

SUPPLEMENTARY INFORMATION

Table S1: Reaction of CMCS with tetrabutylammonium chloride and bromide in CD₃CN at 25 °C

Nucleophile Conc./M	t/min	[CMCS]/M	[CH ₂ Cl ₂]/M	[CH ₂ CIBr]/M
		δ_H	6.13	5.44
			5.44	5.31
Cl ⁻	0	0.300	0	-
	10	0.211	0.086	-
	50	0.203	0.089	-
	135	0.190	0.109	-
	3120	0.179	0.118	-
Br ⁻	0	0.300	0	0
	10	0.233	0.012	0.056
	100	0.214	0.021	0.064
	975	0.200	0.030	0.070
	3120	0.182	0.042	0.077
Br ⁻	0	0.300	0	0
	10	0.133	0.026	0.121
Br ⁻	0	0.300	0	0
	10	0.071	0.027	0.155
I ⁻ 0.075	0	0.300	0	0 ^a
	10	0.113	0	0 ^a
	2400	0.076	0.027	0 ^a

CH ₃ CO ₂ ⁻ 0.075	0	0.300	0	0 ^b
	10	0.185	0.060	0.048 ^b
Cl ⁻ + Br ⁻ 0.0375 each	0	0.300	0	0
	10	0.226	0.038	0.025
	95	0.188	0.068	0.039
	1560	0.176	0.076	0.039
Cl ⁻ + Br ⁻ 0.075 each	0	0.300	0	0
	10	0.151	0.097	0.056

a Chloroiodomethane

b Chloromethyl acetate: δ_H = 2.09, 5.71

Table S2: Reaction of MCS with tetrabutylammonium chloride, bromide, iodide and acetate in CD₃CN at 25 °C

Time/min.	<u>Chloride (0.150 M)</u>		<u>Bromide (0.150 M)</u>		<u>Iodide (0.150 M)</u>		<u>Acetate (0.150 M)</u>				
	MCS	MeCl	MCS	MeCl	MeBr	MCS	MeCl	MeI	MCS	MeCl	MeO ₂ CCH ₃
δ_H	4.23	3.02			2.67			2.16			3.58, 1.97
0	0.300	0	0.300	0	0	0.300	0	0	0.300	0	0
5	0.083	0.129	0.083	0.015	0.111	0.099	0.020	0.109	0.111	0.040	0.055
40	0.064 ^a	0.130 ^a	0.084	0.016	0.131	0.077	0.021	0.110			
70	0.057 ^a	0.135 ^a	0.074	0.016	0.118	0.069	0.025	0.113			
110	0.054 ^a	0.136 ^a	0.069	0.018	0.125	0.064	0.027	0.119			
990	0.013	0.155	0.014	0.019	0.127	0.013	0.030	0.127	0.008	0.045	0.076

^a Interpolated from measurements at other times

Table S3: Products (M) of reaction of CMCS with sodium potassium bromide and sodium acetate in CDCl₃/H₂O containing tetraoctylammonium bromide at 25°C

M ⁺ X ⁻ / %	50			100			200		
	[CMCS]	[CH ₂ Cl ₂]	[CH ₂ CIX]	[CMCS]	[CH ₂ Cl ₂]	[CH ₂ CIX]	[CMCS]	[CH ₂ Cl ₂]	[CH ₂ CIX]
	δ5.97	5.30	5.17 or 5.69						
KBr									
0	0.300	0	0	0.300	0	0	0.300	0	0
5	0.277	0.002	0.016	0.282	0.002	0.022	0.147	0.004	0.147
30				0.139	0.004	0.129	0.072	0.004	0.234
60	0.132	0.018	0.138	0.065	0.004	0.209	0.012	0.004	0.278
120	0.066	0.048	0.154	0.012	0.008	0.242	0	0.004	0.290
180	0.015	0.076	0.160	0	0.009	0.280			
NaOAc^a									
0	0.300	0	0	0.300	0	0	0.300	0	0
	(0.300)	(0)	(0)				(0.300)	(0)	(0)
5	0.270	0	0.012 ^a	0.252	0.002	0.020 ^a	(0.283)	(0)	(0.017) ^a
30	0.260	0.008	0.016 ^a	0.234	0.012	0.034 ^a	0.252	0.021	0.029 ^a
60				0.217	0.027	0.040 ^a	(0.205)	(0.037)	(0.058) ^a
							0.217	0.036	0.056 ^a
120	0.149	0.057	0.027 ^a	0.167	0.080	0.048 ^a	(0.137)	(0.080)	(0.082) ^a
							0.177	0.065	0.069 ^a
240	0.132	0.140	0.026 ^a	0.080	0.160	0.051 ^a	(0.061)	(0.130)	(0.109) ^a
							0.095	0.107	0.087 ^a
							(0.005)	(0.167)	(0.127) ^a

^a Figures in parentheses refer to experiments carried out in the presence of NaHCO₃ (0.9 M); the concentrations of the product CH₂CIX refer to chloromethyl acetate (δ_H = 5.69) containing in each case 0.015M CH₂CIBr (δ_H = 5.17) arising from the phase-transfer catalyst

Table S4: Products (M) of reaction of MCS with potassium chloride, bromide and iodide and sodium acetate in CDCl₃/H₂O containing tetraoctylammonium bromide at 25 °C

Nucleophile ^a Compound(δ_H)	Time/min					
	0	5	15	30	45	
KCl	MCS (4.21)	0.300	0.242	0.092	0.032	0
	MeCl (3.02)	0	0.063	0.149	0.255	0.265
	MeBr (2.65)	0	0.012	0.015	0.016	0.013
KBr	MCS	0.300	0.186		0.005	0
	MeCl	0	0.039		0.174	0.172
	MeBr	0	0.063		0.081	0.080
KI	MCS	0.300	0.174	0.075	0.016	0
	MeCl	0	0.044	0.136	0.188	0.171
	MeBr	0	0.013	0.016	0.011	0.013
	MeI (2.17)	0	0.073	0.084	0.079	0.081
NaOAc	MCS	0.300	0.241	0.146	0.036	0
	MeCl	0	0.037	0.097	0.166	0.219
	MeBr	0	0.013	0.018	0.019	0.015

