00004	177.21
0.008	0.0178 ± 0.0001	179.18
0.009	0.0193 ± 0.0002	175.73
0.010	0.0198 ± 0.0002	190.54
0.015	0.02116 ± 0.00009	195.47
0.020	0.02312 ± 0.00008	208.90
0.025	0.02597 ± 0.00007	228.25
0.030	0.02614 ± 0.00009	256.39
0.040	0.02679 ± 0.00005	258.06
0.050	0.0264 ± 0.0001	264.48
0.075	0.02682 ± 0.00006	260.63
0.100	0.02640 ± 0.00009	264.78

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, [Morph] = 0.01 M, pH = 10.78. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S19. Reaction of **4W-*i*Pr** with Glycinethylester in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.2722 ± 0.0006
0.0250	0.01250	0.6995 ± 0.0008
0.0375	0.01875	1.136 ± 0.003
0.0500	0.02500	1.752 ± 0.002

0.0625	0.03125	2.380 ± 0.001
0.0750	0.03750	2.98 ± 0.01
0.1000	0.05000	4.229 ± 0.008

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 7.43. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S20. Reaction of **4W-*i*Pr** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.995 ± 0.005
0.0250	0.01250	2.146 ± 0.009
0.0375	0.01875	3.206 ± 0.008
0.0500	0.02500	4.46 ± 0.04
0.0625	0.03125	5.517 ± 0.009
0.0750	0.03750	6.46 ± 0.03
0.1000	0.05000	8.24 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S21. Reaction of **4W-*i*Pr** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.560 ± 0.009
0.0250	0.01250	1.42 ± 0.02
0.0375	0.01875	2.12 ± 0.02
0.0500	0.02500	3.04± 0.04
0.0625	0.03125	3.50 ± 0.04
0.0750	0.03750	4.62 ± 0.05
0.1000	0.05000	6.06 ± 0.05

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S22. Reaction of **4W-*i*Pr** with Methoxyethylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.00625	3.1250 10^{-3}	0.199 ± 0.003
0.01250	6.2500 10^{-3}	0.406 ± 0.006

0.01875	9.3750 10^{-3}	0.627 ± 0.003
0.02500	0.0125	0.98 ± 0.01
0.03125	0.0156	1.241 ± 0.008
0.03750	0.0188	1.47 ± 0.03
0.05000	0.0250	1.76 ± 0.04

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 9.39. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S23. Reaction of **4W-*t*Bu** with Glycinethylester in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.1799 ± 0.0002
0.0250	0.01250	0.5020 ± 0.0009
0.0375	0.01875	0.785 ± 0.002
0.0500	0.02500	1.313 ± 0.002
0.0625	0.03125	1.852 ± 0.002
0.0750	0.03750	2.50 ± 0.01
0.1000	0.05000	3.65 ± 0.03

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 7.43. [b] Determined with a *stopped-flow* machine monitoring at 441 nm.

Table S24. Reaction of **4W-*t*Bu** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.706 ± 0.004
0.0250	0.01250	1.643 ± 0.006
0.0375	0.01875	2.508 ± 0.009
0.0500	0.02500	3.54 ± 0.01
0.0625	0.03125	4.417 ± 0.007
0.0750	0.03750	5.30 ± 0.04
0.1000	0.05000	6.91 ± 0.04

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 441 nm.

Table S25. Reaction of **4W-*t*Bu** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]

0.0125	0.00625	0.5249 ± 0.0004
0.0250	0.01250	1.13 ± 0.02
0.0375	0.01875	1.787 ± 0.006
0.0500	0.02500	2.329± 0.008
0.0625	0.03125	2.89 ± 0.02
0.0750	0.03750	3.34 ± 0.03
0.1000	0.05000	4.37 ± 0.05

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*t*Bu**] = 1.0×10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 441 nm.

Table S26. Reaction of **4W-*t*Bu** with Methoxyethylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.00625	$3.1250\ 10^{-3}$	0.278 ± 0.006
0.01250	$6.2500\ 10^{-3}$	0.609 ± 0.005
0.01875	$9.3750\ 10^{-3}$	0.959 ± 0.005
0.02500	0.0125	1.36 ± 0.01
0.03125	0.0156	1.726 ± 0.009
0.03750	0.0188	2.011 ± 0.002
0.05000	0.0250	2.62 ± 0.04

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*t*Bu**] = 1.0×10^{-4} M, p*H* = 9.39. [b] Determined with a *stopped-flow* machine monitoring at 441 nm.

Table S27. Reaction of **4W-*t*Bu** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Nu]_f$, M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.073 ± 0.004
0.0250	0.01250	0.17 ± 0.02
0.0375	0.01875	0.19 ± 0.01
0.0500	0.02500	0.283 ± 0.008
0.0625	0.03125	0.38 ± 0.01
0.0750	0.03750	0.36 ± 0.01
0.1000	0.05000	0.59 ± 0.05

[a] Conditions: ionic strength = 0.1 M (KCl), [**4W-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 441 nm.

Table S28. Reaction of **4Cr-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	$[Morph]_f$, M	k_{obs} , s^{-1} [b]	$k_{A\ corr}$, M^{-1} s^{-1} [c]
0.0125	0.007528	0.00780 ± 0.00009	0.14
0.0250	0.015055	0.0099 ± 0.0003	0.26
0.0375	0.022582	0.0148 ± 0.0002	0.46
0.0500	0.030110	0.0212 ± 0.0003	0.63
0.0625	0.037638	0.0349 ± 0.0003	0.99
0.7500	0.045165	0.0465 ± 0.0007	1.17
0.1000	0.060220	0.0699 ± 0.0006	1.40

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 8.88. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 355 nm.

Table S29. Reaction of **4Cr-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C varying the p*H*.[a]

pH	$[HO^-]$, M	k_{obs}, s^{-1}	$k_{A\ corr}$, M^{-1} s^{-1}
9.588	2.50 10^{-6}	0.02255 ± 0.00007	9.06
9.667	3.00 10^{-6}	0.02096 ± 0.00007	9.45
9.792	4.00 10^{-6}	0.0204 ± 0.0002	11.23
9.889	5.00 10^{-6}	0.02055 ± 0.00009	13.38
10.065	7.50 10^{-6}	0.0175 ± 0.0003	15.83
10.190	1.00 10^{-5}	0.0161 ± 0.0001	18.67
10.366	1.50 10^{-5}	0.0144 ± 0.0001	24.05
10.491	2.00 10^{-5}	0.01478 ± 0.00009	32.24
10.588	2.50 10^{-5}	0.0142 ± 0.0004	38.24

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, [morph] = 0.02 M and [TEA] = 0.01M. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 355 nm.

Table S30. Reaction of **4Cr-*c*Hex** with Morpholine in 50% MeCN- 50% water at 25 °C varying the concentration of the external TEA buffer.[a]

[TEA], M	k_{obs}, s^{-1}	$k_{A\ corr}$, $M^{-1}\ s^{-1}$
0.001	0.0131 ± 0.0002	18.28
0.002	0.0140 ± 0.0002	19.54
0.003	0.0143 ± 0.0001	19.96
0.004	0.0152 ± 0.0002	21.22
0.005	0.01549 ± 0.00007	21.62
0.006	0.0162 ± 0.0002	22.61
0.007	0.01643± 0.00009	22.93
0.010	0.0164 ± 0.0001	22.89
0.015	0.0182 ± 0.0001	25.40
0.020	0.0197 ± 0.0002	27.50
0.025	0.02185 ± 0.00009	30.50
0.030	0.0229 ± 0.0002	31.96
0.035	0.0239 ± 0.0002	33.36

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, [Morph] = 0.02 M, p*H* = 10.78. [b] Determined with a *stopped-flow* machine monitoring at 436 nm and 335 nm.

Table S31. Reaction of **4Cr-*c*Hex** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.137 ± 0.006
0.0250	0.01250	0.256 ± 0.002
0.0375	0.01875	0.38 ± 0.05
0.0500	0.02500	0.482 ± 0.002
0.0625	0.03125	0.574 ± 0.007
0.0750	0.03750	0.683 ± 0.003
0.1000	0.05000	0.852 ± 0.001

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S32. Reaction of **4Cr-*c*Hex** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00250	0.1513 ± 0.0003
0.0250	0.00500	0.345 ± 0.004

0.0375	0.01000	0.783 ± 0.003
0.0500	0.01500	1.268 ± 0.005
0.0625	0.02000	1.748 ± 0.008
0.0750	0.02500	2.27 ± 0.01
0.1000	0.03000	2.85 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S33. Reaction of **4Cr-*c*Hex** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.2416 ± 0.0009
0.0250	0.01250	0.683 ± 0.003
0.0375	0.01875	1.120 ± 0.008
0.0500	0.02500	1.580 ± 0.008
0.0625	0.03125	2.17 ± 0.01
0.0750	0.03750	2.71 ± 0.02
0.1000	0.05000	3.61 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*c*Hex**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 436 nm.

Table S34. Reaction of **4Cr-*i*Pr** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.111 ± 0.002
0.0250	0.01250	0.203 ± 0.002
0.0375	0.01875	0.272 ± 0.003
0.0500	0.02500	0.356 ± 0.001
0.0625	0.03125	0.421 ± 0.001
0.0750	0.03750	0.498 ± 0.003
0.1000	0.05000	0.62 ± 0.01

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 451nm.

Table S35. Reaction of **4Cr-*i*Pr** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.175 ± 0.002
0.0250	0.01250	0.529 ± 0.003
0.0375	0.01875	0.903 ± 0.004
0.0500	0.02500	1.286 ± 0.006
0.0625	0.03125	1.776 ± 0.009
0.0750	0.03750	2.214 ± 0.008
0.1000	0.05000	2.95 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 451nm.

Table S36. Reaction of **4Cr-*i*Pr** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00250	0.1166 ± 0.0006
0.0250	0.00500	0.282 ± 0.001
0.0375	0.01000	0.621 ± 0.005
0.0500	0.01500	0.987 ± 0.005
0.0625	0.02000	1.321 ± 0.009
0.0750	0.02500	1.704 ± 0.008
0.1000	0.03000	2.14 ± 0.01

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*i*Pr**] = 1.0 × 10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 451nm.

Table S37. Reaction of **4Cr-*t*Bu** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.0596 ± 0.0006
0.0250	0.01250	0.110 ± 0.002
0.0375	0.01875	0.154 ± 0.002
0.0500	0.02500	0.204 ± 0.004
0.0625	0.03125	0.244 ± 0.002
0.0750	0.03750	0.29 ± 0.01
0.1000	0.05000	0.367 ± 0.006

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 457nm.

Table S38. Reaction of **4Cr-*t*Bu** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.096 ± 0.001
0.0250	0.01250	0.3217 ± 0.0005
0.0375	0.01875	0.586 ± 0.001
0.0500	0.02500	0.860 ± 0.004
0.0625	0.03125	1.211 ± 0.006
0.0750	0.03750	1.556 ± 0.008
0.1000	0.05000	2.08 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 457nm.

Table S39. Reaction of **4Cr-*t*Bu** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00250	0.0400 ± 0.0008
0.0250	0.00500	0.129 ± 0.001
0.0375	0.01000	0.348 ± 0.002
0.0500	0.01500	0.583 ± 0.006
0.0625	0.02000	0.843 ± 0.002
0.0750	0.02500	1.1067 ± 0.0009
0.1000	0.03000	1.40 ± 0.01

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*t*Bu**] = 1.0 × 10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 457nm.

Table S40. Reaction of **4Cr-*n*Bu** with Butylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.127 ± 0.002
0.0250	0.01250	0.232 ± 0.004
0.0375	0.01875	0.34 ± 0.01
0.0500	0.02500	0.436 ± 0.006
0.0625	0.03125	0.525 ± 0.002
0.0750	0.03750	0.613 ± 0.003

0.1000	0.05000	0.783 ± 0.005

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 10.40. [b] Determined with a *stopped-flow* machine monitoring at 450 nm.

Table S41. Reaction of **4Cr-*n*Bu** with Benzylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00250	0.203 ± 0.0013
0.0250	0.00500	0.471 ± 0.004
0.0375	0.01000	0.975 ± 0.004
0.0500	0.01500	1.50 ± 0.01
0.0625	0.02000	2.06 ± 0.01
0.0750	0.02500	2.613 ± 0.009
0.1000	0.03000	3.22 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 9.12. [b] Determined with a *stopped-flow* machine monitoring at 450 nm.

Table S42. Reaction of **4Cr-*n*Bu** with Furfurylamine in 50% MeCN- 50% water at 25 °C.[a]

[Buffer], M	[Nu], M	k_{obs}, s^{-1} [b]
0.0125	0.00625	0.361 ± 0.005
0.0250	0.01250	0.911 ± 0.004
0.0375	0.01875	1.46 ± 0.01
0.0500	0.02500	2.03 ± 0.01
0.0625	0.03125	2.74 ± 0.02
0.0750	0.03750	3.38 ± 0.01
0.1000	0.05000	4.46 ± 0.02

[a] Conditions: ionic strength = 0.1 M (KCl), [**4Cr-*n*Bu**] = 1.0 × 10^{-4} M, p*H* = 8.58. [b] Determined with a *stopped-flow* machine monitoring at 450 nm.