Supplementary Information

Table S1 Observed BIRD rate constants for the dissociation of R_i–A^- complexes to products R_i and A^-.

Temperature / K	k / s^{-1}									
	R_M–Br^-	**R_M–I^-**	**R_B–I^-**	**R_B–TsO^-**	**R_B–HSO_4^-**	**R_B–NO_3^-**	**R_B–$H_2PO_4^-$**	**R_T–I^-**	**R_T–TsO^-**	**R_T–HSO_4^-**
293		0.0106			0.0007					
316	0.0021	0.0418		0.0070	0.0065					
320			0.0004	0.0072		0.0004				
336-337	0.0079	0.1189	0.0029	0.0306	0.0503	0.0023	0.00026			0.0007
342	0.0167	0.1300		0.0498	0.0615		0.00057		0.0007	0.0015
346-347						0.0058		4.2×10^{-5}	0.0011	
350-352			0.0099	0.0845	0.0809	0.0124	0.0023	0.0002	0.0021	0.0073
354-355	0.0391	0.1931								0.0066
357						0.0250	0.0043		0.0038	
361-362	0.0628	0.2467	0.0186	0.1208				0.0007	0.0072	
363-365						0.0335	0.0083	0.0008		0.0181
367	0.1047	0.3505	0.0285		0.2423		0.0096	0.0012	0.0100	0.0258
372	0.1286	0.3751	0.0384	0.2293	0.2466		0.0104	0.0020	0.0173	0.0259
379			0.0611	0.2760				0.0046	0.0365	
381-383	0.1291	0.4763	0.0854		0.3895	0.0704	0.0275	0.0058		0.0794

Table S2. Calculated free energies of interaction ΔG in comparison to solution phase data. Values indicated are in kJ mol^{-1} and calculated at 298 K.

Receptor	**Anion**	**[a]ΔG(solution) X 10^3**	**ΔG (gas)** B3LYP/ 6-31+G(d,p)
R_{C6F5I}	Cl^-	-12.1	-68.1
	Br^-	-11.3	-66.9
	I^-	-9.3	-52.7
R_M	Cl^-	-19.0	-77.0
	Br^-	-16.8	-75.7
	I^-	-14.3	-61.5
R_B	Cl^-	-18.4	-105.3
	I^-	-	-82.5
	TsO^-	-	-24.7
	HSO_4^-	-	-35.9
	NO_3^-	-	-58.6
	$H_2PO_4^-$	-	-64.6
R_T	Cl^-	-24.2	-
	Br^-	-20.2	-
	I^-	-16.3	-98.1
	TsO^-	< -5.6	-29
	HSO_4^-	< -5.6	-42.9
	NO_3^-	< -5.6	-

a: from Refs. [13,48].

Figure S1

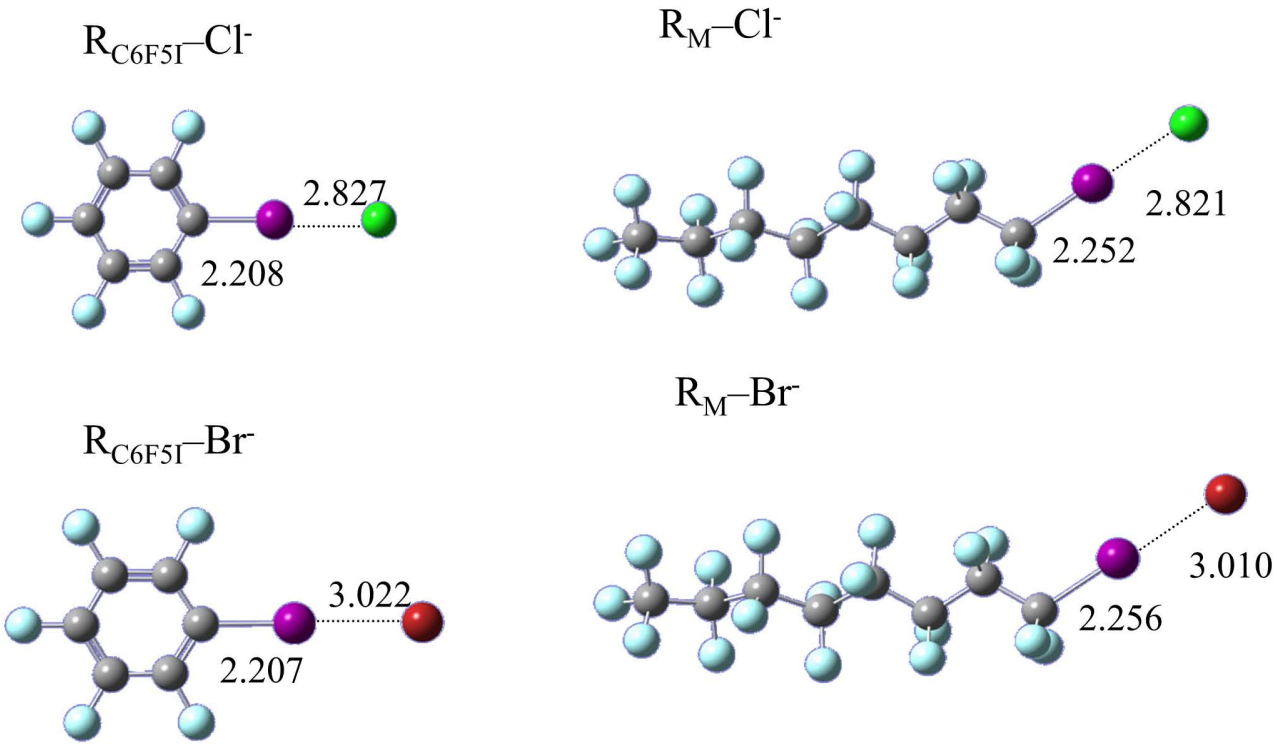

Figure S2