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APPENDICES

Appendix A

Thermodynamic parameters

Table A1 Slope and y-intercept from $\ln k'$ versus $1/T$ plots and thermodynamic parameters of 46 PAMeS on ASiAc column

analytes	temperature range (°C)	retained enantiomer			$-\Delta H$ (kcal/mol)	$-\Delta S$ (cal/mol·K)
		$\ln k' = m(1/T) + c$		R^2		
		m	c			
H	110-170	6319.4	-14.149	0.9998	12.56	17.14
2F	110-170	6393.4	-14.303	0.9998	12.70	17.45
3F	110-170	6375.3	-14.305	0.9998	12.67	17.45
4F	110-170	6447.9	-14.428	0.9998	12.81	17.70
2Cl	130-190	6778.5	-14.359	0.9998	13.47	17.56
3Cl	130-190	6805.3	-14.438	0.9998	13.52	17.72
4Cl	130-190	6917.4	-14.587	0.9998	13.74	18.01
2Br	140-200	6951.3	-14.362	0.9998	13.81	17.57
3Br	140-200	7005.9	-14.475	0.9998	13.92	17.79
4Br	140-200	7130.6	-14.637	0.9998	14.17	18.11
2Me	120-180	6438.7	-14.168	0.9999	12.79	17.18
3Me	120-180	6655.9	-14.513	0.9999	13.23	17.87
4Me	120-180	6688.4	-14.535	0.9999	13.29	17.91
2OMe	140-200	6998.0	-14.948	0.9997	13.91	18.73
3OMe	140-200	7197.6	-14.948	0.9997	14.30	18.73
4OMe	140-200	7227.4	-14.968	0.9997	14.36	18.77
2CF ₃	110-170	6538.7	-14.569	0.9998	12.99	17.98
3CF ₃	100-170	6582.0	-14.925	0.9998	13.08	18.68
4CF ₃	110-170	6655.5	-14.880	0.9998	13.22	18.60

analytes	temperature range (°C)	retained enantiomer			-ΔH (kcal/mol)	-ΔS (cal/mol·K)
		ln k' = m(1/T) + c		R ²		
		m	c			
2NO ₂	160-220	7501.6	-14.744	0.9997	14.91	18.33
3NO ₂	160-220	7515.8	-14.757	0.9997	14.93	18.35
4NO ₂	160-220	7967.6	-15.337	0.9996	15.83	19.50
2CN	160-220	7270.2	-14.538	0.9996	14.45	17.92
3CN	160-220	7265.4	-14.579	0.9997	14.44	18.00
4CN	160-220	7741.9	-15.286	0.9995	15.38	19.40
2,3F	110-170	6530.3	-14.540	0.9998	12.98	17.92
2,4F	100-160	6447.3	-14.621	0.9998	12.81	18.08
2,5F	100-160	6581.7	-14.843	0.9998	13.08	18.52
2,6F	100-160	6384.8	-14.407	0.9998	12.69	17.66
3,4F	100-160	6509.0	-14.755	0.9998	12.93	18.35
3,5F	100-160	6408.3	-14.631	0.9998	12.73	18.10
2,3Cl	150-210	7295.5	-14.626	0.9998	14.50	18.09
2,4Cl	150-210	7296.2	-14.673	0.9998	14.50	18.18
2,5Cl	150-210	7101.1	-14.499	0.9998	14.11	17.84
2,6Cl	150-210	6918.4	-14.115	0.9998	13.75	17.08
3,4Cl	150-210	7179.1	-14.567	0.9998	14.26	17.97
3,5Cl	150-210	7082.8	-14.503	0.9998	14.07	17.85
2,3Me	130-190	6837.5	-14.500	0.9998	13.59	17.84
2,4Me	130-190	6748.1	-14.444	0.9998	13.41	17.73
2,5Me	130-190	6666.2	-14.350	0.9997	13.25	17.54
2,6Me	130-190	6561.7	-14.063	0.9998	13.04	16.97
3,4Me	130-190	7046.0	-14.813	0.9998	14.00	18.46
3,5Me	130-190	6938.1	-14.778	0.9998	13.79	18.39
pentaF	90-150	6320.1	-14.763	0.9997	12.56	18.36



analytes	temperature range (°C)	retained enantiomer			-ΔH (kcal/mol)	-ΔS (cal/mol·K)
		ln k' = m(1/T) + c		R ²		
		m	c			
2,4,6Cl	150-210	7343.9	-14.618	0.9998	14.59	18.07
2,4,6F	90-160	6326.8	-14.648	0.9998	12.57	18.13



Table A2 Slope and y-intercept from $\ln k'$ versus $1/T$ plots of 46 PAMEs on GSiAc column

analytes	temperature range (°C)	less retained enantiomer			more retained enantiomer		
		$\ln k' = m(1/T) + c$		R^2	$\ln k' = m(1/T) + c$		R^2
		m	c		m	c	
H	110-160	7141.8	-15.842	0.9994	7520.3	-16.693	0.9990
2F	100-140	7896.4	-17.646	0.9993	8038.1	-17.980	0.9993
3F	120-160	7239.4	-16.054	0.9996	7598.3	-16.855	0.9993
4F	120-160	7428.9	-16.434	0.9994	7624.1	-16.870	0.9994
2Cl	140-200	7123.0	-14.917	0.9995	7123.0	-14.917	0.9995
3Cl	130-180	7524.6	-15.837	0.9995	7831.9	-16.508	0.9992
4Cl	110-150	8765.1	-18.619	0.9993	8835.2	-18.780	0.9994
2Br	150-210	7241.4	-14.816	0.9998	7241.4	-14.816	0.9998
3Br	140-180	7710.5	-15.844	0.9997	7983.4	-16.434	0.9996
4Br	150-210	7735.0	-15.712	0.9997	7735.0	-15.712	0.9997
2Me	90-130	7526.2	-16.643	0.9996	7640.8	-16.921	0.9996
3Me	120-170	7138.1	-15.428	0.9994	7403.7	-16.021	0.9992
4Me	120-160	7443.3	-16.066	0.9996	7613.8	-16.451	0.9996
2OMe	150-200	7152.2	-14.913	0.9998	7152.2	-14.913	0.9998
3OMe	130-170	7946.0	-16.447	0.9996	8167.8	-16.937	0.9995
4OMe	120-160	8342.3	-17.314	0.9996	8442.8	-17.538	0.9996
2CF ₃	110-150	7248.5	-16.044	0.9996	7452.7	-16.522	0.9995
3CF ₃	120-160	7216.6	-16.159	0.9996	7564.5	-16.947	0.9993
4CF ₃	120-180	7477.9	-16.455	0.9991	7477.9	-16.455	0.9991
2NO ₂	160-220	8188.7	-15.980	0.9994	8188.7	-15.980	0.9994
3NO ₂	140-180	8913.2	-17.571	0.9997	9102.2	-17.983	0.9996
4NO ₂	140-180	10152.0	-19.719	0.9996	10290.0	-20.019	0.9996
2CN	150-190	8315.6	-16.585	0.9996	8461.3	-16.895	0.9996

analytes	temperature range (°C)	less retained enantiomer			more retained enantiomer		
		ln k' = m(1/T) + c		R ²	ln k' = m(1/T) + c		R ²
		m	c		m	c	
3CN	150-190	8221.4	-16.420	0.9997	8411.8	-16.827	0.9997
4CN	150-190	8989.4	-17.724	0.9996	9135.1	-18.032	0.9996
2,3F	90-130	8907.8	-19.987	0.9992	9038.8	-20.301	0.9991
2,4F	110-150	7753.8	-17.408	0.9991	7928.8	-17.809	0.9991
2,5F	100-140	8008.2	-17.983	0.9993	8145.1	-18.309	0.9993
2,6F	80-120	7638.0	-17.288	0.9996	7778.7	-17.640	0.9995
3,4F	110-160	7873.1	-17.409	0.9991	8070.0	-17.841	0.9993
3,5F	110-160	7504.1	-16.873	0.9992	7799.4	-17.539	0.9989
2,3Cl	130-170	8520.3	-17.169	0.9995	8633.5	-17.419	0.9995
2,4Cl	120-160	9215.4	-18.772	0.9995	9323.5	-19.016	0.9995
2,5Cl	150-210	7395.6	-14.987	0.9999	7395.6	-14.987	0.9999
2,6Cl	150-210	7151.2	-14.476	0.9999	7151.2	-14.476	0.9999
3,4Cl	150-190	7867.4	-15.880	0.9997	8095.8	-16.363	0.9996
3,5Cl	110-150	8414.7	-17.399	0.9994	8455.1	-17.492	0.9996
2,3Me	110-150	7557.7	-16.030	0.9997	7684.8	-16.327	0.9997
2,4Me	130-190	7037.2	-14.933	0.9997	7037.2	-14.933	0.9997
2,5Me	130-190	6773.9	-14.461	0.9998	6773.9	-14.461	0.9998
2,6Me	130-190	6736.7	-14.320	0.9998	6736.7	-14.320	0.9998
3,4Me	120-160	7778.0	-16.322	0.9998	7929.0	-16.664	0.9997
3,5Me	130-190	7102.6	-15.002	0.9997	7102.6	-15.002	0.9997
pentaF	100-140	7395.5	-17.060	0.9994	7651.1	-17.676	0.9993
2,4,6Cl	120-160	8104.0	-16.202	0.9998	8257.9	-16.554	0.9998
2,4,6F	110-150	6903.4	15.765	0.9996	7096.0	-16.210	0.9996



Table A3 Thermodynamic parameters of 46 PAMEs on GSiAc column

analytes	enthalpy term (kcal/mol)			entropy term (cal/mol·K)		
	$-\Delta H_1$	$-\Delta H_2$	$-\Delta\Delta H$	$-\Delta S_1$	$-\Delta S_2$	$-\Delta\Delta S$
H	14.19	14.94	0.75	20.51	22.20	1.69
2F	15.69	15.97	0.28	24.09	24.76	0.66
3F	14.38	15.10	0.71	20.93	22.52	1.59
4F	14.76	15.15	0.39	21.68	22.55	0.87
2Cl	14.15	14.15	0.00	18.67	18.67	0.00
3Cl	14.95	15.56	0.61	20.50	21.83	1.33
4Cl	17.42	17.56	0.14	26.02	26.34	0.32
2Br	14.39	14.39	0.00	18.47	18.47	0.00
3Br	15.32	15.86	0.54	20.51	21.68	1.17
4Br	15.37	15.37	0.00	20.25	20.25	0.00
2Me	14.95	15.18	0.23	22.10	22.65	0.55
3Me	14.18	14.71	0.53	19.68	20.86	1.18
4Me	14.79	15.13	0.34	20.95	21.72	0.76
2OMe	14.21	14.21	0.00	18.66	18.66	0.00
3OMe	15.79	16.23	0.44	21.71	22.68	0.97
4OMe	16.58	16.78	0.20	23.43	23.88	0.45
2CF ₃	14.40	14.81	0.41	20.91	21.86	0.95
3CF ₃	14.34	15.03	0.69	21.14	22.70	1.57
4CF ₃	14.86	14.86	0.00	21.72	21.72	0.00
2NO ₂	16.27	16.27	0.00	20.78	20.78	0.00
3NO ₂	17.71	18.09	0.38	23.94	24.76	0.82
4NO ₂	20.17	20.45	0.27	28.21	28.81	0.60
2CN	16.52	16.81	0.29	21.98	22.60	0.62
3CN	16.34	16.71	0.38	21.66	22.46	0.81

analytes	enthalpy term (kcal/mol)			entropy term (cal/mol·K)		
	$-\Delta H_1$	$-\Delta H_2$	$-\Delta\Delta H$	$-\Delta S_1$	$-\Delta S_2$	$-\Delta\Delta S$
4CN	17.86	18.15	0.29	24.25	24.86	0.61
2,3F	17.70	17.96	0.26	28.74	29.37	0.62
2,4F	15.41	15.75	0.35	23.62	24.42	0.80
2,5F	15.91	16.18	0.27	24.76	25.41	0.65
2,6F	15.18	15.46	0.28	23.38	24.08	0.70
3,4F	15.64	16.04	0.39	23.62	24.48	0.86
3,5F	14.91	15.50	0.59	22.56	23.88	1.32
2,3Cl	16.93	17.15	0.22	23.14	23.64	0.50
2,4Cl	18.31	18.53	0.21	26.33	26.81	0.48
2,5Cl	14.70	14.70	0.00	18.81	18.81	0.00
2,6Cl	14.21	14.21	0.00	17.79	17.79	0.00
3,4Cl	15.63	16.09	0.45	20.58	21.54	0.96
3,5Cl	16.72	16.80	0.08	23.60	23.79	0.18
2,3Me	15.02	15.27	0.25	20.88	21.47	0.59
2,4Me	13.98	13.98	0.00	18.70	18.70	0.00
2,5Me	13.46	13.46	0.00	17.76	17.76	0.00
2,6Me	13.39	13.39	0.00	17.48	17.48	0.00
3,4Me	15.45	15.75	0.30	21.46	22.14	0.68
3,5Me	14.11	14.11	0.00	18.84	18.84	0.00
pentaF	14.69	15.20	0.51	22.93	24.15	1.22
2,4,6Cl	16.10	16.41	0.31	21.22	21.92	0.70
2,4,6F	13.72	14.10	0.38	20.35	21.24	0.88



Appendix B

Retention factor, selectivity and resolution

Table B1 Retention factor (k'), selectivity (α) and resolution (R_s) values of 46 PAMEs on ASiAc and GSiAc columns

analytes	temperature (°C)	ASiAc	GSiAc			
		k'	k'_1	k'_2	α	R_s
H	160	1.551	1.954	2.013	1.030	0.94
2F	130	4.688	6.900	7.023	1.018	0.93
3F	130	4.474	6.649	7.244	1.089	4.35
4F	130	4.728	7.265	7.618	1.049	2.53
2Cl	140	7.744	10.463	10.463	1.000	—
3Cl	140	7.634	10.677	11.454	1.073	3.84
4Cl	140	8.631	13.275	13.402	1.010	0.59
2Br	170	3.716	4.564	4.564	1.000	—
3Br	170	3.752	4.736	4.857	1.026	1.18
4Br	170	4.227	5.639	5.639	1.000	—
2Me	120	9.238	12.090	12.266	1.015	0.82
3Me	120	11.374	15.633	17.082	1.093	5.12
4Me	120	12.076	17.834	18.736	1.051	2.88
2OMe	150	6.038	7.385	7.385	1.000	—
3OMe	150	7.839	10.152	10.472	1.032	1.70
4OMe	150	8.248	10.950	11.112	1.015	0.85
2CF ₃	130	5.147	6.831	7.013	1.027	1.35
3CF ₃	130	4.000	5.656	6.079	1.075	3.52
4CF ₃	130	5.034	8.092	8.092	1.000	—
2NO ₂	160	13.345	19.079	19.079	1.000	—

analytes	temperature (°C)	ASiAc	GSiAc			
		k'	k' ₁	k' ₂	α	R _s
3NO ₂	160	13.623	19.902	20.339	1.022	1.40
4NO ₂	160	21.697	40.423	41.159	1.018	1.39
2CN	170	6.478	8.738	8.900	1.018	1.01
3CN	170	6.153	8.342	8.527	1.022	1.16
4CN	170	8.887	12.779	13.037	1.020	1.33
2,3F	110	12.411	25.448	26.118	1.026	1.68
2,4F	110	9.042	17.340	18.353	1.058	3.32
2,5F	110	10.288	18.265	18.832	1.031	1.80
2,6F	110	9.519	13.992	14.218	1.016	0.91
3,4F	110	9.275	23.865	25.740	1.079	4.64
3,5F	110	8.086	15.523	17.347	1.118	6.25
2,3Cl	150	13.877	19.077	19.432	1.019	1.14
2,4Cl	150	13.244	20.031	20.272	1.012	0.85
2,5Cl	150	9.945	12.202	12.202	1.000	–
2,6Cl	150	9.475	11.389	11.389	1.000	–
3,4Cl	150	11.188	15.238	16.171	1.061	3.47
3,5Cl	150	9.481	12.226	12.226	1.000	–
2,3Me	130	11.875	14.948	15.225	1.018	1.04
2,4Me	130	10.064	12.724	12.724	1.000	–
2,5Me	130	9.025	10.574	10.574	1.000	–
2,6Me	130	9.279	11.104	11.104	1.000	–
3,4Me	130	14.555	19.388	19.998	1.031	1.90
3,5Me	130	11.525	13.931	13.931	1.000	–
pentaF	120	3.675	5.639	5.817	1.031	1.50
2,4,6Cl	150	15.661	18.983	19.217	1.012	0.76
2,4,6F	140	1.949	2.563	2.623	1.023	0.93



VITA

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