Supplementary Material (ESI) for Chemical Communications

ESI

Nucleophile-dependent regioselective ring opening of 2-substituted *N*,*N*-dibenzylaziridinium ions: bromide versus hydride

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Table of Contents

Table T1: Cartesian coordinates and energy of B3LYP/6-31++G** optimized conformation for **reactant**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.046278	4.072663	-0.310369
2	6	0	-3.426415	3.895241	-0.429452
3	6	0	-3.943732	2.619660	-0.675329
4	6	0	-3.078701	1.531702	-0.801062
5	6	0	-1.688327	1.702604	-0.688401
6	6	0	-1.176588	2.986570	-0.444119
7	6	0	-0.793866	0.492150	-0.873240
8	6	0	0.452049	0.721358	-1.729413
9	7	0	-0.389845	-0.193577	0.466212
10	6	0	-0.589341	0.492846	1.786535
11	6	0	0.777946	0.387797	1.245487
12	6	0	1.833301	-0.528242	1.838265
13	8	0	2.468870	-1.346363	0.862331
14	6	0	3.617812	-0.911309	0.218558
15	6	0	4.095796	0.400832	0.259208
16	6	0	5.266296	0.710882	-0.444725
17	6	0	5.945940	-0.259848	-1.181472
18	6	0	5.447632	-1.567435	-1.216280
19	6	0	4.287263	-1.897212	-0.517831
20	6	0	-0.546556	-1.695971	0.427326
21	6	0	-1.965928	-2.170486	0.209268
22	6	0	-2.335306	-2.733219	-1.021293
23	6	0	-3.633257	-3.206163	-1.231306
24	6	0	-4.580404	-3.122626	-0.208531
25	6	0	-4.220566	-2.575487	1.026892
26	6	0	-2.921766	-2.109459	1.235403
27	5	0	1.943206	3.320860	1.523387
28	1	0	-0.155443	-2.080856	1.368247
29	1	0	0.114307	-2.049694	-0.365608
30	1	0	-1.404791	-0.277034	-1.346013
31	1	0	1.050497	-0.191241	-1.812515
32	1	0	1.090884	1.517667	-1.340524
33	1	0	0.128178	1.009003	-2.733807
34	1	0	1.404110	-1.222233	2.567530
35	1	0	2.542368	0.119370	2.364711
36	1	0	3.584380	1.190522	0.803072
37	1	0	3.894478	-2.909343	-0.522107
38	1	0	5.966408	-2.336049	-1.782275
39	1	0	5.633101	1.732449	-0.412930
40	1	0	6.851210	-0.003675	-1.723244
41	1	0	-1.600543	-2.811188	-1.818978
42	1	0	-2.655099	-1.704974	2.207530
43	1	0	-4.948064	-2.520037	1.831023
44	1	0	-3.900360	-3.641017	-2.189675
45	1	0	-5.589654	-3.489758	-0.368249

46	1	0	-0.110343	3.151918	-0.317352
47	1	0	-3.486725	0.542605	-0.994983
48	1	0	-5.015434	2.472135	-0.772216
49	1	0	-1.633616	5.055414	-0.105099
50	1	0	-4.096236	4.744508	-0.329697
51	1	0	2.608324	2.505928	2.173964
52	1	0	2.436417	4.432096	1.602372
53	1	0	0.784377	3.321170	1.946727
54	1	0	1.937515	2.961798	0.329008
55	1	0	1.164327	1.304461	0.797091
56	1	0	-0.905176	-0.175919	2.581142
57	1	0	-1.089492	1.452535	1.739076

HF=-1087.3862084

Zero-point correction= 0.481355
(Hartree/Particle)
Thermal correction to Energy= 0.507756
Thermal correction to Enthalpy= 0.508700
Thermal correction to Gibbs Free Energy= 0.422133
Sum of electronic and zero-point Energies= -1086.904853
Sum of electronic and thermal Energies= -1086.878452
Sum of electronic and thermal Enthalpies= -1086.877508
Sum of electronic and thermal Free Energies= -1086.964075

Table T2: Cartesian coordinates and energy of MPW1B95/6-31++G** optimized conformation for **reactant**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.914299	3.914039	-0.374620
2	6	0	-3.277625	3.717825	-0.551760
3	6	0	-3.766871	2.442424	-0.812137
4	6	0	-2.890546	1.369671	-0.894619
5	6	0	-1.518243	1.564162	-0.728363
6	6	0	-1.032284	2.844629	-0.469466
7	6	0	-0.598911	0.379245	-0.824789
8	6	0	0.696867	0.613686	-1.575640
9	7	0	-0.298440	-0.237667	0.546070
10	6	0	-0.537455	0.506578	1.808904
11	6	0	0.835132	0.341288	1.328804
12	6	0	1.835831	-0.579605	1.973908
13	8	0	2.449221	-1.439122	1.041637
14	6	0	3.473677	-0.959051	0.263906
15	6	0	3.899025	0.363549	0.266581
16	6	0	4.939653	0.732205	-0.581225
17	6	0	5.547158	-0.191999	-1.418208
18	6	0	5.106679	-1.512083	-1.407989
19	6	0	4.072730	-1.899248	-0.570950
20	6	0	-0.520844	-1.711038	0.570721
21	6	0	-1.948427	-2.078243	0.282459
22	6	0	-2.283079	-2.674878	-0.931395
23	6	0	-3.602839	-2.994080	-1.224917
24	6	0	-4.603789	-2.717736	-0.303122
25	6	0	-4.278451	-2.136021	0.916698
26	6	0	-2.958740	-1.824018	1.209197
27	5	0	1.921283	3.227549	1.661373
28	1	0	-0.213366	-2.069561	1.550934
29	1	0	0.161702	-2.139140	-0.162814
30	1	0	-1.152971	-0.414217	-1.323316
31	1	0	1.331417	-0.274396	-1.550343
32	1	0	1.270552	1.452814	-1.179707
33	1	0	0.455125	0.833705	-2.615441
34	1	0	1.367629	-1.232519	2.711543
35	1	0	2.556852	0.055339	2.495722
36	1	0	3.441478	1.124652	0.890234
37	1	0	3.724019	-2.923776	-0.541445
38	1	0	5.573204	-2.247422	-2.051973
39	1	0	5.261634	1.765881	-0.579560
40	1	0	6.354664	0.109737	-2.072593
41	1	0	-1.503425	-2.892056	-1.653547
42	1	0	-2.719969	-1.380012	2.167638
43	1	0	-5.053117	-1.929367	1.643949
44	1	0	-3.846971	-3.457139	-2.172390
45	1	0	-5.633596	-2.962726	-0.529784

46	1	0	0.025072	3.016208	-0.296309
47	1	0	-3.272160	0.372341	-1.091868
48	1	0	-4.828878	2.283515	-0.951688
49	1	0	-1.525453	4.899455	-0.153178
50	1	0	-3.960104	4.555901	-0.483492
51	1	0	2.474780	2.363097	2.352245
52	1	0	2.423432	4.315512	1.860989
53	1	0	0.718794	3.238167	1.932350
54	1	0	2.062486	2.923312	0.460740
55	1	0	1.248174	1.228935	0.852844
56	1	0	-0.894707	-0.121397	2.615692
57	1	0	-1.003484	1.476254	1.700248

HF=-1086.8334456

Zero-point correction= 0.488795
(Hartree/Particle)
Thermal correction to Energy= 0.514118
Thermal correction to Enthalpy= 0.515062
Thermal correction to Gibbs Free Energy= 0.432848
Sum of electronic and zero-point Energies= -1086.344651
Sum of electronic and thermal Energies= -1086.319327
Sum of electronic and thermal Enthalpies= -1086.318383
Sum of electronic and thermal Free Energies= -1086.400598

Table T3: Cartesian coordinates, energy and imaginary frequency of B3LYP/6-31++G** optimized conformation for **TS-a**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.381402	3.990555	-0.913623
2	6	0	-0.790718	4.683406	-0.606901
3	6	0	-1.984392	3.978332	-0.427543
4	6	0	-1.997151	2.588242	-0.547334
5	6	0	-0.822472	1.878632	-0.846642
6	6	0	0.365024	2.598630	-1.038262
7	6	0	-0.897351	0.363014	-0.969545
8	6	0	0.043299	-0.238141	-2.020957
9	7	0	-0.712922	-0.342808	0.362312
10	6	0	-0.473592	0.491573	1.853755
11	6	0	0.592872	-0.125166	1.076988
12	6	0	1.414092	-1.285714	1.602025
13	8	0	2.100037	-1.960514	0.548692
14	6	0	3.295733	-1.450792	0.083125
15	6	0	3.883471	-2.177842	-0.962071
16	6	0	5.094645	-1.755518	-1.506057
17	6	0	5.730006	-0.607960	-1.016527
18	6	0	5.136088	0.107543	0.023372
19	6	0	3.917782	-0.299709	0.582356
20	6	0	-1.350480	-1.687991	0.450784
21	6	0	-2.838856	-1.676703	0.169526
22	6	0	-3.353362	-2.377142	-0.929185
23	6	0	-4.728948	-2.405543	-1.178667
24	6	0	-5.606647	-1.728886	-0.329801
25	6	0	-5.103758	-1.029844	0.772604
26	6	0	-3.731021	-1.007705	1.022286
27	5	0	1.659137	1.511591	3.575099
28	1	0	1.206086	0.592163	0.540056
29	1	0	-1.175903	-2.060246	1.461598
30	1	0	-0.834283	-2.368648	-0.234235
31	1	0	-1.925871	0.123430	-1.248358
32	1	0	-0.136659	-1.309308	-2.145202
33	1	0	1.097510	-0.109014	-1.763877
34	1	0	-0.134993	0.247550	-2.984467
35	1	0	0.799023	-2.047244	2.085096
36	1	0	2.086582	-0.879164	2.363645
37	1	0	3.383202	-3.070694	-1.323948
38	1	0	3.488597	0.283057	1.391859
39	1	0	5.616440	0.998119	0.418078
40	1	0	5.545159	-2.327733	-2.312207
41	1	0	6.674861	-0.280898	-1.439281
42	1	0	-2.675873	-2.909241	-1.592501
43	1	0	-3.355199	-0.468846	1.887411
44	1	0	-5.781321	-0.509241	1.442868
45	1	0	-5.110676	-2.955213	-2.033840

46	1	0	-6.675376	-1.749195	-0.520586
47	1	0	1.288653	2.085755	-1.286648
48	1	0	-2.928145	2.044120	-0.406569
49	1	0	-2.902948	4.509154	-0.195605
50	1	0	1.313791	4.529228	-1.050885
51	1	0	-0.775083	5.764540	-0.508334
52	1	0	-1.001340	-0.073729	2.608995
53	1	0	-0.710731	1.534468	1.716477
54	1	0	0.452271	1.158107	3.442820
55	1	0	2.264027	0.535735	4.008959
56	1	0	1.666372	2.449394	4.350111
57	1	0	2.082305	1.837791	2.465103

HF=-1087.378084
W= -511.1708

Zero-point correction= 0.479857
(Hartree/Particle)
Thermal correction to Energy= 0.506012
Thermal correction to Enthalpy= 0.506956
Thermal correction to Gibbs Free Energy= 0.420948
Sum of electronic and zero-point Energies= -1086.898227
Sum of electronic and thermal Energies= -1086.872072
Sum of electronic and thermal Enthalpies= -1086.871128
Sum of electronic and thermal Free Energies= -1086.957136

Table T4: Cartesian coordinates, energy and imaginary frequency of MPW1B95/6-31++G** optimized conformation for **TS-a**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.109759	3.553664	-0.955417
2	6	0	0.125725	4.465634	-0.602740
3	6	0	-1.173417	4.026502	-0.376543
4	6	0	-1.479281	2.678648	-0.496650
5	6	0	-0.494896	1.752186	-0.842907
6	6	0	0.800358	2.205125	-1.080171
7	6	0	-0.868038	0.291960	-0.941046
8	6	0	-0.054508	-0.495005	-1.955673
9	7	0	-0.801603	-0.385526	0.390368
10	6	0	-0.466750	0.424608	1.883018
11	6	0	0.497340	-0.317109	1.098516
12	6	0	1.193415	-1.552228	1.598217
13	8	0	1.886517	-2.200926	0.552967
14	6	0	3.049055	-1.634012	0.105044
15	6	0	3.630968	-2.247972	-1.002611
16	6	0	4.811111	-1.746448	-1.527586
17	6	0	5.418942	-0.630684	-0.959599
18	6	0	4.830178	-0.028125	0.141698
19	6	0	3.645242	-0.516826	0.684426
20	6	0	-1.590115	-1.619327	0.499384
21	6	0	-3.040663	-1.401286	0.167846
22	6	0	-3.663386	-2.153250	-0.822378
23	6	0	-5.010998	-1.965053	-1.110397
24	6	0	-5.745299	-1.016709	-0.412173
25	6	0	-5.129091	-0.258820	0.577836
26	6	0	-3.786725	-0.451475	0.866703
27	5	0	1.644080	1.410499	3.374841
28	1	0	1.181371	0.336460	0.566186
29	1	0	-1.503359	-1.969576	1.528716
30	1	0	-1.154008	-2.392141	-0.139641
31	1	0	-1.922857	0.246345	-1.215786
32	1	0	-0.454629	-1.501168	-2.083388
33	1	0	0.990982	-0.589001	-1.657121
34	1	0	-0.089545	0.006706	-2.922622
35	1	0	0.502127	-2.292245	1.997186
36	1	0	1.851784	-1.238700	2.412189
37	1	0	3.149144	-3.118663	-1.428769
38	1	0	3.219715	-0.012563	1.545023
39	1	0	5.288094	0.839425	0.600213
40	1	0	5.259089	-2.233124	-2.385237
41	1	0	6.340822	-0.240651	-1.371085
42	1	0	-3.092269	-2.893201	-1.372149
43	1	0	-3.313060	0.144134	1.638655
44	1	0	-5.697474	0.479647	1.129159
45	1	0	-5.483538	-2.558654	-1.882687

46	1	0	-6.793871	-0.868044	-0.636357
47	1	0	1.583251	1.509335	-1.359106
48	1	0	-2.492805	2.333772	-0.317510
49	1	0	-1.947356	4.733316	-0.105254
50	1	0	2.125096	3.887111	-1.125791
51	1	0	0.369505	5.515320	-0.500920
52	1	0	-1.091150	-0.077712	2.607371
53	1	0	-0.575860	1.484145	1.721048
54	1	0	0.486779	0.896116	3.413950
55	1	0	2.425133	0.501700	3.628974
56	1	0	1.655413	2.283437	4.217034
57	1	0	1.828597	1.858070	2.246425

HF=-1086.8195253
W= -605.4535

Zero-point correction= 0.486529
(Hartree/Particle)
Thermal correction to Energy= 0.511832
Thermal correction to Enthalpy= 0.512776
Thermal correction to Gibbs Free Energy= 0.430249
Sum of electronic and zero-point Energies= -1086.332997
Sum of electronic and thermal Energies= -1086.307693
Sum of electronic and thermal Enthalpies= -1086.306749
Sum of electronic and thermal Free Energies= -1086.389276

Table T5: Cartesian coordinates, energy and imaginary frequency of B3LYP/6-31++G** optimized conformation for **TS-b**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.169247	4.236565	-0.590259
2	6	0	-2.560677	4.348683	-0.608111
3	6	0	-3.346467	3.199560	-0.735991
4	6	0	-2.737355	1.948319	-0.842854
5	6	0	-1.338261	1.823398	-0.829267
6	6	0	-0.561253	2.984047	-0.705928
7	6	0	-0.731858	0.435290	-0.962583
8	6	0	0.513463	0.363684	-1.852371
9	7	0	-0.462590	-0.248641	0.370990
10	6	0	-0.627020	0.475218	1.654388
11	6	0	0.813942	0.450306	1.423482
12	6	0	1.766353	-0.617603	1.933812
13	8	0	2.277243	-1.459735	0.899294
14	6	0	3.404119	-1.080561	0.198325
15	6	0	4.031488	0.164425	0.316651
16	6	0	5.169949	0.425220	-0.456619
17	6	0	5.676759	-0.527514	-1.340733
18	6	0	5.035300	-1.766980	-1.450680
19	6	0	3.904437	-2.046599	-0.686117
20	6	0	-0.721369	-1.718783	0.369746
21	6	0	-2.181723	-2.093020	0.198713
22	6	0	-2.651933	-2.556698	-1.038998
23	6	0	-3.993626	-2.907723	-1.211889
24	6	0	-4.886264	-2.801895	-0.143114
25	6	0	-4.427814	-2.355078	1.099897
26	6	0	-3.086103	-2.008951	1.269441
27	5	0	1.790548	2.713574	2.736121
28	1	0	-0.333592	-2.118607	1.307007
29	1	0	-0.118109	-2.152177	-0.430053
30	1	0	-1.506696	-0.187068	-1.418849
31	1	0	0.879339	-0.663224	-1.936745
32	1	0	1.335513	0.973799	-1.472184
33	1	0	0.260793	0.720968	-2.854971
34	1	0	1.257101	-1.286008	2.632906
35	1	0	2.572111	-0.118459	2.473022
36	1	0	3.661462	0.934762	0.987330
37	1	0	3.403891	-3.007795	-0.750746
38	1	0	5.419682	-2.522730	-2.129867
39	1	0	5.654740	1.392184	-0.358071
40	1	0	6.559580	-0.311752	-1.934409
41	1	0	-1.960717	-2.656837	-1.872546
42	1	0	-2.743288	-1.684792	2.247971
43	1	0	-5.112194	-2.285622	1.940190
44	1	0	-4.337262	-3.267498	-2.177205

45	1	0	-5.928819	-3.076159	-0.273171
46	1	0	0.521701	2.929930	-0.678150
47	1	0	-3.353286	1.057461	-0.939764
48	1	0	-4.429702	3.276403	-0.753170
49	1	0	-0.549597	5.119741	-0.472797
50	1	0	-3.030059	5.323876	-0.518786
51	1	0	1.264391	1.587238	2.968361
52	1	0	2.022382	3.195553	3.830167
53	1	0	0.984167	3.368529	2.088157
54	1	0	2.819965	2.520791	2.092541
55	1	0	1.223065	1.256426	0.833053
56	1	0	-1.017028	-0.147829	2.456013
57	1	0	-1.121135	1.439535	1.589224

HF=-1087.3731085
W= -548.4066

Zero-point correction= 0.479803
(Hartree/Particle)
Thermal correction to Energy= 0.506060
Thermal correction to Enthalpy= 0.507004
Thermal correction to Gibbs Free Energy= 0.419901
Sum of electronic and zero-point Energies= -1086.893306
Sum of electronic and thermal Energies= -1086.867048
Sum of electronic and thermal Enthalpies= -1086.866104
Sum of electronic and thermal Free Energies= -1086.953208

Table T6: Cartesian coordinates, energy and imaginary frequency of MPW1B95/6-31++G** optimized conformation for **TS-b**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.978597	4.179580	-0.459392
2	6	0	-2.358457	4.304964	-0.534109
3	6	0	-3.143333	3.178098	-0.751273
4	6	0	-2.543397	1.935160	-0.891429
5	6	0	-1.155904	1.800186	-0.825681
6	6	0	-0.378788	2.935340	-0.610037
7	6	0	-0.562277	0.421839	-0.973670
8	6	0	0.748954	0.363029	-1.737765
9	7	0	-0.417968	-0.297869	0.331293
10	6	0	-0.666848	0.377863	1.607152
11	6	0	0.779830	0.363299	1.483186
12	6	0	1.678534	-0.758236	1.946280
13	8	0	2.155868	-1.553690	0.880696
14	6	0	3.257550	-1.134546	0.190265
15	6	0	3.880071	0.094581	0.381388
16	6	0	4.996196	0.411915	-0.387524
17	6	0	5.486222	-0.468975	-1.339870
18	6	0	4.847835	-1.691709	-1.524653
19	6	0	3.738997	-2.027108	-0.765358
20	6	0	-0.714269	-1.739253	0.259890
21	6	0	-2.184122	-2.030351	0.111802
22	6	0	-2.743450	-2.255204	-1.145847
23	6	0	-4.105687	-2.486273	-1.288701
24	6	0	-4.928299	-2.503479	-0.169861
25	6	0	-4.379818	-2.305231	1.091278
26	6	0	-3.017938	-2.075949	1.229368
27	5	0	1.625711	2.463786	2.856733
28	1	0	-0.319438	-2.205752	1.160922
29	1	0	-0.144513	-2.144265	-0.576730
30	1	0	-1.302008	-0.163185	-1.524194
31	1	0	1.122452	-0.661069	-1.787930
32	1	0	1.528864	0.963310	-1.269690
33	1	0	0.600692	0.730313	-2.753417
34	1	0	1.135414	-1.432982	2.608664
35	1	0	2.500531	-0.325327	2.514053
36	1	0	3.518539	0.816131	1.105259
37	1	0	3.239304	-2.979762	-0.887225
38	1	0	5.219151	-2.393862	-2.260976
39	1	0	5.478017	1.369109	-0.231463
40	1	0	6.354690	-0.209813	-1.931211
41	1	0	-2.103487	-2.265069	-2.021829
42	1	0	-2.599458	-1.949368	2.221230
43	1	0	-5.011401	-2.338593	1.969991
44	1	0	-4.522019	-2.660800	-2.272847

45	1	0	-5.989968	-2.685330	-0.278396
46	1	0	0.699278	2.866149	-0.536921
47	1	0	-3.156040	1.053919	-1.052885
48	1	0	-4.220840	3.267155	-0.810618
49	1	0	-0.360625	5.047473	-0.270338
50	1	0	-2.822307	5.276392	-0.418229
51	1	0	1.177653	1.290465	3.031067
52	1	0	1.832174	2.883536	3.976661
53	1	0	0.764020	3.086414	2.255611
54	1	0	2.654344	2.374305	2.195855
55	1	0	1.219604	1.176700	0.923762
56	1	0	-1.107163	-0.272571	2.355614
57	1	0	-1.153202	1.344809	1.545278

HF=-1086.8149294
W= -647.6705

Zero-point correction= 0.487136
(Hartree/Particle)
Thermal correction to Energy= 0.512262
Thermal correction to Enthalpy= 0.513206
Thermal correction to Gibbs Free Energy= 0.431544
Sum of electronic and zero-point Energies= -1086.327793
Sum of electronic and thermal Energies= -1086.302667
Sum of electronic and thermal Enthalpies= -1086.301723
Sum of electronic and thermal Free Energies= -1086.383385

Table T7: Cartesian coordinates, energy and imaginary frequency of B3LYP/6-31++G** optimized conformation for **product-a**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.979758	3.647554	-1.559302
2	6	0	0.010821	4.500952	-1.031527
3	6	0	-1.176958	3.960395	-0.525487
4	6	0	-1.381536	2.581141	-0.545240
5	6	0	-0.414690	1.708506	-1.072922
6	6	0	0.766896	2.263430	-1.581000
7	6	0	-0.707347	0.204945	-1.078279
8	6	0	0.203426	-0.605618	-2.016537
9	7	0	-0.811060	-0.303451	0.308055
10	6	0	-0.165379	0.488895	2.555475
11	6	0	0.327452	-0.106107	1.217666
12	6	0	1.190446	-1.350386	1.533130
13	8	0	1.858460	-1.928017	0.410120
14	6	0	3.103894	-1.487198	0.048419
15	6	0	3.741329	-2.240947	-0.950223
16	6	0	5.010163	-1.880057	-1.395423
17	6	0	5.665647	-0.767247	-0.853384
18	6	0	5.027705	-0.020708	0.136635
19	6	0	3.749139	-0.367336	0.590719
20	6	0	-1.580470	-1.535249	0.467040
21	6	0	-3.041145	-1.401677	0.063367
22	6	0	-3.609954	-2.278078	-0.868448
23	6	0	-4.964270	-2.185937	-1.208377
24	6	0	-5.768472	-1.210786	-0.616155
25	6	0	-5.210749	-0.329669	0.317523
26	6	0	-3.859607	-0.425756	0.652525
27	5	0	0.611023	1.388127	5.504952
28	1	0	0.975125	0.638554	0.746410
29	1	0	-1.555038	-1.804558	1.529042
30	1	0	-1.140988	-2.391449	-0.073974
31	1	0	-1.725498	0.106264	-1.474959
32	1	0	-0.091373	-1.658814	-2.014723
33	1	0	1.254488	-0.562448	-1.724872
34	1	0	0.113033	-0.235233	-3.043769
35	1	0	0.565699	-2.156726	1.927115
36	1	0	1.918750	-1.098433	2.312694
37	1	0	3.225009	-3.105099	-1.355677
38	1	0	3.275500	0.241562	1.351420
39	1	0	5.518954	0.848628	0.564667
40	1	0	5.492257	-2.473952	-2.166834
41	1	0	6.655917	-0.488943	-1.199900
42	1	0	-2.988135	-3.039211	-1.334147
43	1	0	-3.426220	0.260633	1.374622
44	1	0	-5.831025	0.429739	0.785832

45	1	0	-5.386485	-2.872902	-1.936460
46	1	0	-6.819877	-1.135358	-0.878207
47	1	0	1.534694	1.622671	-2.001732
48	1	0	-2.303616	2.164524	-0.149800
49	1	0	-1.943668	4.614605	-0.119259
50	1	0	1.905418	4.053488	-1.957956
51	1	0	0.174136	5.574796	-1.017713
52	1	0	-0.838602	-0.199364	3.078301
53	1	0	-0.704722	1.418860	2.366667
54	1	0	0.684407	0.704950	3.220350
55	1	0	1.280884	0.418289	5.690510
56	1	0	-0.563274	1.347697	5.706496
57	1	0	1.122300	2.406507	5.152578

HF=-1087.4595897

Zero-point correction= 0.480962
(Hartree/Particle)
Thermal correction to Energy= 0.508335
Thermal correction to Enthalpy= 0.509279
Thermal correction to Gibbs Free Energy= 0.416632
Sum of electronic and zero-point Energies= -1086.978628
Sum of electronic and thermal Energies= -1086.951255
Sum of electronic and thermal Enthalpies= -1086.950310
Sum of electronic and thermal Free Energies= -1087.042958

Table T8: Cartesian coordinates and energy of MPW1B95/6-31++G** optimized conformation for **product-a**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.533190	3.754190	-1.633109
2	6	0	-0.457467	4.514242	-1.030862
3	6	0	-1.518283	3.874941	-0.395584
4	6	0	-1.574687	2.490627	-0.362159
5	6	0	-0.583253	1.713218	-0.964233
6	6	0	0.468588	2.363391	-1.602060
7	6	0	-0.709669	0.200670	-0.900376
8	6	0	0.321026	-0.541064	-1.739325
9	7	0	-0.778383	-0.226871	0.497745
10	6	0	-0.107662	0.843104	2.571389
11	6	0	0.372559	0.088795	1.336342
12	6	0	1.221525	-1.099872	1.792894
13	8	0	1.742320	-1.884916	0.741938
14	6	0	2.932484	-1.547342	0.181373
15	6	0	3.449483	-2.467365	-0.730684
16	6	0	4.652043	-2.213425	-1.366931
17	6	0	5.358649	-1.042903	-1.104279
18	6	0	4.838219	-0.131551	-0.198796
19	6	0	3.626891	-0.369113	0.444960
20	6	0	-1.414274	-1.509495	0.715459
21	6	0	-2.853711	-1.522404	0.267514
22	6	0	-3.313259	-2.454360	-0.656513
23	6	0	-4.648328	-2.469170	-1.047986
24	6	0	-5.538669	-1.546864	-0.516580
25	6	0	-5.088467	-0.610823	0.409446
26	6	0	-3.756693	-0.600035	0.795818
27	5	0	2.050215	2.361651	3.206080
28	1	0	1.014812	0.758033	0.756318
29	1	0	-1.401571	-1.707913	1.791159
30	1	0	-0.876414	-2.344980	0.240105
31	1	0	-1.697445	-0.037898	-1.309101
32	1	0	0.208534	-1.617403	-1.604705
33	1	0	1.341902	-0.281131	-1.456730
34	1	0	0.195093	-0.312423	-2.799479
35	1	0	0.617239	-1.787036	2.387117
36	1	0	2.028821	-0.742662	2.439802
37	1	0	2.890749	-3.374603	-0.920427
38	1	0	3.242143	0.371575	1.132276
39	1	0	5.371029	0.787189	0.013826
40	1	0	5.042823	-2.937487	-2.071263
41	1	0	6.299814	-0.846469	-1.600845
42	1	0	-2.618280	-3.173406	-1.076529
43	1	0	-3.399349	0.130438	1.513458
44	1	0	-5.779178	0.109421	0.830942
45	1	0	-4.989378	-3.199397	-1.771548

46	1	0	-6.577812	-1.554912	-0.821124
47	1	0	1.250386	1.789872	-2.083207
48	1	0	-2.395065	1.986735	0.136206
49	1	0	-2.302050	4.458536	0.072249
50	1	0	1.363110	4.240069	-2.131635
51	1	0	-0.408062	5.595754	-1.056243
52	1	0	-0.828925	0.248824	3.140193
53	1	0	-0.581312	1.778562	2.283035
54	1	0	0.711796	1.045792	3.288052
55	1	0	2.779475	1.482309	3.558233
56	1	0	1.498018	3.030821	4.022247
57	1	0	1.996738	2.658603	2.053181

HF=-1086.894933

Zero-point correction= 0.488488
(Hartree/Particle)
Thermal correction to Energy= 0.514893
Thermal correction to Enthalpy= 0.515837
Thermal correction to Gibbs Free Energy= 0.430303
Sum of electronic and zero-point Energies= -1086.406445
Sum of electronic and thermal Energies= -1086.380040
Sum of electronic and thermal Enthalpies= -1086.379096
Sum of electronic and thermal Free Energies= -1086.464630

Table T9: Cartesian coordinates and energy of B3LYP/6-31++G** optimized conformation for **product-b**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.804157	-3.862075	-1.446237
2	6	0	4.020040	-3.709540	-0.780635
3	6	0	4.294905	-2.504535	-0.123518
4	6	0	3.358046	-1.472156	-0.132614
5	6	0	2.126756	-1.612365	-0.795768
6	6	0	1.867327	-2.820797	-1.454486
7	6	0	1.152771	-0.429215	-0.792134
8	6	0	-0.066748	-0.614360	-1.717878
9	7	0	0.842732	-0.013758	0.589281
10	6	0	0.292830	-0.988625	1.517956
11	6	0	-1.208144	-1.405576	1.472558
12	6	0	-2.234042	-0.451562	2.095488
13	8	0	-2.570128	0.673536	1.276946
14	6	0	-3.531912	0.557949	0.308087
15	6	0	-4.189899	-0.630774	-0.035638
16	6	0	-5.163413	-0.612461	-1.042330
17	6	0	-5.484012	0.567869	-1.712074
18	6	0	-4.818779	1.750154	-1.363998
19	6	0	-3.851524	1.749692	-0.362508
20	6	0	0.431627	1.380364	0.748885
21	6	0	1.538437	2.374176	0.429546
22	6	0	1.349424	3.377430	-0.528502
23	6	0	2.353071	4.315213	-0.796450
24	6	0	3.563993	4.259206	-0.104329
25	6	0	3.764657	3.261394	0.856771
26	6	0	2.760453	2.328544	1.118308
27	5	0	-2.169532	-4.254298	1.959014
28	1	0	0.138442	1.508853	1.797205
29	1	0	-0.461994	1.640047	0.161693
30	1	0	1.717273	0.417350	-1.205129
31	1	0	-0.733408	0.249263	-1.645000
32	1	0	-0.653861	-1.505361	-1.478998
33	1	0	0.255425	-0.697003	-2.761735
34	1	0	-1.828849	-0.012314	3.013358
35	1	0	-3.148186	-0.992538	2.366624
36	1	0	-3.956959	-1.566571	0.457753
37	1	0	-3.337155	2.661016	-0.074583
38	1	0	-5.058114	2.680064	-1.872144
39	1	0	-5.667591	-1.539342	-1.301220
40	1	0	-6.238696	0.570193	-2.492188
41	1	0	0.407988	3.425664	-1.071010
42	1	0	2.918670	1.552471	1.862590
43	1	0	4.702869	3.214102	1.402973
44	1	0	2.188217	5.084117	-1.546152
45	1	0	4.345684	4.984998	-0.309568

46	1	0	0.932732	-2.964817	-1.985845
47	1	0	3.571650	-0.539765	0.381161
48	1	0	5.241524	-2.369536	0.392750
49	1	0	2.577769	-4.790704	-1.962946
50	1	0	4.747773	-4.515977	-0.774950
51	1	0	-1.256833	-2.329484	2.082129
52	1	0	-2.006169	-4.243240	3.141237
53	1	0	-1.325172	-4.693900	1.242035
54	1	0	-3.207711	-3.884637	1.501849
55	1	0	-1.512684	-1.678531	0.459804
56	1	0	0.499597	-0.626019	2.535688
57	1	0	0.877206	-1.906595	1.396005

HF=-1087.457019

Zero-point correction= 0.481847
(Hartree/Particle)
Thermal correction to Energy= 0.509618
Thermal correction to Enthalpy= 0.510562
Thermal correction to Gibbs Free Energy= 0.415512
Sum of electronic and zero-point Energies= -1086.975172
Sum of electronic and thermal Energies= -1086.947401
Sum of electronic and thermal Enthalpies= -1086.946457
Sum of electronic and thermal Free Energies= -1087.041507

Table T10: Cartesian coordinates and energy of MPW1B95/6-31++G** optimized conformation for **product-b**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.553563	4.191539	-1.522582
2	6	0	-1.729109	4.717191	-1.009128
3	6	0	-2.641835	3.870487	-0.386580
4	6	0	-2.371447	2.515451	-0.281123
5	6	0	-1.190241	1.973598	-0.791923
6	6	0	-0.286858	2.829167	-1.414521
7	6	0	-0.956887	0.481767	-0.651251
8	6	0	0.246728	-0.033627	-1.433542
9	7	0	-1.003994	0.097738	0.759515
10	6	0	-0.233747	0.840817	1.725144
11	6	0	1.298548	0.711620	1.769095
12	6	0	1.874574	-0.660938	2.084817
13	8	0	1.991290	-1.494574	0.946359
14	6	0	3.060439	-1.334459	0.122918
15	6	0	4.009363	-0.322968	0.249196
16	6	0	5.063305	-0.256334	-0.657608
17	6	0	5.179872	-1.176203	-1.687457
18	6	0	4.223754	-2.181136	-1.807595
19	6	0	3.171529	-2.262988	-0.912099
20	6	0	-1.166364	-1.320351	1.007472
21	6	0	-2.468649	-1.860838	0.468227
22	6	0	-2.502270	-3.054091	-0.245699
23	6	0	-3.705988	-3.571886	-0.711751
24	6	0	-4.892935	-2.893404	-0.472795
25	6	0	-4.869453	-1.696836	0.236894
26	6	0	-3.666678	-1.187527	0.703796
27	5	0	2.857119	2.715605	2.752727
28	1	0	-1.163635	-1.451825	2.095200
29	1	0	-0.338013	-1.932454	0.625794
30	1	0	-1.837329	-0.001014	-1.092988
31	1	0	0.352574	-1.110543	-1.302549
32	1	0	1.186132	0.426146	-1.126760
33	1	0	0.111717	0.157715	-2.499965
34	1	0	1.213809	-1.201943	2.764810
35	1	0	2.848827	-0.572383	2.574500
36	1	0	3.944538	0.417653	1.033762
37	1	0	2.425432	-3.043420	-0.989376
38	1	0	4.299315	-2.910895	-2.604297
39	1	0	5.796142	0.533827	-0.549673
40	1	0	6.001960	-1.114903	-2.388366
41	1	0	-1.575236	-3.582735	-0.439993
42	1	0	-3.639163	-0.254157	1.254401
43	1	0	-5.792229	-1.162231	0.427407
44	1	0	-3.713956	-4.501622	-1.267336
45	1	0	-5.831488	-3.291016	-0.838530

46	1	0	0.635060	2.439386	-1.826484
47	1	0	-3.077234	1.853698	0.207597
48	1	0	-3.566133	4.269164	0.013740
49	1	0	0.163791	4.839826	-2.010852
50	1	0	-1.936696	5.776633	-1.093760
51	1	0	1.593977	1.372405	2.612390
52	1	0	2.284296	2.956524	3.771972
53	1	0	2.626858	3.354056	1.774692
54	1	0	3.769636	1.945555	2.765598
55	1	0	1.754208	1.108840	0.861362
56	1	0	-0.617242	0.564783	2.714040
57	1	0	-0.460386	1.901039	1.591118

HF=-1086.8912655

Zero-point correction= 0.489882
(Hartree/Particle)
Thermal correction to Energy= 0.516059
Thermal correction to Enthalpy= 0.517003
Thermal correction to Gibbs Free Energy= 0.429747
Sum of electronic and zero-point Energies= -1086.401384
Sum of electronic and thermal Energies= -1086.375207
Sum of electronic and thermal Enthalpies= -1086.374262
Sum of electronic and thermal Free Energies= -1086.461518

Table T11: Cartesian coordinates and single point energy of B3LYP/6-31++G** for **2A**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.737496	-2.194423	1.092622
2	6	0	-1.764710	-2.120944	0.083370
3	6	0	-2.085097	-2.599385	-1.195628
4	6	0	-3.352518	-3.120799	-1.468081
5	6	0	-4.317789	-3.171156	-0.460188
6	6	0	-4.006161	-2.709146	0.822212
7	6	0	-0.376266	-1.592260	0.366293
8	7	0	-0.301121	-0.091985	0.529956
9	6	0	0.822104	0.483828	1.376009
10	6	0	1.916298	-0.421241	1.912552
11	8	0	2.609258	-1.122135	0.885775
12	6	0	3.742538	-0.576171	0.301495
13	6	0	4.148651	0.751434	0.457612
14	6	0	5.311057	1.179052	-0.196359
15	6	0	6.052685	0.308966	-0.996339
16	6	0	5.625939	-1.015648	-1.146649
17	6	0	4.474794	-1.461921	-0.499542
18	6	0	-0.721588	0.679223	-0.756913
19	6	0	0.522715	1.042814	-1.567704
20	6	0	-1.682436	1.821938	-0.491587
21	6	0	-3.059802	1.588300	-0.644283
22	6	0	-3.983808	2.615492	-0.447229
23	6	0	-3.539481	3.891932	-0.088827
24	6	0	-2.172784	4.131019	0.070592
25	6	0	-1.244090	3.106603	-0.134217
26	6	0	-0.556700	0.472420	1.897565
27	1	0	0.021032	-2.032035	1.280180
28	1	0	0.314293	-1.844636	-0.439957
29	1	0	-1.283241	-0.079509	-1.302128
30	1	0	1.170506	0.172699	-1.713127
31	1	0	1.112016	1.836888	-1.103350
32	1	0	0.198714	1.394539	-2.551448
33	1	0	1.514309	-1.194251	2.574758
34	1	0	2.581676	0.217230	2.503271
35	1	0	3.587552	1.465970	1.053892
36	1	0	4.137075	-2.489459	-0.593443
37	1	0	6.193572	-1.707009	-1.763138
38	1	0	5.621928	2.212364	-0.074777
39	1	0	6.950779	0.655768	-1.498146
40	1	0	-1.335508	-2.573078	-1.982825
41	1	0	-2.507338	-1.857641	2.099278
42	1	0	-4.747388	-2.758018	1.614139
43	1	0	-3.581690	-3.488953	-2.463499
44	1	0	-5.303382	-3.576277	-0.668435
45	1	0	-0.190260	3.316600	0.025879
46	1	0	-3.411185	0.598448	-0.925573
47	1	0	-5.044485	2.420492	-0.576212

48	1	0	-1.816612	5.113870	0.362776
49	1	0	-4.255383	4.693905	0.066704
50	1	0	1.165256	1.453155	1.010944
51	1	0	-0.847832	-0.274900	2.629106
52	1	0	-1.106948	1.405261	1.918577

HF=-1059.9852059

Table T12: Cartesian coordinates and single point energy of B3LYP/6-31++G** for **2A** in geometry of **TS-a**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.668770	-1.098715	0.983963
2	6	0	-2.735464	-1.675453	0.108161
3	6	0	-3.199008	-2.286848	-1.063940
4	6	0	-4.564750	-2.317632	-1.362413
5	6	0	-5.483625	-1.732687	-0.489314
6	6	0	-5.031770	-1.123224	0.685947
7	6	0	-1.257254	-1.684971	0.438771
8	7	0	-0.644814	-0.326200	0.488600
9	6	0	0.631968	-0.148485	1.264148
10	6	0	1.459036	-1.335602	1.715424
11	8	0	2.193020	-1.904328	0.632278
12	6	0	3.392722	-1.335214	0.254016
13	6	0	4.029380	-1.958413	-0.828926
14	6	0	5.248929	-1.469294	-1.292266
15	6	0	5.844164	-0.357550	-0.684043
16	6	0	5.201751	0.254511	0.392414
17	6	0	3.974273	-0.221021	0.871739
18	6	0	-0.799632	0.489166	-0.783112
19	6	0	0.187295	-0.001896	-1.849185
20	6	0	-0.759918	1.989486	-0.527627
21	6	0	-1.958123	2.649712	-0.209179
22	6	0	-1.977798	4.024176	0.030246
23	6	0	-0.793555	4.763004	-0.046293
24	6	0	0.401991	4.120073	-0.370785
25	6	0	0.418262	2.744142	-0.615338
26	6	0	-0.471965	0.379720	2.053743
27	1	0	1.247722	0.623381	0.812532
28	1	0	-1.108518	-2.140397	1.419209
29	1	0	-0.704908	-2.294468	-0.284024
30	1	0	-1.813275	0.256653	-1.116965
31	1	0	0.033515	-1.061239	-2.071365
32	1	0	1.229588	0.122937	-1.545596
33	1	0	0.030967	0.562350	-2.772886
34	1	0	0.844102	-2.146848	2.109544
35	1	0	2.097573	-0.984903	2.532046
36	1	0	3.559716	-2.825147	-1.283454
37	1	0	3.506790	0.281703	1.713072
38	1	0	5.650483	1.115784	0.878732
39	1	0	5.737408	-1.961413	-2.128613
40	1	0	6.795549	0.021484	-1.044100
41	1	0	-2.489265	-2.747415	-1.746766
42	1	0	-3.332790	-0.630426	1.904765
43	1	0	-5.741579	-0.674709	1.374697
44	1	0	-4.906743	-2.797646	-2.274444
45	1	0	-6.544844	-1.755110	-0.718012

46	1	0	1.359895	2.271061	-0.874853
47	1	0	-2.881905	2.079161	-0.148108
48	1	0	-2.914182	4.516663	0.275098
49	1	0	1.327161	4.684923	-0.428777
50	1	0	-0.803336	5.831612	0.145514
51	1	0	-1.012650	-0.258148	2.738765
52	1	0	-0.725772	1.426266	1.998655

HF=-1059.9741222

Table T13: Cartesian coordinates and single point energy of B3LYP/6-31++G** for **2A** in geometry of **TS-b**.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.947418	-2.154006	1.078627
2	6	0	-2.010825	-2.074595	0.035594
3	6	0	-2.424727	-2.410947	-1.261933
4	6	0	-3.743532	-2.796260	-1.517933
5	6	0	-4.669348	-2.853340	-0.473955
6	6	0	-4.266561	-2.534819	0.826509
7	6	0	-0.574550	-1.660989	0.296326
8	7	0	-0.383873	-0.191274	0.474834
9	6	0	-0.616944	0.370967	1.826753
10	6	0	0.829479	0.434364	1.641952
11	6	0	1.815556	-0.644102	2.057304
12	8	0	2.393132	-1.337878	0.950279
13	6	0	3.520334	-0.832270	0.334847
14	6	0	4.086199	0.416096	0.615845
15	6	0	5.232425	0.813113	-0.084579
16	6	0	5.806851	-0.008075	-1.055096
17	6	0	5.226421	-1.252538	-1.327581
18	6	0	4.088897	-1.666886	-0.637690
19	6	0	-0.647308	0.630845	-0.779520
20	6	0	0.624154	0.716107	-1.630278
21	6	0	-1.320445	1.967012	-0.507701
22	6	0	-2.722895	2.033032	-0.552776
23	6	0	-3.391704	3.236340	-0.323031
24	6	0	-2.663512	4.395219	-0.038356
25	6	0	-1.269424	4.341080	0.012168
26	6	0	-0.601424	3.137481	-0.226503
27	1	0	-0.194876	-2.150108	1.193711
28	1	0	0.069954	-1.972500	-0.527693
29	1	0	-1.379727	0.033299	-1.329415
30	1	0	1.039115	-0.277556	-1.819925
31	1	0	1.406399	1.312340	-1.155782
32	1	0	0.383166	1.176347	-2.592985
33	1	0	1.318457	-1.410235	2.657944
34	1	0	2.582225	-0.177137	2.676416
35	1	0	3.662673	1.086885	1.358016
36	1	0	3.635125	-2.634493	-0.828607
37	1	0	5.663845	-1.907268	-2.076040
38	1	0	5.669279	1.781821	0.140183
39	1	0	6.694906	0.312518	-1.590778
40	1	0	-1.706814	-2.384098	-2.078322
41	1	0	-2.647113	-1.931422	2.098625
42	1	0	-4.976429	-2.592595	1.646290
43	1	0	-4.043374	-3.055768	-2.528928
44	1	0	-5.694169	-3.154738	-0.668786
45	1	0	0.481689	3.126627	-0.169584

46	1	0	-3.294237	1.134074	-0.771485
47	1	0	-4.476437	3.268497	-0.366827
48	1	0	-0.694585	5.230188	0.250519
49	1	0	-3.179587	5.332588	0.146868
50	1	0	1.217245	1.320275	1.161729
51	1	0	-0.999910	-0.356996	2.538302
52	1	0	-1.152951	1.314426	1.856531

HF=-1059.9679025

Preparation of 6: To a solution of 2-(aryloxymethyl)aziridine **5a** (0.23 g, 0.694 mmol) in CH_3CN (2.3 mL) was added 0.13 g of benzyl bromide (0.763 mmol) at rt. The resulting mixture was refluxed for 12 h and then quenched with H_2O. The mixture was extracted with CH_2Cl_2 and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography provided analytically pure product **6a** in 95% yield.

6a: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, J=6.9 Hz, CH_3); 2.98 (2H, J=7.2 Hz, $CHCH_2N$); 3.59 (1H, J=6.5, 10.0 Hz, (HCH)O); 3.66 and 3.69 (2H, J=13.5 Hz, Ar(HCH)N); 3.78 (3H, OCH_3); 3.93-4.1 (3H, CHBr, CHN and (HCH)O); 6.66 and 6.80 (2H and 2H, J=9.0, 9.3 Hz, CH_{arom}), 7.22-7.38 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9 (CH_3); 49.6 (CHBr); 54.0 ($CHCH_2N$); 56.0 ($ArCH_2N$); 58.1 (CHN); 70.1 (CH_2O); 114.3, 115.8, 127.1, 127.3, 128.1, 128.2, 128.4, 128.9, 139.7, 142.6, 152.4, 154.1 (CH_{arom}, CO, NCH_2C_{quat} and $NCHC_{quat}$). HRMS m/z exact mass calcd for $C_{25}H_{28}BrNO_2$: 453.1303; Found 453.1306.

6b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, J=6.9 Hz, CH_3); 2.98 (2H, J=7.2 Hz, $CHCH_2N$); 3.59 (1H, J=6.5, 10.0 Hz, (HCH)O); 3.66 and 3.69 (2H, J=13.5 Hz, Ar(HCH)N); 3.93-4.51 (3H, CHBr, CHN and (HCH)O); 6.59-6.64, 6.91-6.95 and 7.13-7.41 (2H, 1H and 11H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9 (CH_3); 49.6 (CHBr); 54.0 ($CHCH_2N$); 56.0 ($ArCH_2N$); 58.1 (CHN); 70.1 (CH_2O); 113.2, 114.7, 121.0, 127.1, 127.3, 128.0, 128.1, 128.4, 128.9 and 129.98 (CH_{arom}); 134.7 (CCl); 139.4 and 142.5 (NCH_2C_{quat} and $NCHC_{quat}$); 158.9 (CO). HRMS m/z exact mass calcd for $C_{24}H_{25}BrClNO$: 457.0808; Found 457.0810.

6c: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, J=6.9 Hz, CH_3); 2.98 (2H, J=7.2 Hz, $CHCH_2N$); 3.62 (1H, J=6.5, 10.0 Hz, (HCH)O); 3.66 and 3.69 (2H, J=13.5 Hz, Ar(HCH)N); 3.93-4.1 (3H, CHBr, CHN and (HCH)O); 6.59-6.64, 7.15-7.21 and 7.22-7.41 (2H, 2H and 10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9 (CH_3); 49.6 (CHBr); 54.0 ($CHCH_2N$); 56.0 ($ArCH_2N$); 58.1 (CHN); 70.1 (CH_2O); 115.9, 125.5, 126.8, 127.0, 127.8, 128.2, 128.4, 128.5, 129.5, 142.4, 144.7, 157.8 (CH_{arom}). HRMS m/z exact mass calcd for $C_{24}H_{25}BrClNO$: 457.0808; Found 457.0811.

6d: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, J=6.9 Hz, CH_3); 2.98 (2H, J=7.2 Hz, $CHCH_2N$); 3.62 (1H, J=6.5, 10.0 Hz, (HCH)O); 3.66 and 3.69 (2H, J=13.5 Hz, Ar(HCH)N); 3.93-4.2 (3H, CHBr, CHN and (HCH)O); 6.69-6.72, 6.92-6.96 and 7.20-7.40 (2H, 1H and 12H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.9 (CH_3); 49.6 (CHBr); 54.0 ($CHCH_2N$); 56.0 ($ArCH_2N$); 58.1 (CHN); 70.1 (CH_2O); 114.4, 120.3, 126.8, 127.0, 127.8, 128.2, 128.4, 128.8, 129.3, 138.6, 145.2, 159.4 (CH_{arom}). HRMS m/z exact mass calcd for $C_{24}H_{26}BrNO$: 423.1198; Found 423.1196.

6e: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41 (3H, J=7.0 Hz, $CHCH_3$); 2.91 (2H, J=8.5, 1.5 Hz, $N\underline{CH_2}CHBr$); 3.18 (3H, CH_3O); 3.30 (1H, J=4.5, 6.5 Hz, $OC\underline{H_2}CHBr$); 3.56 (1H, J=4.0, 7.0 Hz, $OC\underline{H_2}CHBr$); 3.63 (2H, J=2.5, CH_2Ar); 3.85-3.92 (1H, BrCH); 3.95 (1H, CH_3CHN), 3.94 (1H, J=6.9, $ArCHCH_3$), 7.22-7.42 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 52.0, 54.8, 55.9, 58.6, 58.8, 74.8, 127.2, 127.3, 128.3, 128.5, 129.0, 129.0, 140.1, 142.8
HRMS m/z exact mass calcd for $C_{19}H_{24}BrNO$: 361.1041; Found 361.1043.

6f: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (3H, J=7.2 Hz, OCH_2CH_3); 1.41 (3H, J=6.9 Hz, $CHCH_3$); 2.91 (2H, J=7.5 Hz, NCH_2CHBr); 3.30 and 3.34 (1H and 2H, J=4.5 and 6.9 Hz, $CHCH_2O$ and CH_3CH_2O; 3.59 (1H, J=4.5, $CHCH_2O$); 3.62 (2H, CH_2Ar); 3.82-3.88 (1H, $BrCHCH_2$), 3.94 (1H, J=6.9, $ArCHCH_3$), 7.22-7.42 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.5, 13.6, 52.1, 54.7, 56.0, 58.6, 58.9, 74.8, 127.2, 127.3, 128.3, 128.5, 129.0, 129.0, 140.1, 142.8. HRMS m/z exact mass calcd for $C_{20}H_{26}BrNO$: 375.1198; Found 375.1196.

Preparation of 7: To a mixture of $NaBH_4$ (0.016 g, 0.43 mmol) in THF (0.5 mL) was added 2-bromopropylamine **6a** (650 mg, 0.14 mmol) at rt. The resulting mixture was refluxed for 4 h and then quenched with H_2O. The mixture was extracted with CH_2Cl_2 and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography provided analytically pure product **7a** in 90% yield.

7a: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96, 1.35 (3H, J=6.9 Hz, CH_3); 3.36 (1H, $NCHCH_3$); 3.68 and 3.72 (2H, J=6.9, 7.8, 9.3 Hz, $CHCH_2O$, Ar(HCH)N); 3.88-3.98 (3H, $CHCH_2O$, Ar(HCH)N, CHN); 6.70-6.82, 7.15-7.44 (4H, 10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 19.6, 50.5,

51.8, 55.9, 58.4, 72.3, 114.8, 115.5, 126.6, 126.8, 127.8, 128.2, 128.3, 128.3, 142.4, 144.8, 153.4, 153.8. HRMS m/z exact mass calcd for $C_{25}H_{29}NO_2$: 375.2198; Found 375.2196.

7b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96, 1.35 (3H, J=6.9 Hz, CH_3); 3.36 (1H, $NCHCH_3$); 3.68 and 3.72 (2H, J=6.9, 7.8, 9.3 Hz, $CHCH_2O$, Ar(HCH)N); 3.88-3.98 (3H, $CHCH_2O$, Ar(HCH)N, CHN); 6.70-6.74, 6.82-6.85, 6.88-6.92, 7.12-7.44 (3x1H, 11H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 20.1, 50.5, 51.7, 58.6, 71.9, 112.5, 115.2, 120.4, 127.2, 127.3, 128.4, 128.4, 128.8, 128.8, 130.7, 136.1, 138.6, 145.2, 158.8. HRMS m/z exact mass calcd for $C_{24}H_{26}ClNO$: 379.1703; Found 379.1706.

7c: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96, 1.35 (3H, J=6.9 Hz, CH_3); 3.36 (1H, $NCHCH_3$); 3.68 and 3.72 (2H, J=6.9, 7.8, 9.3 Hz, $CHCH_2O$, Ar(HCH)N); 3.88-4.00 (3H, $CHCH_2O$, Ar(HCH)N, CHN); 6.74, 7.16-7.44 (2H, 12H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 19.9, 50.5, 51.7, 58.7, 71.9, 115.9, 125.5, 126.8, 127.0, 127.9, 128.2, 128.4, 128.5, 129.5, 142.4, 144.7, 157.8. HRMS m/z exact mass calcd for $C_{24}H_{26}ClNO$: 379.1703; Found 379.1705.

7d: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96, 1.35 (3H, J=6.9 Hz, CH_3); 3.38 (1H, $NCHCH_3$); 3.68 and 3.72 (2H, J=6.9, 7.8, 9.3 Hz, $CHCH_2O$, Ar(HCH)N); 3.88-4.05 (3H, $CHCH_2O$, Ar(HCH)N, CHN); 6.83, 6.91, 7.15-7.46 (2H, 1H, 12H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 20.1, 50.5, 51.8, 58.7, 71.8, 114.5, 120.3, 127.2, 127.3, 128.4, 128.5, 128.8, 128.9, 129.3, 138.6, 145.2, 159.4. HRMS m/z exact mass calcd for $C_{24}H_{27}NO$: 345.2093; Found 345.2097.

7e: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87, 1.31 (3H, J=6.5, 7.0 Hz, CH_3); 3.10-3.19 (1H, $NC\underline{H}CH_3$); 3.19 (1H, J=1.5, 7.0, 7.5 Hz, $CHCH_2O$); 3.28 (3H, OCH_3); 3.47 (1H, J=5.0, 5.5, 4.0, $CHCH_2O$); 3.66 and 3.83 (1H and 1H, J=15.0, 15.5 Hz, $\underline{CH_2}Ar$); 3.92 (1H, J=6.5, 7.0 Hz, CH_3CHN); 7.18-7.44 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 19.8, 51.8, 59.3, 59.7, 61.4, 79.3, 127.2, 127.3, 128.3, 128.4, 128.7, 128.8, 139.6, 142.8. HRMS m/z exact mass calcd for $C_{19}H_{25}NO$: 283.1936; Found 283.1939.

7f: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (3H, J=7.0 Hz, CH_3); 1.11 (3H, J=7.2 Hz, $OCH_2\underline{CH_3}$); 1.31 (3H, J=7.0 Hz, CH_3); 3.11-3.20 (1H, $NC\underline{H}CH_3$); 3.21 (1H, J=1.4, 7.0, 7.4 Hz, $CHCH_2O$);

3.31 (2H, J=6.9 Hz, OCH_2CH_3); 3.47 (1H, J=5.0, 5.5, 4.0, $CHCH_2O$); 3.67 and 3.82 (1H and 1H, J=15.0, 15.5 Hz, $\underline{CH_2}Ar$); 3.92 (1H, J=6.5, 7.0 Hz, CH_3CHN); 7.17-7.44 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.5, 13.6, 19.9, 52.1, 59.3, 59.7, 61.5, 79.8, 127.2, 127.3, 128.3, 128.5, 128.7, 128.8, 139.8, 142.8. HRMS m/z exact mass calcd for $C_{20}H_{27}NO$: 297.2093; Found 297.2090.

Reaction of 6 with $LiAlH_4$: To a mixture of $LiAlH_4$ (3 mg, 79 μmol) in THF (0.33 mL) was added 2-bromopropylamine **6a** (30 mg, 66 μmol) at rt. The resulting mixture was stirred for 4 h at rt and then quenched with EtOAc and H_2O. The mixture was extracted with CH_2Cl_2 and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography provided analytically pure product **7a** (40%) and **8** (30%).

8: ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (3H, J=6.7 Hz, CH_3); 2.98 and 3.14 (1H and 1H, J=6.3, 8.4 Hz, $CHCH_2N$); 3.51 (2H, J=14.1, 17.4 Hz, Ar(HCH)N); 3.94 (1H, J=6.9 Hz, CH_3CHN); 5.06-5.21 (2H, J=12.3, 19.5 Hz, $CH=\underline{CH_2}$); 5.78-5.94 (1H, $\underline{CH}=CH_2$); 7.15-7.46 (10H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9, 52.6, 53.9, 57.8, 117.1, 126.9, 126.9, 128.0, 128.3, 128.4, 128.8, 136.9, 140.9, 144.0. HRMS m/z exact mass calcd for $C_{18}H_{21}N$: 251.1674; Found 251.1679.