Electronic Supplementary Information #2

Revisiting Secondary Interactions in Neighboring Group Participation, Exemplified by Reactivity Changes of Iminylium Intermediates

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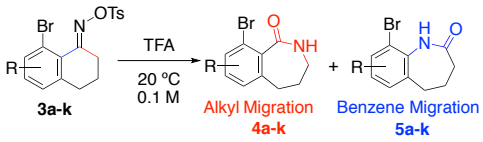
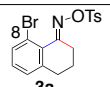
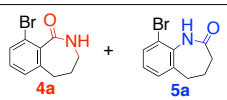
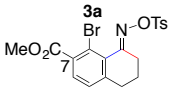
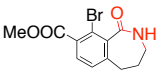
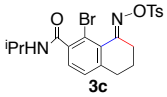
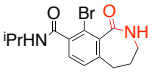
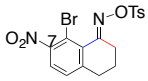
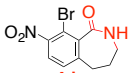
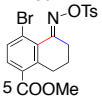
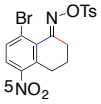
Table S1. Migration Generality of 8-Br derivatives: comparison of isolation ratio and NMR ratio (in parentheses).



Tosylated Oxime	Reaction Time	Isolated Ratio[a] (Alkyl : Benzene)	isomer ratios
 **3a**	1 h	 **4a** + **5a**	89 : 11 (90 : 10)
 **3b**	1 h	 **4b**	100 : 0 (100 : 0)
 **3c**	1 h	 **4c**	100 : 0 (100 : 0)
 **3d**	1 h	 **4d**	—
 **3e**	3 h	 **4e**	100 : 0 (100 : 0)
 **3f**	8 h	 **4f**	100 : 0 (100 : 0)

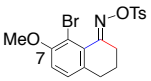
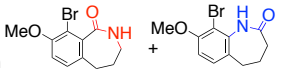
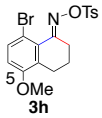
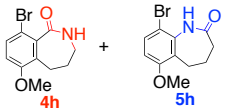
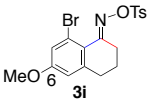
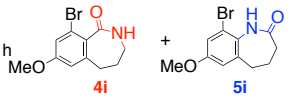
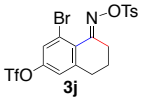
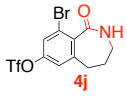
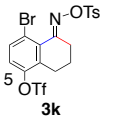
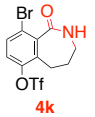
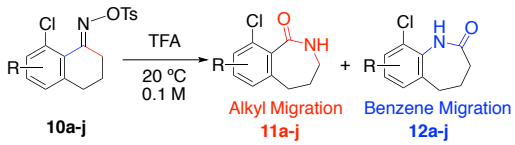
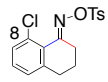
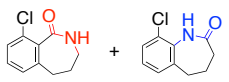
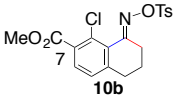
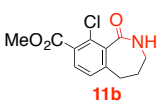
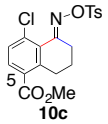
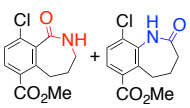
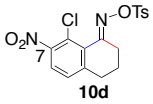
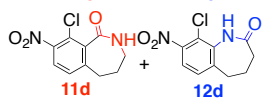
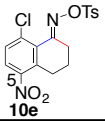
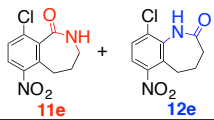
Tosylated Oxime	Reaction Time	Isolated Ratio[a] (Alkyl : Benzene)	isomer ratios
 **3g**	1 h	 **4g** + **5g**	93 : 7 (95 : 5)
 **3h**	1 h	 **4h** + **5h**	93 : 7 (93 : 7)
 **3i**	1 h	 **4i** + **5i**	49 : 51 (44 : 56)
 **3j**	4 h	 **4j**	100 : 0 (100 : 0)
 **3k**	1 h	 **4k**	100 : 0 (100 : 0)

Table S2. Migration Generality of 8-Cl derivatives: comparison of isolation ratio and NMR ratio (in parentheses).



Tosylated Oxime	Reaction Time	Isolated Ratio[a] (Alkyl : Benzene)	isomer ratio
 **10a**	1 h	 **11a** **12a**	66 : 34 (69 : 31)
 **10b**	1 h	 **11b**	– 100 : 0 (100 : 0)
 **10c**	3 h	 **11c** **12c**	67 : 33 (71 : 29)
 **10d**	16 h	 **11d** **12d**	97 : 3 (95 : 5)
 **10e**	48 h	 **11e** **12e**	87 : 13 (89 : 11)

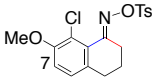
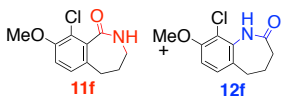
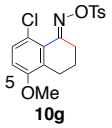
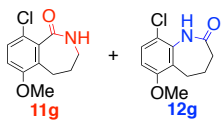
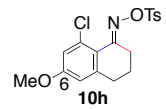
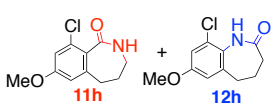
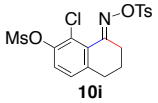
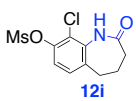
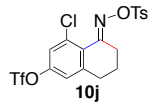
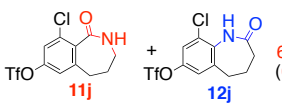
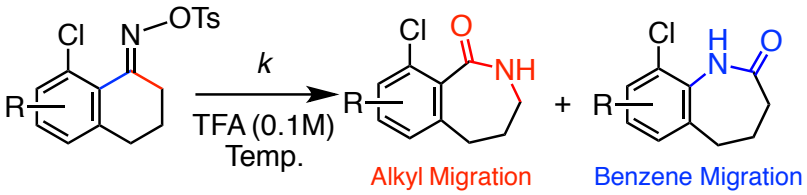
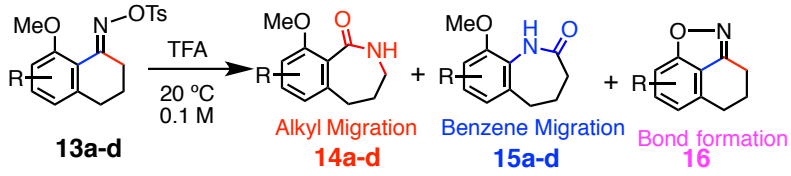
Tosylated Oxime	Reaction Time	Isolated Ratio[a] (Alkyl : Benzene)	isomer ratio
 **10f**	1 h	 **11f** **12f**	75 : 25 (78 : 22)
 **10g**	1 h	 **11g** **12g**	73 : 27 (75 : 25)
 **10h**	1 h	 **11h** **12h**	8 : 92 (6 : 94)
 **10i**	18 h	–  **12i**	0 : 100 (0 : 100)
 **10j**	17 h	 **11j** **12j**	63 : 37 (60 : 40)

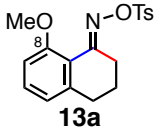
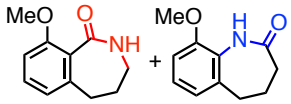
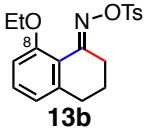
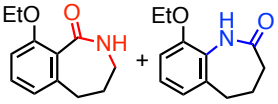
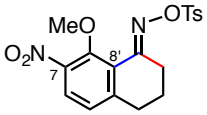
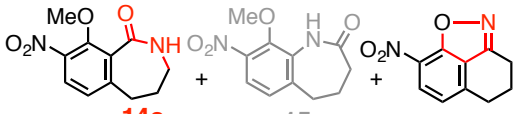
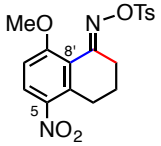
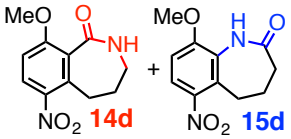
Table S3. Kinetic data of *peri*-Cl compounds, based on consumption rate of oxime.



	Tosylated Oxime	Temp. [°C]	10^4 x k [s^{-1}]	Relative rate
10a	**R= H**	-12	1.68 ± 0.03	1
10b	**R= 7-CO_2Me**	-12	8.95 ± 0.21	5.33
10f	**R= 7-OMe**	-12	2.13 ± 0.05	1.27
10g	**R= 5-OMe**	-12	1.87 ± 0.02	1.11
10d	**R= 7-NO_2**	45	26.32 ± 0.96	3.17
10e	**R= 5-NO_2**	45	8.29 ± 0.11	1

Table S4. Migration Generality of 8-MeO derivatives: comparison of isolation ratio and NMR ratio (in parentheses).

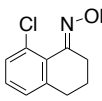
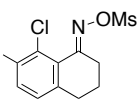
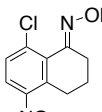
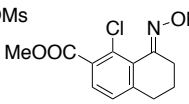
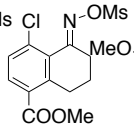
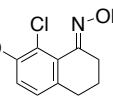
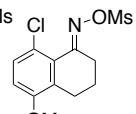


entry	Tosylated Oxime	Reaction Time	Isolated Ratio (Alkyl : Benzene)	Isolated Yield
1	 13a	1 h	 14a 91 : 9 15a	**15a** 80% **16a** 8% (89 : 11)
2	 13b	1 h	 14b 87 :13 15b	**15b** 74% **16b**11% (90 : 20)
3	 13c	1 h	 14c 100 : 0 15c 16c	**15c** 9% **16c** 80% (100 : 0)
4	 13d	1 h	 14d 90 : 10 15d	**15d** 82% **16d** 9% (88 : 12)

Notes for Tables S1, S3 and S4:
1). NMR ratios were determined with crude mixtures of reactions after aqueous work-up. 2). Reactions were carried out twice to check the reproducibility.

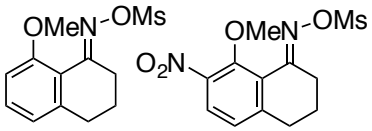
II. Computation results of *peri*-Br, *peri*-Cl and *peri*-OMe compounds.

Table S5. Calculated Energetics of the migrations of *peri*-Cl Oximes[a, b]

(kcal/mol)	 10a-Ms	 10d-Ms	 10e-Ms	 10b-Ms	 10c-Ms	 10f-Ms	 10g-Ms
ΔHs	**21.4**	**23.3**	**24.5**	**18.9**	**22.4**	**20.8**	**20.5**
ΔH_R	19.8	18.8	22.7	12.6	20.2	18.2	18.8
ΔH_A	3.1	5.6	3.4	7.4	3.2	2.9	3.3
ΔH_B	23.1	28.3	28.7	24.6	26.7	22.7	23.2

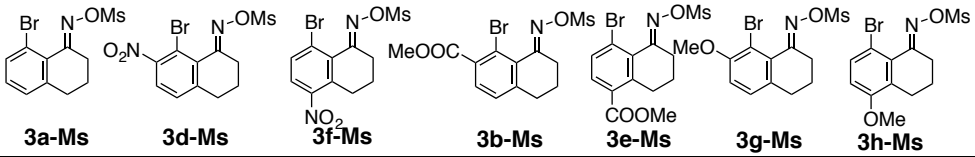
(a) In kcal/mol. Relative energy compared with the initial compound. Zero point energy was corrected. (b) ΔH_s: Activation energy of substitution process; ΔH_R: activation energy of the substitution intermediate with respect to the initial compound; ΔH_A: activation energy of the alkyl migration process. ΔH_B: activation energy of benzene migration process.

Table S6 Calculated energetics of migrations of *peri*-OMe Oximes[a a, b]

(kcal/mol)		
	13a-Ms	**13c-Ms**
ΔHs	**19.1**	**20.8**
ΔH_R	11.0	14.6
ΔH_A	3.8	7.8

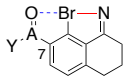
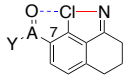
(a) In kcal/mol, relative to the initial compound. (b) ΔH_s: Activation energy of substitution process (**Figure S9**: Substitution); ΔH_R: activation energy of the substitution intermediate with respect to the initial compound; ΔH_A: activation energy of the alkyl migration process (**Figure S9**: Alkyl migration). ΔH_B: activation energy of benzene migration process (**Figure S9**). (c) In boldface: rate-determining step in alkyl migration reaction was shown.

Table S7 Calculated energetics of migrations of *peri*-Br Oximes [a, b]

(kcal/mol)							
	3a-Ms	**3d-Ms**	**3f-Ms**	**3b-Ms**	**3e-Ms**	**3g-Ms**	**3h-Ms**
ΔHs	**19.2**	19.0	**20.9**	17.5	**19.9**	**17.4**	**18.0**
ΔH_R	8.8	3.4	9.5	1.2	8.2	6.3	6.9
ΔH_A	12.1	**21.1**	16.0	**21.9**	14.8	14.4	13.8
ΔH_B	23.4	29.8	31.9	24.3	24.9	22.9	23.1

(a) In kcal/mol, relative to the initial compound. (b) ΔH_s: Activation energy of substitution process (**Figure S9**: Substitution); ΔH_R: activation energy of the substitution intermediate with respect to the initial compound; ΔH_A: activation energy of the alkyl migration process (**Figure S9**: Alkyl migration). ΔH_B: activation energy of benzene migration process (**Figure S9**). (c) In boldface: rate-determining step in alkyl migration reaction was shown.

Table S8 Summary of Calculated Atomic Distance

		atomic distance (Å)				atomic distance (Å)	
							
		O-Br (Å)	Br-N (Å)			O-Cl (Å)	Cl-N (Å)
3a-Ms (*peri*- Br)	Reactant	-	3.099	**10a-Ms** (*peri*- Cl)	Reactant	-	2.968
	TS	-	2.302		TS	-	2.292
	IM	-	2.000		IM	-	1.958
3b-Ms (7-COOMe, *peri*- Br)	Reactant	4.218	3.096	**10b-Ms** (7-COOMe, *peri*- Cl)	Reactant	3.030	2.962
	TS	2.891	2.369		TS	2.827	2.115
	IM	2.883	1.982		IM	2.829	1.878
3e-Ms (5-COOMe, *peri*- Br)	Reactant	-	3.071	**10c-Ms** (5-COOMe, *peri*- Cl)	Reactant	-	2.975
	TS	-	2.313		TS	-	2.296
	IM	-	2.001		IM	-	1.957
3d-Ms (7-NO_2, *peri*- Br)	Reactant	3.113	3.005	**10d-Ms** (7-NO_2, *peri*- Cl)	Reactant	3.001	2.955
	TS	2.835	2.339		TS	2.778	2.153
	IM	2.855	1.984		IM	2.807	1.910
3f-Ms (5-NO_2, *peri*- Br)	Reactant	-	3.116	**10e-Ms** (5-NO_2, *peri*- Cl)	Reactant	-	2.966
	TS	-	2.311		TS	-	2.303
	IM	-	1.999		IM	-	1.959

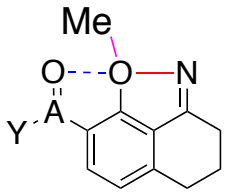
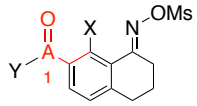
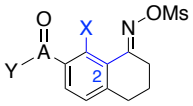
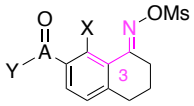
		atomic distance (Å)		
				
		O-O (Å)	O-N (Å)	O-Me (Å)
13a-Ms (*peri*- OMe)	Reactant	-	2.630	1.427
	TS	-	1.888	1.472
	IM	-	1.580	1.505
13c-Ms (7-NO_2-*peri*- OMe)	Reactant	2.758	2.720	1.441
	TS	2.838	1.870	1.493
	IM	2.871	1.599	1.520

Table S9. Summary of Calculated Dihedral Angles of **6b-IM**, **10b-IM** and **14c-IM**

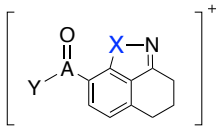






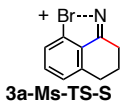
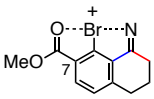
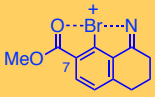
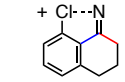
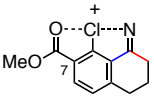
	1(O-A-C-C)			2 (X-C-C-C)			3 (N-C-C-C)		
	reactant	TS	IM	reactant	TS	IM	reactant	TS	IM
3b (X=Br)	-135.9°	-1.1°	-0.3°	-11.5°	1.1°	0.4	-42.5°	-3.1°	0.4°
10b (X=Cl)	-42.2°	-1.9°	-1.6°	-4.5°	0.3°	4.2	-37.8°	0.7°	0.02°
14c (X=O)	-33.5°	-13.1°	-8.5°	-7.3°	-4.1°	-1.1°	-31.7°	0.9°	1.2°

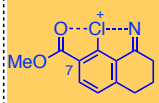
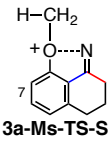
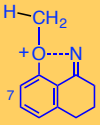
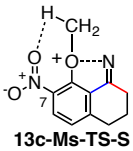
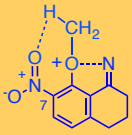
Table S10. Summary of CHelpG charges and Hirshfeld charges for **6b-IM**, **10b-IM** and **14c-IM**.



	CHELPG charges			**Hirshfeld charges**		
	O	X	N	O	X	N
3b(X=Br)	-0.51	+0.58	-0.37	-0.24	+0.44	-0.10
10b (X=Cl)	-0.50	+0.44	-0.32	-0.24	+0.35	-0.07
14c (X=OMe)	-0.40	+0.40	-0.33	-0.17	+0.34	-0.02

Table S11 QTAIM analyses of TS structures and intermediates [a)]

species	electron density $\rho(\mathbf{r})_b$ (e/bohr^3)	Laplacian of electron density (e/bohr^5)
 **3a-Ms-TS-S**	Br-N (bcp) 0.067	Br-N +0.089
 **3a-IM**	Br-N (bcp) 0.122	Br-N +0.064
 **3b-Ms-TS-S**	Br-N (bcp1) 0.061 O-Br (bcp2) 0.019	Br-N +0.079 O-Br +0.059
 **3b-IM**	Br-N (bcp1) 0.130 O-Br (bcp2) 0.018 C-Br (σ bond) 0.141	Br-N +0.046 O-Br +0.058 C-Br (σ bond) -0.081
 **10a-Ms-TS-S**	Cl-N (bcp) 0.058	Cl-N +0.113
 **10a-IM**	Cl-N (bcp) 0.121	Cl-N +0.105
 **10b-Ms-TS-S**	Cl-N (bcp1) 0.088 O-Cl (bcp2) 0.017	Cl-N +0.118 O-Cl +0.064

species	electron density $\rho(\mathbf{r})_b$ (e/bohr^3)	Laplacian of electron density (e/bohr^5)
 **10b-IM**	Cl-N (bcp1) 0.147 O-Cl (bcp2) 0.017 C-Cl (σ bond) 0.181	Cl-N +0.060 O-Cl +0.063 C-Cl (σ bond) -0.203
 **13a-Ms-TS-S**	$(CH_3)O$-N (bcp_1) 0.092 (CH_3)-O 0.210	$(CH_3)O$-N +0.194 (CH_3)-O -0.287
 **13a-IM**	$(CH_3)O$-N (bcp_1) 0.179 (CH_3)-O 0.202	$(CH_3)O$-N +0.160 (CH_3)-O -0.233
 **13c-Ms-TS-S**	$(CH_3)O$-N (bcp_1) 0.096 $(NO_2)O$-$CH_3(OCH_3)$ (bcp_2) 0.016 (CH_3)-O 0.195	$(CH_3)O$-N +0.196 $(NO_2)O$-$CH_3(OCH_3)$ +0.063 (CH_3)-O -0.214
 **13c-IM**	$(CH_3)O$-N (bcp_1) 0.182 $(NO_2)O$-$CH_3(OCH_3)$ (bcp_2) 0.018 $C(H_3)$ - O (σ bond) 0.181	$(CH_3)O$-N +0.151 $(NO_2)O$-$CH_3(OCH_3)$ +0.068 $C(H_3)$ - O (σ bond) -0.159

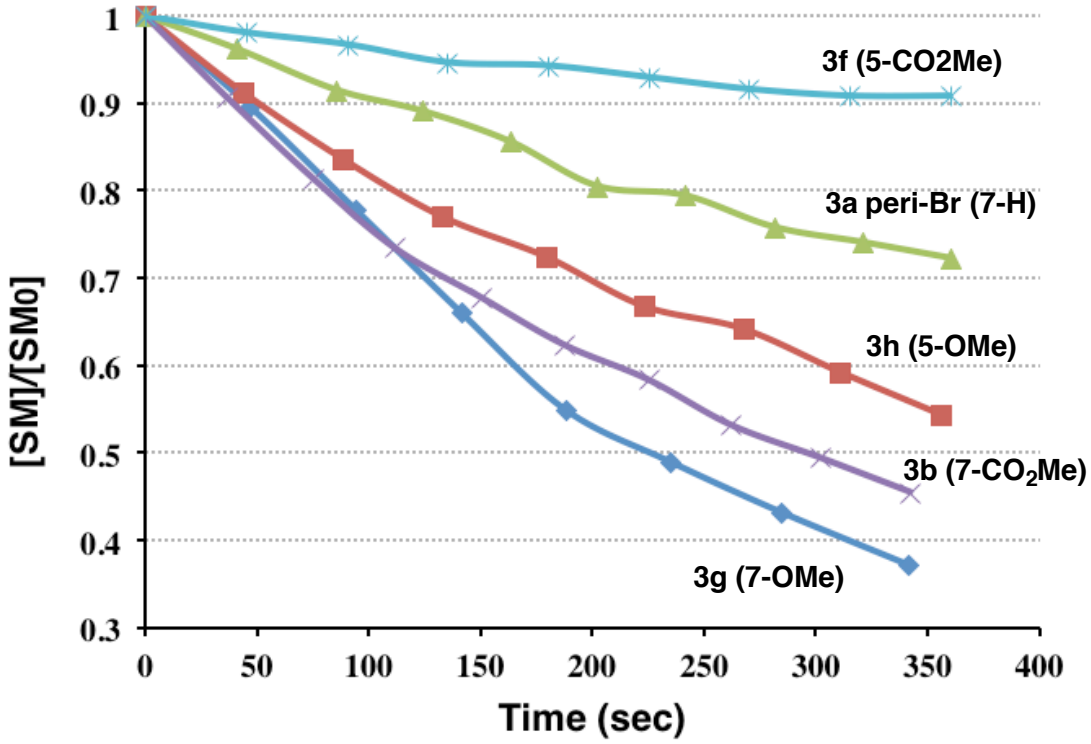
a) For the definition of bond critical points (bcp), see **Figure 8 and Figure S16**.

Full description of *Peri*-chloro-7-ester Derivative: In a similar manner to the *peri*-Br case, QTAIM analysis again identified the presence of secondary interaction involving the third neighboring group (7-ester), i.e., bcp1 between the *peri*-chloride atom and the nitrogen atom and bcp2 between the *peri*-chloride atom and the ester oxygen atom in TS and intermediate **10b-IM** (**Figure 8(b)**), indicating that the three adjacent heteroatoms (O, Cl and N) are interacting simultaneously in the TS and the intermediate (**Figure 1(b)**, **B2**; see also **Table 3**). The interactions in the O --- Cl --- N system are nonequivalent: a larger electron density $\rho(\mathbf{r})_b$ value (0.147 e/bohr^3) at the former bcp1 (Cl --- N) and a small $\rho(\mathbf{r})_b$ value (0.017 e/bohr^3) at the latter bcp2 (O – Cl) were calculated, the former primary interaction being stronger than the latter secondary interaction, and in fact as strong as covalent σ bonding (e.g., C-Cl in **10b-IM**: $\rho(\mathbf{r})_b$=

0.181 e/bohr^3) (**Figure 8(b)**). The former bcp1 (Cl -- N) of **10b-IM** has a larger electron density than that of the 7-unsubstituted **10a-IM** (**Table S11** and **Figure S16**), indicating that the bonding nature of Cl – N is enforced by the presence of another neighboring group (the 7-ester group). Small positive values of the Laplacians of the electron density ($\nabla^2\rho(\mathbf{r})$) (+0.060 e/bohr^5 (Cl – N) and +0.063 e/bohr^5 (O – Cl)) at the relevant regions of **10b-IM** were found, providing a sharp contrast to large negative values of covalent σ bonding (e.g., C-Cl in **10b-IM**: $\nabla^2\rho(\mathbf{r})$= -0.203 e/bohr^5) (**Table S11**). The bonding nature of O --- Cl, that is, a small electron density and a positive small Laplacian of the electron density, is consistent with that of halogen bonding, in a similar manner to the *peri*-Br case (**3b-IM**).[22] Therefore, substitution of the 7-ester group increased the electron density between the *peri*-halogen and N atoms, which will lead to lower activation energies and stabilization of the subsequent intermediates. This cannot be simply described in terms of the resonance structures shown in **Figure 1**.

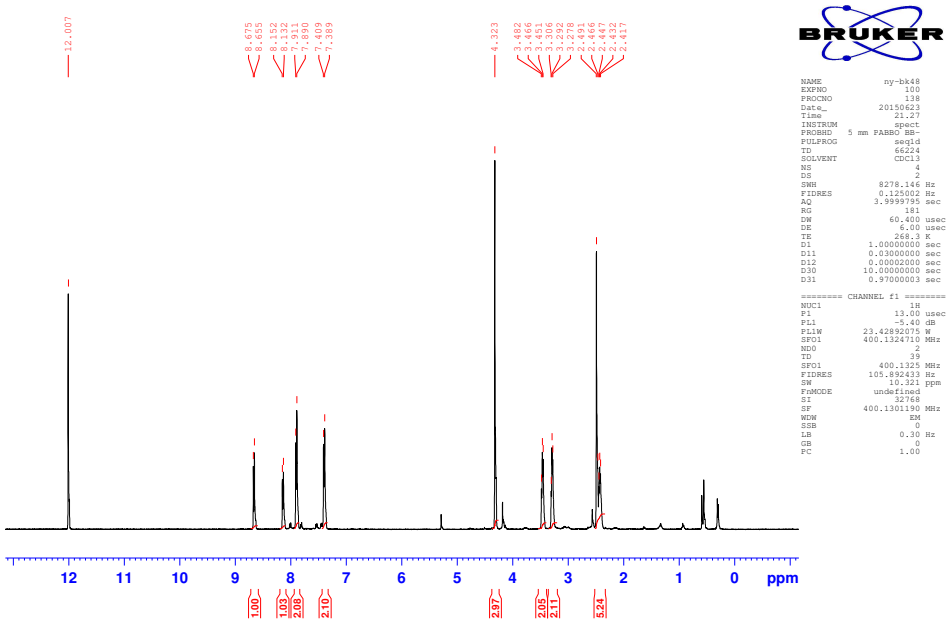
III. Kinetic study of *peri*-Br compounds.

Figure S1 Kinetic study of *peri*-Br compounds



IV. Characterization of 3b-IM in TFA solution: Supporting spectra.

(a) ^{1}H NMR spectrum of 3b-IM in TFA-d (full range)



(b) ^{13}C NMR spectrum of 3b-IM in TFA-d at -12 °C

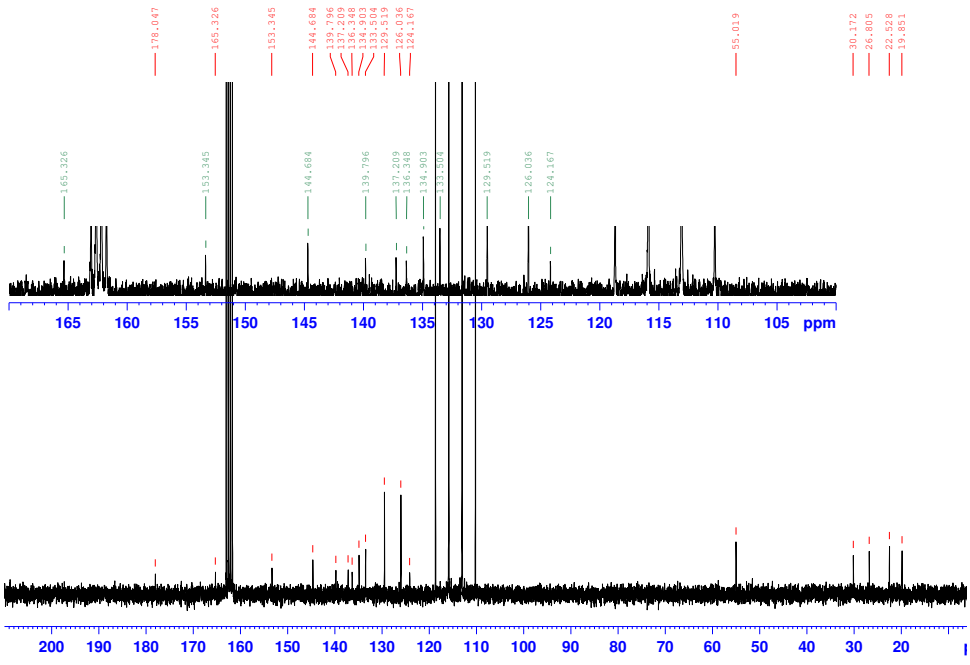


Figure S2. ^{1}H NMR (a) and ^{13}C-NMR (b) spectra of 3b-IM in TFA-*d* (chemical shift calibrated by CH_2Cl_2 in capillary) at -12 °C

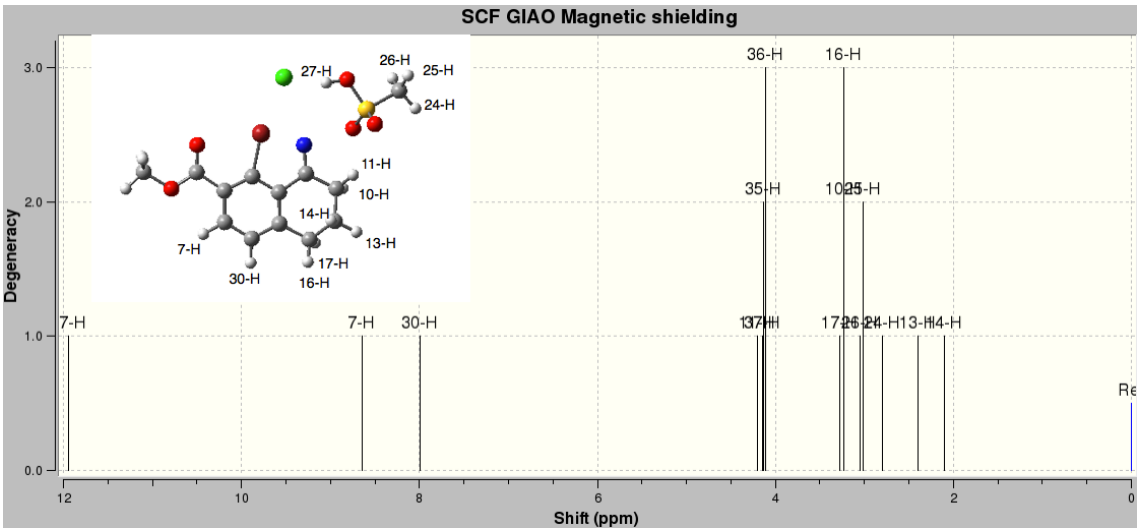


Figure S3. Calculated ^{1}H NMR spectrum for intermediate **3b-IM**. TMS is used as internal reference. The computation results are in good consistence with *in situ* measured chemical shifts shown in **Figure S2(a)**.

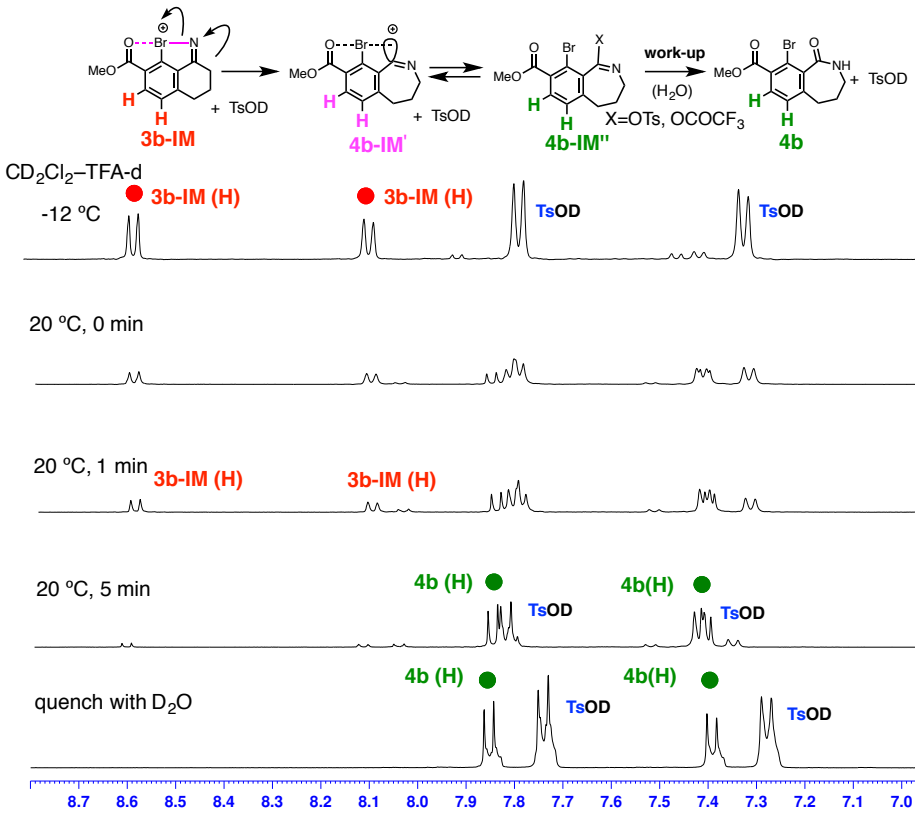


Figure S4. Transformation of **3b-IM** into the alkyl migration product **4b** at 20 °C.

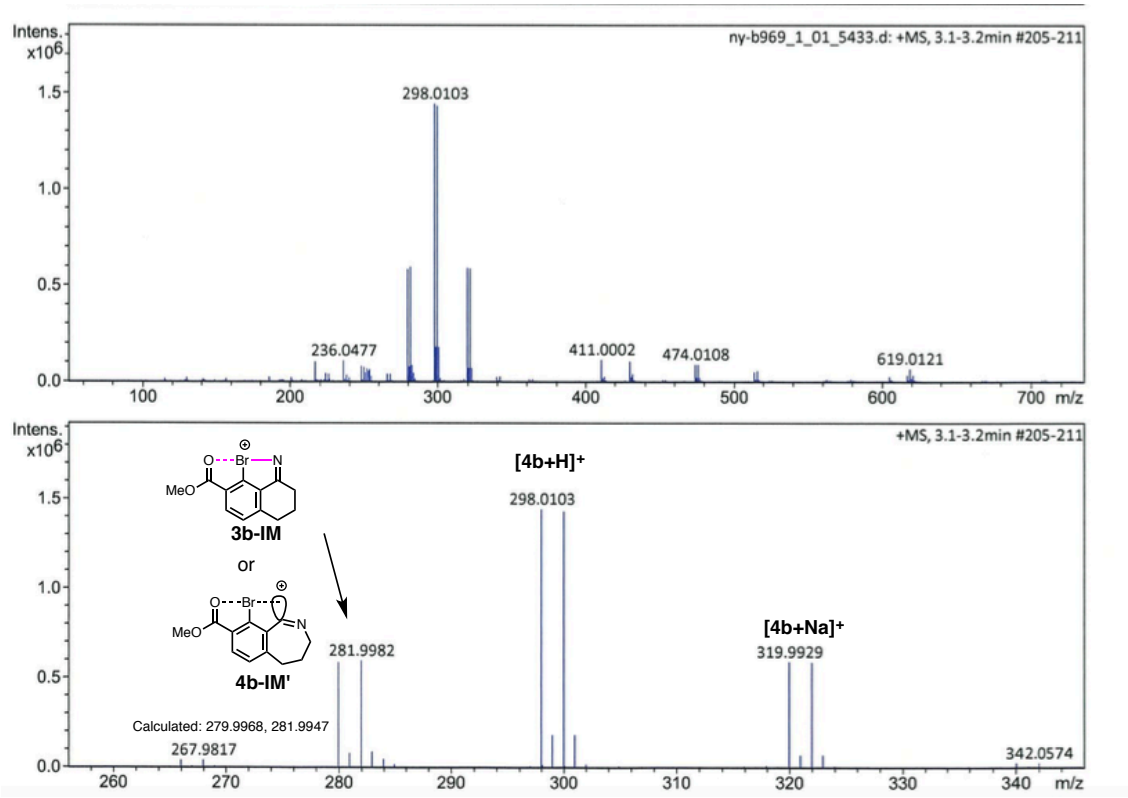
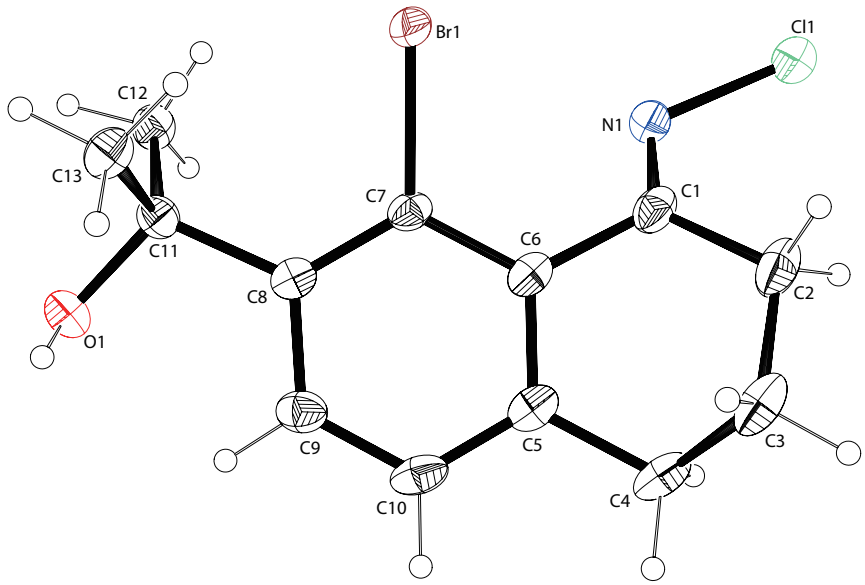


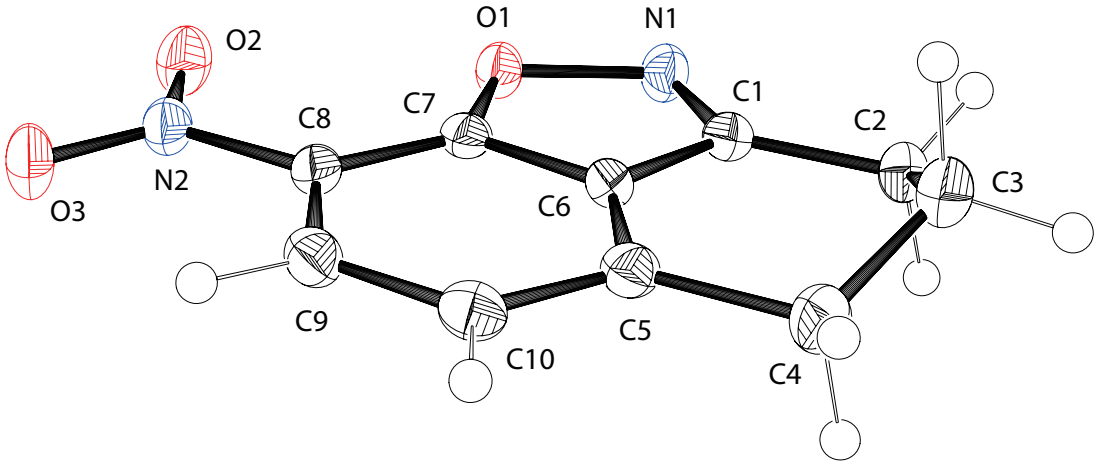
Figure S5. High-resolution mass spectra of **3b** in TFA, reacted at -10 ºC for 1hr. The spectrum suggest the clevage of N-O bond and a peak corresponding to **3b-IM** or **4b-IM'** was observed, accompanied with that of the alkyl migration product **4b**.

V. Crystal structures of 7 and 16c.



7

Figure S6. Crystal Structure of 7



16c

Figure S7. Crystal Structure of 16c.

VI. Kinetic study of *peri*-OMe compounds

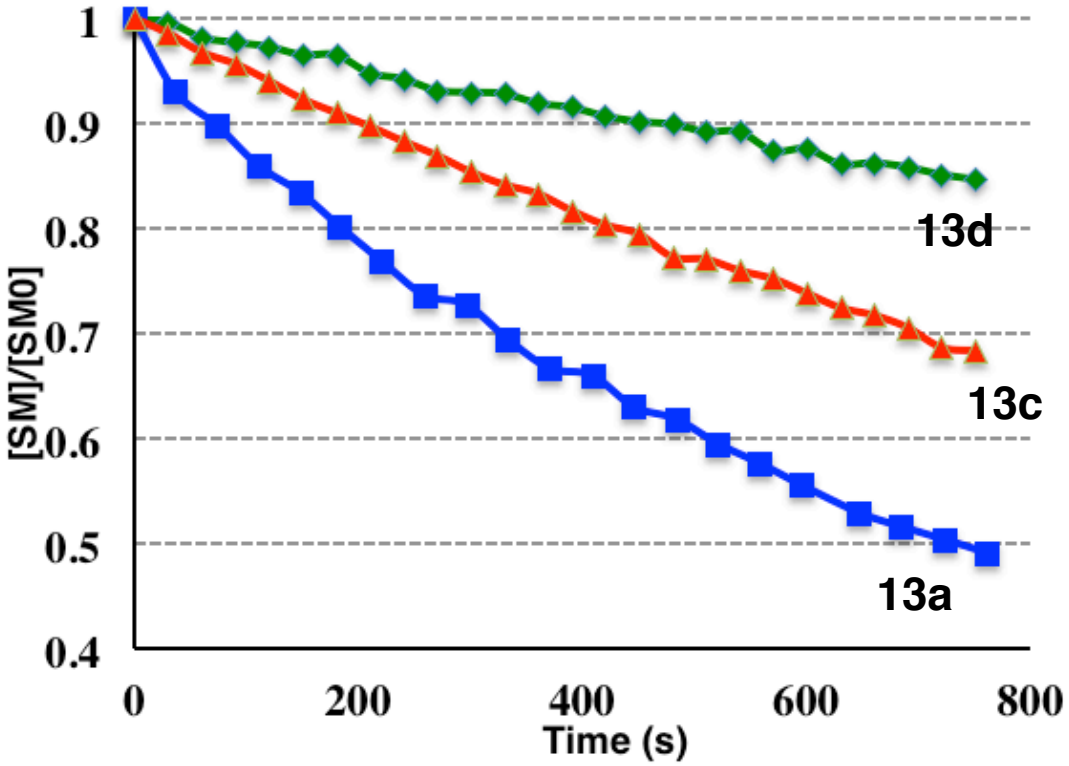


Figure S8. Substituent effects on the reaction rate of 8-methoxytetralone oxime derivatives. Consumption profile of the starting oxime derivatives.

VII. Computational study

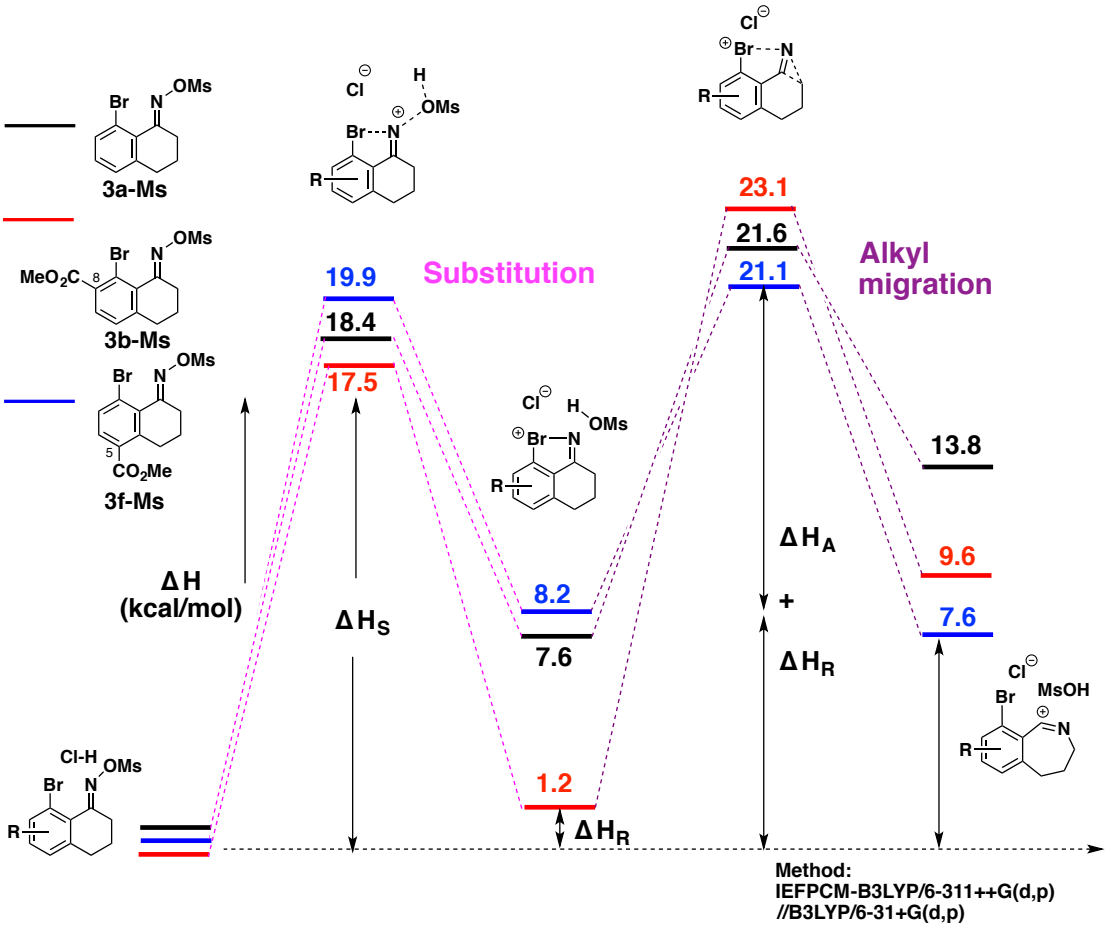


Figure S9. Reaction diagrams for alkyl migration step of CO_2Me-substituted *peri*-Br oxime derivatives 3

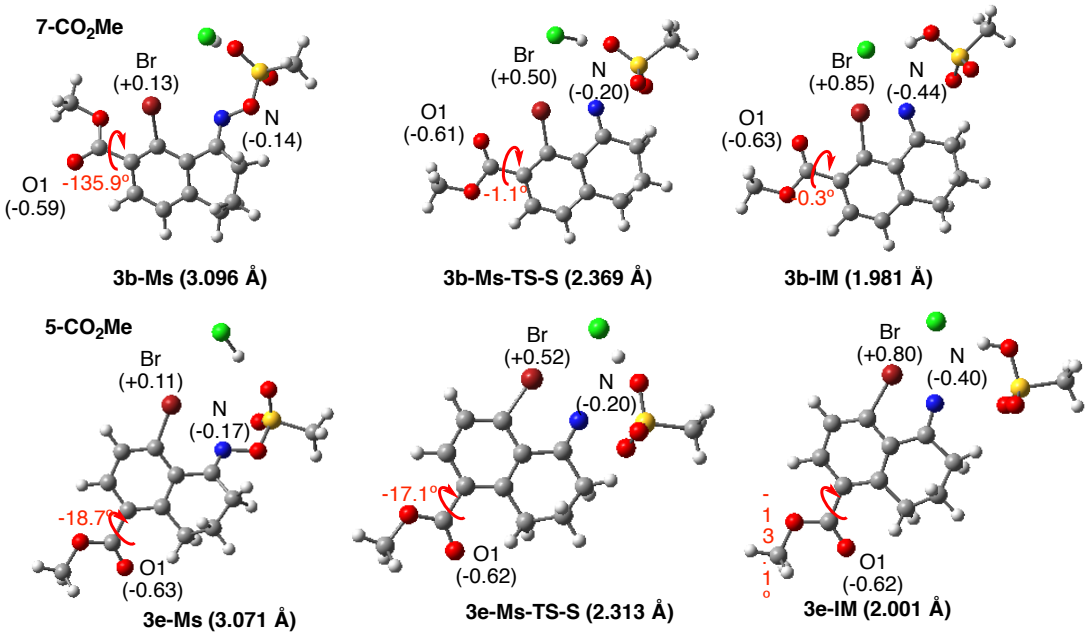


Figure S10. Front view for calculated structures and NPA charges of the reactant, TS of the substitution process, and the resultant intermediate in the substitution of 7-CO_2Me-substituted *peri*-Br compound (**3b-Ms**, top) and 5-CO_2Me-*peri*-Br compound (**3e-Ms**, bottom) (Br-N distance is shown in parentheses).

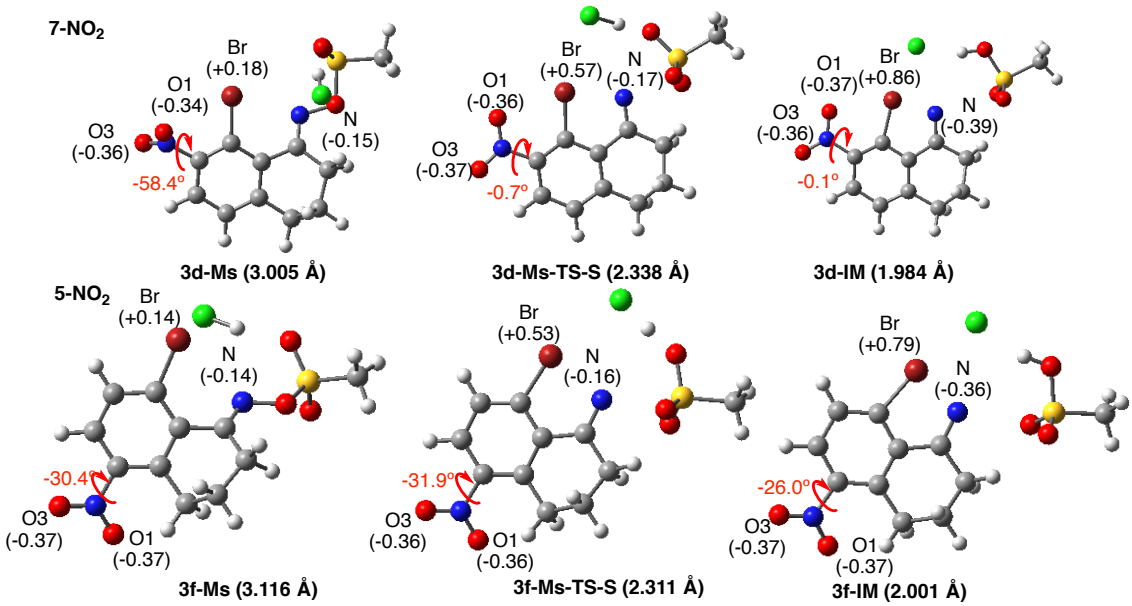


Figure S11. Front view for calculated structures and NPA charges of the reactant, TS of the substitution process, and the resultant intermediate in the substitution of 7-NO_2-*peri*-Br compound (**3d-Ms**, top) and 5-NO_2-*peri*-Br compound (**3f-Ms**, bottom) (Br-N distance is shown in parentheses).

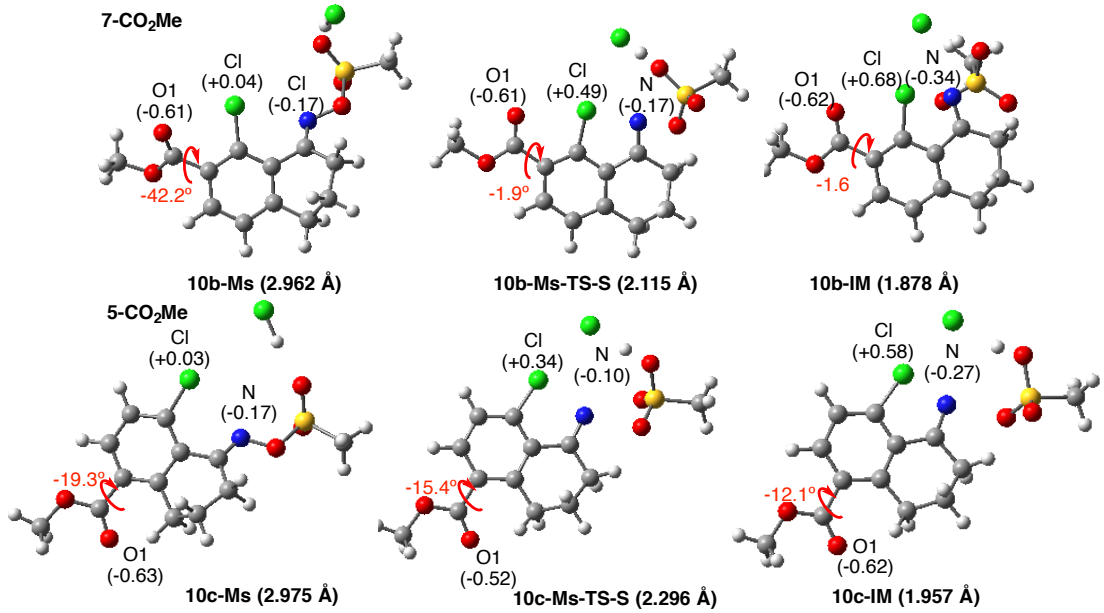


Figure S12. Front view for calculated structures and NPA charges of the reactant, TS of the substitution process, and the resultant intermediate in the substitution of 7-CO_2Me-substituted *peri*-Cl compound (**10b-Ms**, top), 5-CO_2Me-*peri*-Cl compound (**10c-Ms**, bottom) (Cl-N distance is shown in parentheses).

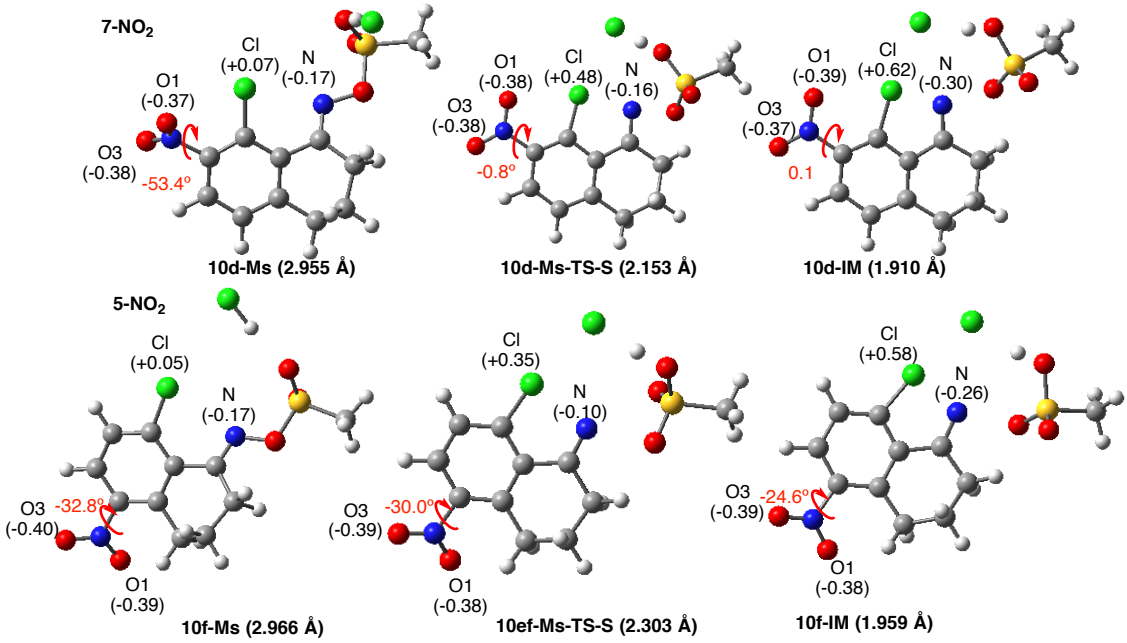


Figure S13. Front view for calculated structures and NPA charges of the reactant, TS of the substitution process, and the resultant intermediate in the substitution of 7-NO_2-substituted *peri*-Cl compound (**10d-Ms**, top), 5-NO_2-*peri*-Cl compound (**10f-Ms**, bottom) (Cl-N distance is shown in parentheses).

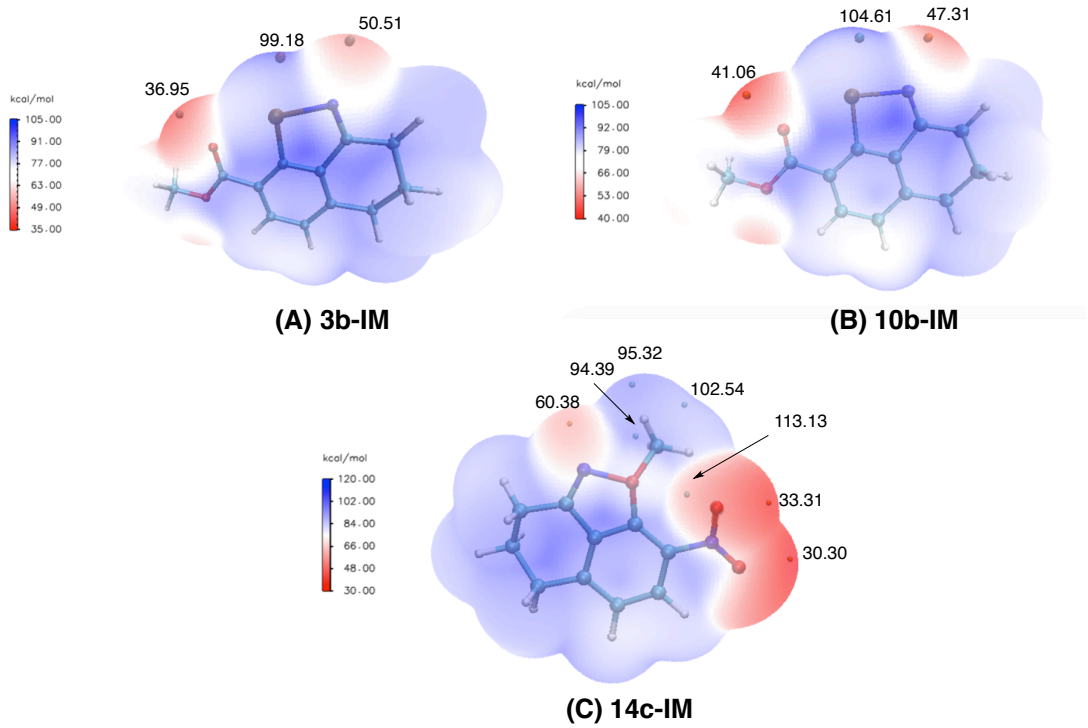
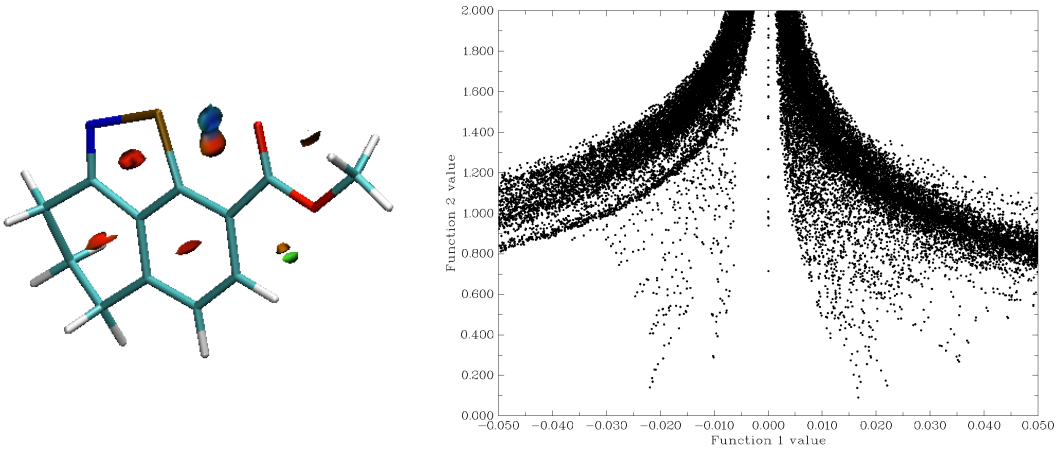
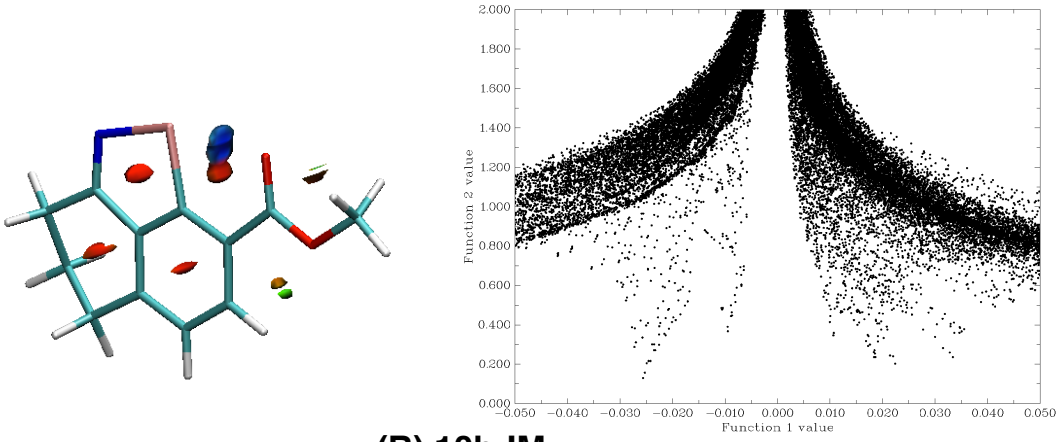


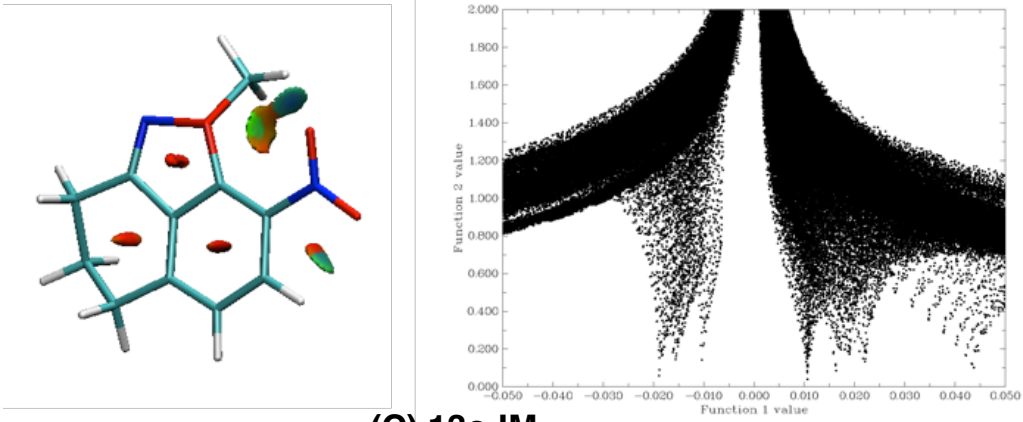
Figure S14. Electron static potential of cationic intermediate **3b-IM (A)**, **10b-IM (B) and 14c-IM (C)** on 0.001 electrons/bohr^3 surface. Selected local minimums (orange balls) and local maximums (cyan balls) are shown.



(A) 3b-IM



(B) 10b-IM



(C) 13c-IM

Figure S15. Gradient isosurfaces (s = 0.5 au, left) and plot of the reduced density gradients versus sign(λ_2)ϱ (right) for 3b-IM (A, top), 10b-IM (B, middle) and 13c-IM (C, bottom).

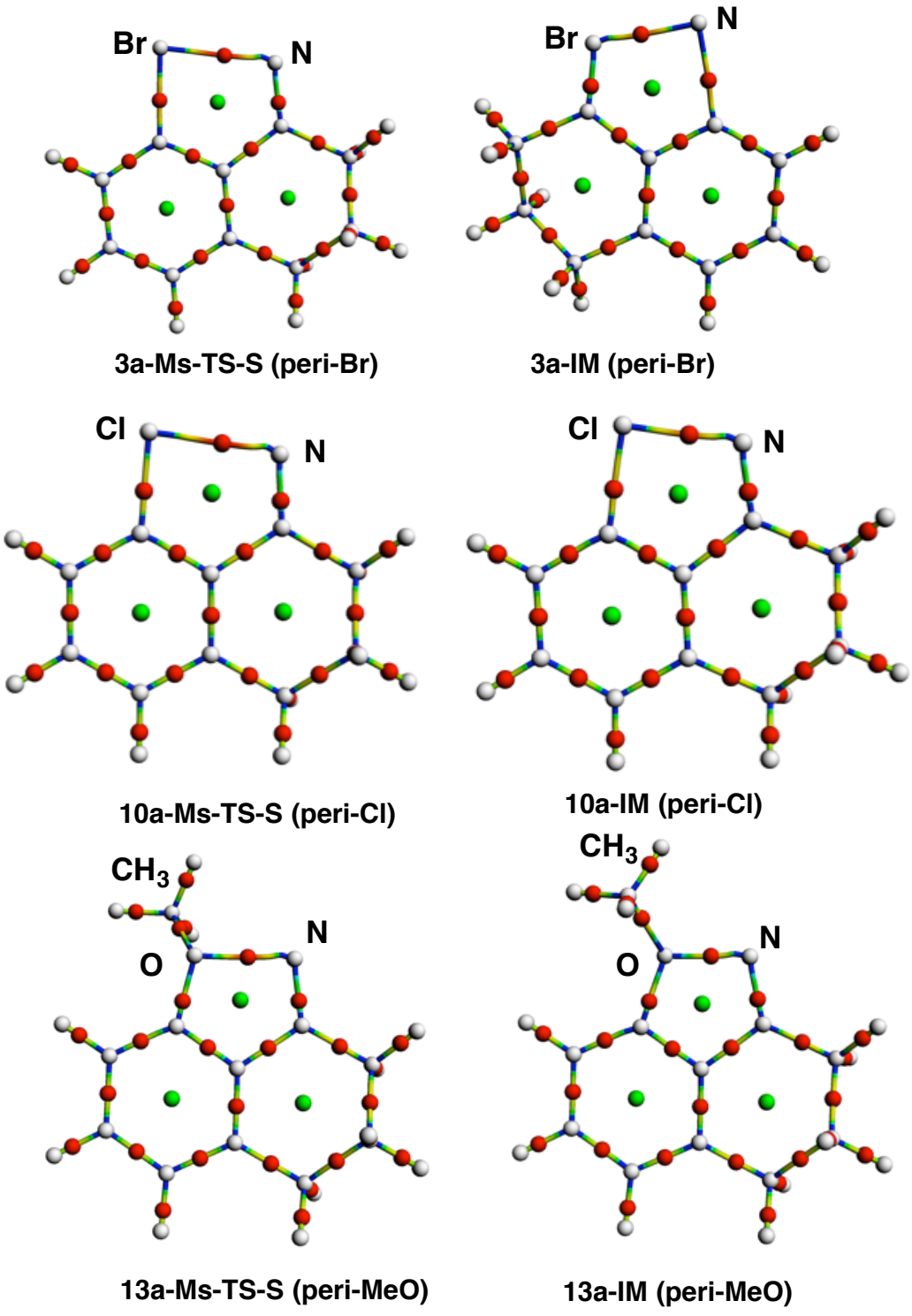


Figure S16. Molecular Graph of TS and Intermediates for Substitution Process (Calculations were done after omitting counter anions). See Table 4 in the Text.

VIII Computational Studies

Energy profiles of reactions:

We carried out computational studies by using Gaussian 09suites of programe[1]. The geometries of the reactant complexes (Rs), intermediates (IMs), transition states (TSs), and products (Ps) for aromatic Beckmann rearrangement nucleophilic substitution of halogen atom onto the N atom of the oxime bearing a OMs group (reaction S), and subsequent alkyl migration (reaction A) were fully optimized using the B3LYP/6-31G+(d,p) level. Harmonic vibrational frequency computations characterized the optimized structures. Intrinsic reaction coordinate (IRC) computations of the transition structures verified the reactants, intermediates, and products on the potential energy surface (PES). Bulk solvation effects (self-consistent reaction field, SCRF) were simulated by the IEFPCM method in formic acid with the Gaussian 09 suites of programs. All the Single point energies were calculated with B3LYP/6-311++G (d, p) on the basis of the B3LYP/6-31+G(d,p) optimized structures. The energies were corrected with the zero-point-energies without scailing, obtained in the geometry optimization steps.

All the natural population analyses (NPA)[2] were carried out on the above mentioned structures at B3LYP/6-311++G (d, p) level.

Population analysis (CHelpg charges[3] and Hirshfeld charges[4]) was calculated at B3LYP/6-311++G (d, p) level with Multiwfn.

Electrostatic potential surface and reduced density gradient[5] were generated with Multiwfn[6] and visualized with VMD.[7]

Basin analysis with Atoms in molecular theory was performed at B3LYP/TZVP level with ADF.[8, 9]

Structures of *peri*-Br compounds in TSs and IMs for substitution reaction

3a-Ms-TS-S

Zero-point correction= 0.224071 (Hartree/Particle)
HF=-4137.4440199 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.386062	0.547637	0.724188
2	6	0	4.170162	-0.803428	0.512474
3	6	0	2.930066	-1.284192	0.117360
4	6	0	1.900770	-0.362404	-0.070303
5	6	0	2.136104	0.989034	0.158757
6	6	0	3.365096	1.468495	0.550730
7	1	0	5.362531	0.892424	1.029012
8	1	0	4.980056	-1.503204	0.656488
9	1	0	3.524894	2.520597	0.720258
10	6	0	0.546640	-0.769302	-0.465869
11	6	0	0.314930	-2.237004	-0.749756
12	1	0	-0.121412	-2.636313	0.169147
13	1	0	-0.450826	-2.313786	-1.509406
14	6	0	1.595981	-2.943087	-1.137717
15	1	0	1.373347	-4.001944	-1.253829
16	1	0	1.944375	-2.583983	-2.106728
17	6	0	2.678919	-2.742381	-0.100613
18	1	0	2.369811	-3.192718	0.845580
19	1	0	3.605552	-3.230960	-0.394351
20	7	0	-0.403953	0.066646	-0.558784
21	8	0	-2.178083	-1.131126	-0.937042
22	16	0	-2.763772	-1.084813	0.440368
23	8	0	-1.959289	-1.826440	1.405068
24	8	0	-3.089960	0.294347	0.853760
25	6	0	-4.319396	-1.911708	0.281744
26	1	0	-4.137797	-2.935255	-0.025202
27	1	0	-4.801903	-1.883918	1.252862
28	1	0	-4.914504	-1.385332	-0.455441
29	1	0	-2.730478	1.607748	0.076900
30	17	0	-2.452088	2.792657	-0.489501
31	35	0	0.637614	2.047365	-0.094813

3a-IM

Zero-point correction= 0.228893 (Hartree/Particle)
HF=-4137.4653059 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	-4.302091	0.821622	0.449155
3	6	0	-3.034469	1.323781	0.133043
4	6	0	-1.983494	0.403266	-0.039361
5	6	0	-2.228882	-0.968751	0.122354
6	6	0	-3.483754	-1.468617	0.437099
7	1	0	-5.519539	-0.909842	0.842042
8	1	0	-5.126513	1.516592	0.579809
9	1	0	-3.652287	-2.532578	0.556218
10	6	0	-0.605878	0.824614	-0.371999
11	6	0	-0.342754	2.321194	-0.557668
12	1	0	0.047285	2.668588	0.408681
13	1	0	0.469519	2.435235	-1.272106

14	6	0	-1.610040	3.073186	-0.970212
15	1	0	-1.377352	4.143256	-0.992418
16	1	0	-1.899115	2.789022	-1.989826
17	6	0	-2.772892	2.805445	-0.010890
18	1	0	-2.534459	3.220913	0.979134
19	1	0	-3.685360	3.307927	-0.348403
20	7	0	0.347575	-0.018199	-0.487996
21	8	0	2.232785	1.148430	-0.967892
22	16	0	2.954310	1.034109	0.364599
23	8	0	2.286962	1.783129	1.451506
24	8	0	3.278336	-0.399665	0.716633
25	6	0	4.560955	1.799219	0.066551
26	1	0	4.397856	2.846804	-0.189042
27	1	0	5.137250	1.709675	0.988765
28	1	0	5.048495	1.265751	-0.749816
29	1	0	2.762451	-1.606675	0.112459
30	17	0	2.339970	-2.854162	-0.366107
31	35	0	-0.684695	-2.037845	-0.110294

3b-Ms-TS-S

Zero-point correction= 0.267526 (Hartree/Particle)
HF=-4365.3305865 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.528036	1.684574	0.331761
2	6	0	-2.711847	2.808300	0.291626
3	6	0	-1.336752	2.700399	0.053220
4	6	0	-0.793560	1.416632	-0.154933
5	6	0	-1.630615	0.288227	-0.099113
6	6	0	-3.005210	0.394957	0.136876
7	1	0	-4.590699	1.790033	0.514362
8	6	0	0.656012	1.216374	-0.413127
9	6	0	1.540089	2.461538	-0.501856
10	1	0	2.005131	2.562889	0.488094
11	1	0	2.351173	2.246154	-1.193507
12	6	0	0.751766	3.710728	-0.892871
13	1	0	1.425947	4.572137	-0.839721
14	1	0	0.412970	3.634783	-1.933856
15	6	0	-0.451280	3.922492	0.026555
16	1	0	-0.100456	4.124664	1.049419
17	1	0	-1.040678	4.793210	-0.278935
18	7	0	1.164493	0.048005	-0.541245
19	8	0	3.312807	0.319889	-0.846500
20	16	0	3.888565	-0.084233	0.510879
21	8	0	3.581133	0.901243	1.572022
22	8	0	3.559918	-1.505335	0.864666
23	6	0	5.672480	-0.059434	0.233225
24	1	0	5.966335	0.957913	-0.027273
25	1	0	6.145580	-0.373374	1.165225
26	1	0	5.904320	-0.755494	-0.573341
27	1	0	2.586960	-2.502821	0.113205
28	17	0	1.773208	-3.441549	-0.431510
29	35	0	-0.709741	-1.336450	-0.345732
30	1	0	-3.145960	3.791478	0.447041
31	6	0	-3.887214	-0.808252	0.182708
32	8	0	-3.502420	-1.949290	0.007861
33	8	0	-5.169049	-0.489956	0.441565

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  34   6   0   -6.090631 -1.600720  0.509181
  35   1   0   -5.790534 -2.290739  1.300406
  36   1   0   -7.059307 -1.154389  0.729102
  37   1   0   -6.113221 -2.129978 -0.445707
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3b-IM

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Zero-point correction=  0.271604 (Hartree/Particle)
HF=-4365.3575584 NIMAG=0
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 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
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  1  6  0  -3.572210  1.666082  0.337863
  2  6  0  -2.763673  2.798518  0.305332
  3  6  0  -1.387950  2.700367  0.070788
  4  6  0  -0.849409  1.417988 -0.137935
  5  6  0  -1.672951  0.288199 -0.088222
  6  6  0  -3.043860  0.378203  0.141414
  7  1  0  -4.636541  1.763715  0.515964
  8  6  0  0.576188  1.182779 -0.403934
  9  6  0  1.494725  2.400467 -0.498633
  10  1  0  1.975717  2.486756  0.485599
  11  1  0  2.297063  2.169967 -1.196378
  12  6  0  0.722962  3.670528 -0.874913
  13  1  0  1.413072  4.518349 -0.813804
  14  1  0  0.383527  3.611594 -1.916837
  15  6  0  -0.480972  3.906360  0.043282
  16  1  0  -0.129889  4.102880  1.067097
  17  1  0  -1.052414  4.787933 -0.265559
  18  7  0  1.042374 -0.005110 -0.543078
  19  8  0  3.398978  0.326665 -0.887415
  20 16  0  3.919266 -0.052501  0.470383
  21  8  0  3.595280  0.929023  1.535627
  22  8  0  3.560993 -1.478892  0.849795
  23  6  0  5.711916 -0.058071  0.263956
  24  1  0  6.016398  0.954422 -0.004809
  25  1  0  6.167531 -0.362224  1.207506
  26  1  0  5.957717 -0.761659 -0.532185
  27  1  0  2.684856 -2.390061  0.157989
  28 17  0  1.836169 -3.384707 -0.387095
  29 35  0  -0.676315 -1.304911 -0.342798
  30  1  0  -3.208105  3.776725  0.462672
  31  6  0  -3.900490 -0.837827  0.173144
  32  8  0  -3.478405 -1.966477 -0.009305
  33  8  0  -5.185349 -0.545809  0.424858
  34  6  0  -6.096932 -1.665696  0.481859
  35  1  0  -5.793097 -2.356734  1.270627
  36  1  0  -7.070252 -1.229366  0.700470
  37  1  0  -6.110348 -2.188054 -0.476884
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3c-Ms-TS-S

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Zero-point correction=  0.226942 (Hartree/Particle)
HF=-4341.9410443 NIMAG=1
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 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
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3	6	0	-1.881627	2.411361	0.048270
4	6	0	-1.195697	1.197459	-0.153739
5	6	0	-1.877601	-0.028323	-0.050112
6	6	0	-3.241353	-0.046052	0.236685
7	1	0	-4.986643	1.114492	0.644992
8	6	0	0.258147	1.164898	-0.456941
9	6	0	0.995780	2.501336	-0.548040
10	1	0	1.438421	2.659015	0.444991
11	1	0	1.832051	2.376536	-1.232603
12	6	0	0.064171	3.643259	-0.953839
13	1	0	0.629898	4.580578	-0.919599
14	1	0	-0.269019	3.509574	-1.990950
15	6	0	-1.149804	3.729244	-0.027967
16	1	0	-0.819261	4.002713	0.985522
17	1	0	-1.843218	4.514083	-0.349712
18	7	0	0.887711	0.061614	-0.608399
19	8	0	3.030921	0.565217	-0.896824
20	16	0	3.576823	0.257925	0.492463
21	8	0	3.130317	1.222901	1.516627
22	8	0	3.384703	-1.183859	0.872251
23	6	0	5.357610	0.451857	0.281002
24	1	0	5.565385	1.485651	-0.000331
25	1	0	5.832424	0.212113	1.234719
26	1	0	5.692404	-0.236130	-0.496743
27	1	0	2.563413	-2.211612	0.102868
28	17	0	1.830991	-3.235082	-0.462166
29	35	0	-0.758324	-1.527704	-0.290454
30	1	0	-3.793350	3.292511	0.486528
31	7	0	-4.013624	-1.295571	0.349440
32	8	0	-5.207875	-1.193406	0.615831
33	8	0	-3.424060	-2.359978	0.169679

3c-IM

Zero-point correction= 0.231273 (Hartree/Particle)

HF=-4341.9691464 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.072915	1.060208	0.381190
2	6	0	-3.446099	2.308324	0.307265
3	6	0	-2.068120	2.418457	0.081642
4	6	0	-1.345832	1.219607	-0.084872
5	6	0	-1.967633	-0.029875	-0.007760
6	6	0	-3.332955	-0.116980	0.227042
7	1	0	-5.140043	0.981427	0.556248
8	6	0	0.086158	1.184957	-0.339717
9	6	0	0.890212	2.432538	-0.437414
10	1	0	1.318247	2.602229	0.562312
11	1	0	1.764826	2.275653	-1.082375
12	6	0	-0.024456	3.597416	-0.866034
13	1	0	0.541167	4.532140	-0.817090
14	1	0	-0.324504	3.467791	-1.913660
15	6	0	-1.289850	3.716574	0.014334
16	1	0	-0.992182	3.982716	1.039824
17	1	0	-1.937773	4.524111	-0.341392
18	7	0	0.643061	0.032685	-0.458981
19	8	0	3.287045	0.595901	-1.009417
20	16	0	3.746756	0.240522	0.347901

21	8	0	3.262605	1.105713	1.446431
22	8	0	3.442135	-1.260916	0.704209
23	6	0	5.543250	0.259784	0.421327
24	1	0	5.860995	1.287522	0.236447
25	1	0	5.858317	-0.069564	1.411451
26	1	0	5.928040	-0.407700	-0.351460
27	1	0	2.771475	-1.804684	0.151139
28	17	0	1.700880	-2.836053	-0.484569
29	35	0	-0.664326	-1.463120	-0.255703
30	1	0	-4.046273	3.204490	0.431871
31	7	0	-3.984729	-1.426507	0.310263
32	8	0	-5.193000	-1.466749	0.514147
33	8	0	-3.255386	-2.417912	0.169200

3d-Ms-TS-S

Zero-point correction= 0.225643 (Hartree/Particle)
HF=-4341.9409653 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.665273	1.440667	-0.396371
2	6	0	-3.690957	0.057313	-0.208004
3	6	0	-2.549624	-0.696115	0.118284
4	6	0	-1.340609	0.029567	0.216132
5	6	0	-1.319758	1.415508	-0.005067
6	6	0	-2.466983	2.136358	-0.305963
7	1	0	-4.593278	1.953298	-0.618255
8	1	0	-2.432286	3.206969	-0.470909
9	6	0	-0.044738	-0.631132	0.518174
10	6	0	-0.044086	-2.146693	0.710989
11	1	0	0.164914	-2.568350	-0.281598
12	1	0	0.799069	-2.409745	1.345702
13	6	0	-1.384657	-2.616397	1.266865
14	1	0	-1.367484	-3.709344	1.340467
15	1	0	-1.521804	-2.232828	2.286045
16	6	0	-2.557293	-2.187627	0.384741
17	1	0	-2.520600	-2.712504	-0.579281
18	1	0	-3.506049	-2.482003	0.836966
19	7	0	1.044195	0.029754	0.581025
20	8	0	2.717135	-1.403912	0.948538
21	16	0	3.339866	-1.414304	-0.434747
22	8	0	2.463187	-1.973968	-1.476545
23	8	0	3.947651	-0.068356	-0.796637
24	6	0	4.775875	-2.485922	-0.253691
25	1	0	4.426824	-3.488215	0.000720
26	1	0	5.305417	-2.495115	-1.208454
27	1	0	5.412407	-2.083035	0.535180
28	1	0	3.623756	1.093455	-0.229999
29	17	0	3.394710	2.464771	0.260702
30	35	0	0.396286	2.209409	0.110172
31	7	0	-5.010620	-0.581472	-0.382019
32	8	0	-5.040000	-1.756414	-0.745084
33	8	0	-6.002380	0.114488	-0.175044

3d-IM

Zero-point correction= 0.231124 (Hartree/Particle)
HF=-4341.9640082 NIMAG=0

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	-3.684656	1.447614	-0.385181
2	6	0	-3.707986	0.062055	-0.208341
3	6	0	-2.565722	-0.698093	0.097372
4	6	0	-1.353622	0.023977	0.188809
5	6	0	-1.334954	1.411974	-0.018697
6	6	0	-2.483229	2.140749	-0.300508
7	1	0	-4.613100	1.965932	-0.592925
8	1	0	-2.448121	3.212632	-0.453967
9	6	0	-0.056896	-0.640114	0.475132
10	6	0	-0.063317	-2.150278	0.704759
11	1	0	0.152240	-2.597753	-0.275031
12	1	0	0.773814	-2.399551	1.352157
13	6	0	-1.409125	-2.609385	1.257715
14	1	0	-1.392497	-3.700898	1.343830
15	1	0	-1.553035	-2.214475	2.271291
16	6	0	-2.574458	-2.188813	0.361775
17	1	0	-2.524168	-2.713593	-0.601335
18	1	0	-3.526796	-2.485148	0.805201
19	7	0	1.038081	0.016594	0.512872
20	8	0	2.686184	-1.431804	0.935337
21	16	0	3.382461	-1.413331	-0.418103
22	8	0	2.542512	-1.948811	-1.507821
23	8	0	4.000383	-0.062913	-0.718859
24	6	0	4.800865	-2.504635	-0.202449
25	1	0	4.428509	-3.507767	0.008088
26	1	0	5.364018	-2.487056	-1.136845
27	1	0	5.403424	-2.124892	0.622820
28	1	0	3.659719	1.172213	-0.187734
29	17	0	3.419850	2.506367	0.261774
30	35	0	0.381417	2.192002	0.102471
31	7	0	-5.028296	-0.579221	-0.367574
32	8	0	-5.061569	-1.724889	-0.816490
33	8	0	-6.017552	0.085096	-0.059918

3e-Ms-TS-S

Zero-point correction= 0.256800 (Hartree/Particle)
HF=-4251.9727729 NIMAG=1

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	-4.083011	0.806710	0.433188
2	6	0	-3.495101	2.070236	0.331251
3	6	0	-2.139575	2.239540	0.044784
4	6	0	-1.374886	1.075172	-0.150514
5	6	0	-1.964729	-0.185913	-0.043282
6	6	0	-3.319134	-0.354283	0.249904
7	1	0	-5.141361	0.731498	0.655416
8	1	0	-4.116624	2.948993	0.481327
9	6	0	0.070111	1.115220	-0.456837
10	6	0	0.740341	2.488826	-0.540495
11	1	0	1.159698	2.666071	0.459192
12	1	0	1.590082	2.412213	-1.216207
13	6	0	-0.258240	3.573997	-0.952758
14	1	0	0.256352	4.540964	-0.920326
15	1	0	-0.574419	3.415641	-1.991808

16	6	0	-1.486423	3.600659	-0.037448
17	1	0	-1.180393	3.915928	0.971336
18	1	0	-2.215986	4.340807	-0.385459
19	7	0	0.756161	0.051603	-0.619038
20	8	0	2.964901	0.672175	-0.904161
21	16	0	3.473420	0.368736	0.487709
22	8	0	2.938669	1.271201	1.526802
23	8	0	3.357670	-1.098355	0.836654
24	6	0	5.250921	0.654100	0.371034
25	1	0	5.417794	1.704289	0.124658
26	1	0	5.693622	0.413795	1.339775
27	1	0	5.657006	0.005626	-0.406806
28	1	0	2.614853	-2.077622	0.090519
29	17	0	1.920719	-3.160507	-0.500546
30	35	0	-0.768111	-1.628542	-0.287794
31	8	0	-3.773474	-1.627077	0.328742
32	6	0	-5.145128	-1.841068	0.652224
33	1	0	-5.804663	-1.408605	-0.109938
34	1	0	-5.274668	-2.923384	0.674066
35	1	0	-5.390498	-1.422355	1.635634

3e-IM

Zero-point correction= 0.261386 (Hartree/Particle)

HF=-4251.994477 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.117235	0.796894	0.391364
2	6	0	-3.530140	2.063744	0.311363
3	6	0	-2.166888	2.239572	0.062873
4	6	0	-1.389198	1.079593	-0.116153
5	6	0	-1.979333	-0.184270	-0.027708
6	6	0	-3.342366	-0.358662	0.221088
7	1	0	-5.180626	0.716703	0.583655
8	1	0	-4.158584	2.939316	0.447924
9	6	0	0.065054	1.132112	-0.387491
10	6	0	0.714474	2.513927	-0.497947
11	1	0	1.139511	2.715063	0.494791
12	1	0	1.558243	2.435569	-1.179937
13	6	0	-0.293069	3.587527	-0.916428
14	1	0	0.214795	4.557654	-0.886582
15	1	0	-0.605923	3.423054	-1.955263
16	6	0	-1.522253	3.605145	-0.003694
17	1	0	-1.220469	3.912445	1.008328
18	1	0	-2.255550	4.342000	-0.348264
19	7	0	0.765549	0.069826	-0.509419
20	8	0	2.891830	0.712581	-0.893734
21	16	0	3.526109	0.376238	0.448001
22	8	0	3.045119	1.242562	1.546575
23	8	0	3.464395	-1.099376	0.753743
24	6	0	5.281027	0.718576	0.199971
25	1	0	5.395203	1.781022	-0.018104
26	1	0	5.794552	0.455132	1.126035
27	1	0	5.636474	0.105968	-0.628983
28	1	0	2.659777	-2.147622	0.080319
29	17	0	1.960284	-3.221184	-0.448175
30	35	0	-0.789522	-1.624941	-0.250268
31	8	0	-3.794109	-1.635332	0.277209

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  32   6   0   -5.176811 -1.866244  0.550649
  33   1   0   -5.810489 -1.433439 -0.232064
  34   1   0   -5.294552 -2.949430  0.557793
  35   1   0   -5.457995 -1.459910  1.528980
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3f-Ms-TS-S

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Zero-point correction=  0.266418 (Hartree/Particle)
HF=-4365.3274601 NIMAG=1
---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
 ---------------------------------------
  1  6  0  3.359051  1.505905  0.243742
  2  6  0  3.396104  0.118845  0.081713
  3  6  0  2.256405 -0.659453 -0.185644
  4  6  0  1.032734  0.045645 -0.253450
  5  6  0  1.001199  1.435607 -0.060897
  6  6  0  2.146735  2.182311  0.182761
  7  1  0  4.285612  2.038565  0.421438
  8  1  0  2.101342  3.255327  0.325191
  9  6  0  -0.262066 -0.638926 -0.498483
  10  6  0  -0.241031 -2.151321 -0.711385
  11  1  0  -0.424979 -2.590382  0.278604
  12  1  0  -1.091240 -2.419045 -1.333891
  13  6  0  1.095958 -2.598888 -1.294225
  14  1  0  1.091826 -3.691430 -1.367903
  15  1  0  1.208183 -2.213599 -2.315480
  16  6  0  2.278306 -2.152849 -0.433645
  17  1  0  2.259991 -2.667220  0.536196
  18  1  0  3.222740 -2.441706 -0.898391
  19  7  0  -1.366546  0.002600 -0.514926
  20  8  0  -3.004009 -1.470009 -0.877778
  21 16  0  -3.666080 -1.445506  0.493210
  22  8  0  -2.791069 -1.958099  1.566207
  23  8  0  -4.293974 -0.100508  0.794882
  24  6  0  -5.074555 -2.557982  0.325522
  25  1  0  -4.694435 -3.558477  0.116361
  26  1  0  -5.613658 -2.537233  1.273944
  27  1  0  -5.703195 -2.195342 -0.487900
  28  1  0  -3.983381  1.136804  0.240178
  29 17  0  -3.773553  2.466220 -0.229533
  30 35  0  -0.727381  2.192564 -0.145772
  31  6  0  4.785879 -0.530163  0.219239
  32  8  0  5.121334 -1.710341  0.128621
  33  8  0  5.756298  0.381682  0.480460
  34  6  0  7.029284 -0.258552  0.600901
  35  1  0  7.779493  0.475552  0.808692
  36  1  0  6.996323 -0.970605  1.398895
  37  1  0  7.264550 -0.759660 -0.314763
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3f-IM

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Zero-point correction=  0.271379 (Hartree/Particle)
HF=-4365.3503197 NIMAG=0
---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
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  1  6  0  3.580350  1.404134  0.206654
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2	6	0	3.590930	-0.002588	0.100586
3	6	0	2.382079	-0.716625	-0.068365
4	6	0	1.203147	0.051695	-0.092963
5	6	0	1.222057	1.438385	0.018647
6	6	0	2.401406	2.149388	0.168036
7	1	0	4.526760	1.918149	0.324102
8	1	0	2.423054	3.230305	0.254369
9	6	0	-0.138570	-0.510524	-0.224846
10	6	0	-0.307812	-2.009200	-0.338762
11	1	0	-0.457637	-2.389971	0.680572
12	1	0	-1.220177	-2.233599	-0.894503
13	6	0	0.954020	-2.612464	-0.972700
14	1	0	0.861242	-3.703223	-0.973977
15	1	0	1.018347	-2.301473	-2.023242
16	6	0	2.247614	-2.216833	-0.239975
17	1	0	2.277992	-2.684681	0.754246
18	1	0	3.118925	-2.610957	-0.764450
19	7	0	-1.182374	0.234929	-0.251301
20	8	0	-3.568563	-1.805890	-1.085729
21	16	0	-4.126589	-1.401265	0.214190
22	8	0	-3.264505	-1.542561	1.396650
23	8	0	-4.767614	0.065415	0.135167
24	6	0	-5.661412	-2.291604	0.490726
25	1	0	-5.399271	-3.347957	0.565916
26	1	0	-6.105746	-1.933689	1.419524
27	1	0	-6.320535	-2.114003	-0.359095
28	1	0	-4.112803	0.824139	0.016285
29	17	0	-3.224992	2.654180	-0.186671
30	35	0	-0.600163	2.139327	-0.058914
31	6	0	4.899188	-0.723635	0.196961
32	8	0	5.024739	-1.922108	0.368620
33	8	0	5.954022	0.112566	0.085363
34	6	0	7.255760	-0.498691	0.202712
35	1	0	7.966769	0.319970	0.099484
36	1	0	7.359725	-0.984430	1.175405
37	1	0	7.398814	-1.238346	-0.587993

3g-Ms-TS-S

Zero-point correction= 0.256702 (Hartree/Particle)
HF=-4251.9730233 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.892322	1.160512	0.449311
2	6	0	3.850544	-0.222179	0.233110
3	6	0	2.641959	-0.863792	-0.115421
4	6	0	1.489648	-0.075562	-0.217820
5	6	0	1.548152	1.308839	0.008544
6	6	0	2.734083	1.936490	0.339011
7	1	0	4.823493	1.649547	0.709187
8	1	0	2.775591	3.005421	0.515822
9	6	0	0.167525	-0.655630	-0.535754
10	6	0	0.079586	-2.173283	-0.710471
11	1	0	-0.176299	-2.561275	0.284738
12	1	0	-0.769357	-2.395560	-1.353752
13	6	0	1.398883	-2.740551	-1.236628
14	1	0	1.308537	-3.831766	-1.282886
15	1	0	1.568202	-2.392886	-2.263833

16	6	0	2.592201	-2.353756	-0.359055
17	1	0	2.530747	-2.871218	0.610051
18	1	0	3.533465	-2.677347	-0.812981
19	7	0	-0.882777	0.060911	-0.624185
20	8	0	-2.694676	-1.348539	-0.943264
21	16	0	-3.236950	-1.332958	0.468062
22	8	0	-2.347156	-1.973765	1.456290
23	8	0	-3.722534	0.040084	0.883314
24	6	0	-4.747325	-2.313587	0.365818
25	1	0	-4.479427	-3.331044	0.075140
26	1	0	-5.218034	-2.308910	1.350991
27	1	0	-5.406712	-1.860461	-0.375942
28	1	0	-3.417497	1.252170	0.216793
29	17	0	-3.197279	2.561035	-0.304706
30	35	0	-0.134144	2.175541	-0.145995
31	8	0	4.930951	-1.041376	0.334831
32	6	0	6.192279	-0.476125	0.673966
33	1	0	6.163968	-0.001911	1.662795
34	1	0	6.893906	-1.310963	0.692771
35	1	0	6.517020	0.256144	-0.075803

3g-IM

Zero-point correction= 0.261457 (Hartree/Particle)
HF=-4251.9941433 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.027486	1.076554	0.398526
2	6	0	3.937760	-0.311312	0.205789
3	6	0	2.699885	-0.923793	-0.081433
4	6	0	1.578537	-0.091742	-0.148578
5	6	0	1.687113	1.298118	0.052282
6	6	0	2.898100	1.903829	0.325236
7	1	0	4.985001	1.535445	0.612128
8	1	0	2.994244	2.972131	0.482586
9	6	0	0.224658	-0.572431	-0.408421
10	6	0	0.005413	-2.065944	-0.603366
11	1	0	-0.251071	-2.458649	0.390611
12	1	0	-0.875166	-2.252160	-1.224969
13	6	0	1.287111	-2.708232	-1.158668
14	1	0	1.130627	-3.790886	-1.205340
15	1	0	1.450944	-2.368097	-2.189047
16	6	0	2.537002	-2.406085	-0.316553
17	1	0	2.465938	-2.912671	0.657195
18	1	0	3.437127	-2.799648	-0.797753
19	7	0	-0.790844	0.214322	-0.462637
20	8	0	-2.848808	-1.275022	-0.961405
21	16	0	-3.463618	-1.229501	0.378438
22	8	0	-2.654096	-1.840702	1.460300
23	8	0	-3.921567	0.200188	0.760846
24	6	0	-5.026639	-2.127716	0.326696
25	1	0	-4.796852	-3.169791	0.099264
26	1	0	-5.508298	-2.042754	1.301619
27	1	0	-5.648856	-1.686286	-0.452805
28	1	0	-3.473057	1.183749	0.180724
29	17	0	-2.958480	2.489970	-0.380742
30	35	0	-0.059580	2.087826	-0.092616
31	8	0	5.000224	-1.155410	0.275997

32	6	0	6.296328	-0.626453	0.555498
33	1	0	6.321597	-0.141279	1.538144
34	1	0	6.968289	-1.484422	0.556877
35	1	0	6.610228	0.082508	-0.219563

Structures of peri-Cl compounds in TSs and IMs for substitution Reactions

10a-Ms-TS-S

Zero-point correction= 0.224415 (Hartree/Particle)
HF=-2025.894027 NIMAG=1

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	4.612601	1.163744	0.239532
2	6	0	4.557657	-0.232595	0.265895
3	6	0	3.340907	-0.911535	0.142372
4	6	0	2.176054	-0.142337	-0.032984
5	6	0	2.243502	1.255261	-0.038925
6	6	0	3.451248	1.929081	0.097183
7	1	0	5.570251	1.666090	0.336650
8	1	0	5.472039	-0.805066	0.392124
9	1	0	3.485264	3.012615	0.092833
10	6	0	0.832364	-0.750673	-0.177063
11	6	0	0.736239	-2.280588	-0.177854
12	1	0	0.434304	-2.565126	0.837010
13	1	0	-0.078517	-2.567345	-0.836553
14	6	0	2.057476	-2.937022	-0.586371
15	1	0	1.952186	-4.019134	-0.451887
16	1	0	2.239985	-2.765523	-1.654386
17	6	0	3.242440	-2.415452	0.229554
18	1	0	3.113486	-2.698694	1.284730
19	1	0	4.180446	-2.871920	-0.102188
20	7	0	-0.201565	-0.026327	-0.281141
21	8	0	-1.924043	-1.522783	-0.190849
22	16	0	-3.174659	-0.814939	0.246709
23	8	0	-3.365972	-0.710516	1.694525
24	8	0	-3.372550	0.540698	-0.507508
25	6	0	-4.530374	-1.732134	-0.498760
26	1	0	-4.396262	-2.782741	-0.237571
27	1	0	-5.457946	-1.341052	-0.078343
28	1	0	-4.491614	-1.583989	-1.577845
29	1	0	-2.836849	1.435381	-0.247236
30	17	0	-2.119916	3.040622	-0.090726
31	17	0	0.708066	2.075621	-0.172892

10a-IM

Zero-point correction= 0.228146 (Hartree/Particle)
HF=-2025.8996728 NIMAG=0

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	4.536151	1.205231	0.412138
2	6	0	4.510836	-0.188895	0.322985
3	6	0	3.312267	-0.880482	0.115157
4	6	0	2.133589	-0.122804	-0.007315
5	6	0	2.172922	1.274724	0.083714
6	6	0	3.363823	1.958361	0.294124
7	1	0	5.480481	1.716459	0.572303

8	1	0	5.435952	-0.750644	0.414724
9	1	0	3.378112	3.040125	0.362256
10	6	0	0.806406	-0.744448	-0.218285
11	6	0	0.743780	-2.276756	-0.292939
12	1	0	0.526271	-2.614173	0.728443
13	1	0	-0.105535	-2.556764	-0.910811
14	6	0	2.063950	-2.860759	-0.801368
15	1	0	1.986344	-3.952963	-0.767386
16	1	0	2.211251	-2.584259	-1.852471
17	6	0	3.258212	-2.389105	0.032899
18	1	0	3.179803	-2.799184	1.050539
19	1	0	4.197783	-2.767651	-0.382509
20	7	0	-0.238106	-0.030830	-0.305816
21	8	0	-1.980809	-1.524588	-0.465544
22	16	0	-3.062657	-0.799212	0.292456
23	8	0	-2.785991	-0.569309	1.713712
24	8	0	-3.521121	0.472643	-0.473486
25	6	0	-4.530851	-1.821569	0.111299
26	1	0	-4.321272	-2.778878	0.590151
27	1	0	-5.350413	-1.305083	0.612514
28	1	0	-4.736124	-1.947357	-0.951660
29	1	0	-2.929325	1.415733	-0.387274
30	17	0	-2.173493	2.920467	-0.396314
31	17	0	0.631893	2.075820	-0.081884

10b-Ms-TS-S

Zero-point correction= 0.266867 (Hartree/Particle)
HF=-2253.7788318 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.427557	1.596647	0.514411
2	6	0	-2.618318	2.730817	0.454507
3	6	0	-1.280239	2.642264	0.052741
4	6	0	-0.796234	1.371017	-0.291849
5	6	0	-1.617072	0.242736	-0.229604
6	6	0	-2.953551	0.314813	0.176045
7	1	0	-4.459298	1.708587	0.829304
8	1	0	-3.032052	3.697784	0.724814
9	6	0	0.588563	1.122309	-0.712178
10	6	0	1.553669	2.303917	-0.750026
11	1	0	2.044295	2.288271	0.233969
12	1	0	2.333122	2.102974	-1.483349
13	6	0	0.792734	3.610141	-1.010630
14	1	0	1.507226	4.437092	-0.943671
15	1	0	0.391241	3.619298	-2.031752
16	6	0	-0.346844	3.828322	-0.004481
17	1	0	0.076675	3.980706	0.998927
18	1	0	-0.915872	4.732647	-0.244493
19	7	0	0.986185	-0.051358	-1.003784
20	8	0	3.502655	0.095428	-0.803854
21	16	0	3.591496	-0.291033	0.646298
22	8	0	3.054099	0.750831	1.564427
23	8	0	3.020951	-1.664203	0.922587
24	6	0	5.354000	-0.452759	1.001825
25	1	0	5.826230	0.516111	0.833873
26	1	0	5.455075	-0.758614	2.044158
27	1	0	5.767410	-1.209148	0.333712

28	1	0	2.301517	-2.552842	-0.031732
29	17	0	1.570416	-3.453023	-0.788058
30	17	0	-0.763697	-1.209283	-0.669896
31	6	0	-3.810601	-0.914109	0.230223
32	8	0	-3.344290	-1.989836	-0.115152
33	8	0	-5.161444	-0.805706	0.686703
34	6	0	-5.790388	-2.088508	0.625486
35	1	0	-5.264073	-2.774241	1.256090
36	1	0	-6.804177	-2.004888	0.957358
37	1	0	-5.773524	-2.446253	-0.382797

10b-IM

Zero-point correction= 0.270521 (Hartree/Particle)
HF=-2253.7902437 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.444572	1.502291	0.501722
2	6	0	-2.660414	2.653543	0.440772
3	6	0	-1.321505	2.596856	0.033968
4	6	0	-0.809621	1.338638	-0.314181
5	6	0	-1.603008	0.189765	-0.252976
6	6	0	-2.935690	0.236379	0.157338
7	1	0	-4.479070	1.566814	0.818476
8	1	0	-3.095455	3.610083	0.714569
9	6	0	0.576027	1.119364	-0.737971
10	6	0	1.520352	2.317134	-0.771456
11	1	0	2.006729	2.305886	0.214805
12	1	0	2.305566	2.134869	-1.503656
13	6	0	0.732607	3.608040	-1.030049
14	1	0	1.430599	4.448901	-0.961190
15	1	0	0.332632	3.610683	-2.051800
16	6	0	-0.412933	3.802831	-0.025242
17	1	0	0.005347	3.967051	0.978406
18	1	0	-1.000914	4.694043	-0.268565
19	7	0	0.997940	-0.044113	-1.036347
20	8	0	3.537608	0.146261	-0.768446
21	16	0	3.569867	-0.250299	0.679074
22	8	0	2.959072	0.765006	1.581137
23	8	0	3.026397	-1.643772	0.918251
24	6	0	5.315812	-0.368765	1.121621
25	1	0	5.767928	0.614718	0.986425
26	1	0	5.373581	-0.682805	2.164759
27	1	0	5.783462	-1.105929	0.467949
28	1	0	2.351428	-2.510425	-0.050488
29	17	0	1.645125	-3.414762	-0.842021
30	17	0	-0.710974	-1.240170	-0.698848
31	6	0	-3.758717	-1.005336	0.211722
32	8	0	-3.342082	-2.099181	-0.120545
33	8	0	-5.001704	-0.778994	0.664728
34	6	0	-5.860958	-1.939857	0.753821
35	1	0	-5.425504	-2.676347	1.431901
36	1	0	-6.806746	-1.564415	1.141020
37	1	0	-5.992203	-2.385543	-0.234201

10c-Ms-TS-S

Zero-point correction= 0.266912 (Hartree/Particle)

HF=-2253.7780373 NIMAG=1

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	3.315229	1.639048	0.138180
2	6	0	3.395095	0.245814	0.057101
3	6	0	2.271532	-0.580263	-0.123471
4	6	0	1.029294	0.087803	-0.185325
5	6	0	0.947337	1.483054	-0.076092
6	6	0	2.080954	2.273947	0.081570
7	1	0	4.229158	2.209765	0.250990
8	1	0	2.001259	3.351798	0.160536
9	6	0	-0.257950	-0.643315	-0.328227
10	6	0	-0.204731	-2.171963	-0.422891
11	1	0	-0.308999	-2.540490	0.605675
12	1	0	-1.073906	-2.513230	-0.978795
13	6	0	1.113871	-2.619750	-1.046640
14	1	0	1.139012	-3.714652	-1.048068
15	1	0	1.156317	-2.301122	-2.095433
16	6	0	2.327074	-2.084990	-0.284759
17	1	0	2.385100	-2.541889	0.711740
18	1	0	3.251309	-2.373149	-0.788789
19	7	0	-1.358562	-0.014680	-0.340286
20	8	0	-2.963815	-1.613827	-0.381873
21	16	0	-4.070725	-0.960304	0.409675
22	8	0	-3.756442	-0.677363	1.811625
23	8	0	-4.654674	0.258428	-0.363678
24	6	0	-5.459101	-2.095555	0.298252
25	1	0	-5.157617	-3.025286	0.782238
26	1	0	-6.296120	-1.634447	0.824163
27	1	0	-5.693440	-2.254117	-0.754214
28	1	0	-4.136050	1.227286	-0.296542
29	17	0	-3.467801	2.802545	-0.327496
30	17	0	-0.650196	2.168168	-0.150165
31	6	0	4.808724	-0.352171	0.182264
32	8	0	5.178282	-1.525153	0.149062
33	8	0	5.757997	0.602132	0.354298
34	6	0	7.054101	0.008404	0.466115
35	1	0	7.273737	-0.539268	-0.426474
36	1	0	7.787222	0.775609	0.603331
37	1	0	7.071154	-0.655389	1.305156

10c-IM

Zero-point correction= 0.270787 (Hartree/Particle)

HF=-2253.7843715 NIMAG=0

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	3.315514	1.637204	0.207236
2	6	0	3.437009	0.241016	0.094195
3	6	0	2.291831	-0.562949	-0.121134
4	6	0	1.044647	0.095088	-0.176349
5	6	0	0.954247	1.487994	-0.045914
6	6	0	2.081924	2.276232	0.139658
7	1	0	4.211559	2.226748	0.356965
8	1	0	1.999720	3.352658	0.235452
9	6	0	-0.241084	-0.633223	-0.327848
10	6	0	-0.188490	-2.162272	-0.424503

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 11   1   0  -0.282660 -2.529704  0.605475
 12   1   0  -1.061673 -2.505083 -0.972832
 13   6   0  1.127847 -2.602525 -1.057076
 14   1   0  1.155375 -3.697647 -1.064507
 15   1   0  1.160459 -2.279063 -2.105041
 16   6   0  2.345425 -2.066006 -0.304077
 17   1   0  2.419073 -2.537425  0.685596
 18   1   0  3.266493 -2.343029 -0.817362
 19   7   0  -1.346063 -0.011985 -0.344084
 20   8   0  -2.958498 -1.619754 -0.400013
 21  16   0  -4.068351 -0.964681  0.385478
 22   8   0  -3.763130 -0.692525  1.792799
 23   8   0  -4.643069  0.256223 -0.382688
 24   6   0  -5.455809 -2.102002  0.265090
 25   1   0  -5.155939 -3.033286  0.747184
 26   1   0  -6.296216 -1.644032  0.788308
 27   1   0  -5.685518 -2.257795 -0.788845
 28   1   0  -4.133793  1.251484 -0.303231
 29  17   0  -3.509982  2.806916 -0.319454
 30  17   0  -0.647808  2.162330 -0.126100
 31   6   0  4.795502 -0.372542  0.240278
 32   8   0  5.014759 -1.550430  0.455872
 33   8   0  5.780137  0.543731  0.123544
 34   6   0  7.124803  0.049362  0.297359
 35   1   0  7.353480 -0.699536 -0.463939
 36   1   0  7.766776  0.922138  0.186096
 37   1   0  7.239560 -0.395029  1.288378
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10d-Ms-TS-S

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Zero-point correction=  0.225028 (Hartree/Particle)
HF=-2230.3874447 NIMAG=1
---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
 ---------------------------------------
  1  6  0  -4.058163  0.644646  0.379382
  2  6  0  -3.573417  1.946296  0.259754
  3  6  0  -2.217314  2.191274  0.003093
  4  6  0  -1.382496  1.074585 -0.149173
  5  6  0  -1.860315 -0.231841 -0.060415
  6  6  0  -3.203787 -0.452936  0.227006
  7  1  0  -5.103793  0.450874  0.589081
  8  6  0  0.051356  1.165617 -0.429284
  9  6  0  0.697259  2.542449 -0.447905
 10  1  0  1.025807  2.721120  0.585281
 11  1  0  1.603172  2.504236 -1.050711
 12  6  0  -0.318374  3.594897 -0.917131
 13  1  0  0.148713  4.581866 -0.842097
 14  1  0  -0.550588  3.435184 -1.977088
 15  6  0  -1.619479  3.575940 -0.096529
 16  1  0  -1.419797  3.936148  0.923295
 17  1  0  -2.356950  4.262535 -0.525499
 18  7  0  0.735501  0.109488 -0.632977
 19  8  0  3.006934  0.808558 -0.844854
 20 16  0  3.441935  0.237304  0.456417
 21  8  0  2.684465  0.716211  1.631656
 22  8  0  3.555258 -1.310198  0.397506
 23  6  0  5.171279  0.666780  0.693548
 24  1  0  5.240756  1.755752  0.687723
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 25   1   0   5.489727   0.262889   1.655202
 26   1   0   5.746566   0.233952  -0.124851
 27   1   0   2.851457  -2.078480  -0.173240
 28  17   0   1.935443  -3.234437  -0.758899
 29   1   0  -4.259999   2.780235   0.367740
 30   7   0  -3.749862  -1.809868   0.352350
 31   8   0  -4.941141  -1.920616   0.631377
 32   8   0  -2.970058  -2.745394   0.170393
 33  17   0  -0.711235  -1.555871  -0.306738
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10d-IM

```
Zero-point correction=  0.230610 (Hartree/Particle)
HF=-2230.3967003 NIMAG=0
 ---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
 ---------------------------------------
  1  6  0  -4.108911   0.795670   0.462071
  2  6  0  -3.543341   2.070585   0.377021
  3  6  0  -2.183646   2.237136   0.082127
  4  6  0  -1.434409   1.070606  -0.122922
  5  6  0  -1.983960  -0.200725  -0.047743
  6  6  0  -3.332271  -0.349954   0.250838
  7  1  0  -5.160951   0.663752   0.688263
  8  6  0  -0.017141   1.051043  -0.446411
  9  6  0   0.740288   2.357134  -0.525950
 10  1  0   1.166827   2.519330   0.472959
 11  1  0   1.587555   2.255091  -1.206329
 12  6  0  -0.223132   3.492678  -0.921315
 13  1  0   0.317641   4.442636  -0.872584
 14  1  0  -0.537800   3.360958  -1.963851
 15  6  0  -1.471137   3.566549  -0.017142
 16  1  0  -1.172861   3.873548   0.996182
 17  1  0  -2.164217   4.332971  -0.379707
 18  7  0   0.571208  -0.069257  -0.637879
 19  8  0   3.649608   0.830403  -0.917549
 20 16  0   3.750180   0.136430   0.377220
 21  8  0   2.810962   0.560091   1.431696
 22  8  0   3.748106  -1.445871   0.196861
 23  6  0   5.429426   0.292319   0.994274
 24  1  0   5.600973   1.354918   1.172172
 25  1  0   5.509737  -0.276299   1.920779
 26  1  0   6.111272  -0.090298   0.234718
 27  1  0   2.877901  -1.873257  -0.132834
 28 17  0   1.403729  -3.039127  -0.691772
 29  1  0  -4.172887   2.939974   0.539797
 30  7  0  -3.948295  -1.677220   0.342426
 31  8  0  -5.145828  -1.738530   0.608516
 32  8  0  -3.210342  -2.644419   0.143652
 33 17  0  -0.720029  -1.446314  -0.346546
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```

10e-Ms-TS-S

```
Zero-point correction=  0.227172 (Hartree/Particle)
HF=-2230.3911685 NIMAG=1
 ---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
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```

```
  1   6   0   3.673114   1.638253   0.253811
  2   6   0   3.745027   0.245917   0.154254
  3   6   0   2.619625  -0.570327  -0.056178
  4   6   0   1.383064   0.106512  -0.129364
  5   6   0   1.308455   1.500659  -0.002598
  6   6   0   2.443830   2.282006   0.185958
  7   1   0   4.588757   2.201364   0.389073
  8   1   0   2.369587   3.359165   0.278566
  9   6   0   0.093647  -0.613098  -0.307321
  10   6   0   0.138333  -2.141244  -0.413038
  11   1   0   0.016814  -2.515613   0.611659
  12   1   0  -0.723964  -2.474642  -0.984501
  13   6   0   1.463779  -2.593565  -1.019349
  14   1   0   1.481456  -3.688585  -1.027330
  15   1   0   1.523754  -2.269048  -2.065456
  16   6   0   2.669947  -2.072975  -0.236532
  17   1   0   2.715938  -2.543358   0.754200
  18   1   0   3.598496  -2.358008  -0.734778
  19   7   0  -1.000841   0.026202  -0.334066
  20   8   0  -2.620430  -1.547236  -0.496368
  21  16   0  -3.740227  -0.974868   0.337510
  22   8   0  -3.435735  -0.800929   1.759644
  23   8   0  -4.342888   0.292576  -0.337204
  24   6   0  -5.113439  -2.114995   0.129552
  25   1   0  -4.804616  -3.073346   0.548745
  26   1   0  -5.961362  -1.703329   0.678491
  27   1   0  -5.335347  -2.199841  -0.934028
  28   1   0  -3.799444   1.246330  -0.273833
  29  17   0  -3.108993   2.815522  -0.295619
  30  17   0  -0.284826   2.194616  -0.091492
  31   7   0   5.093393  -0.338265   0.285442
  32   8   0   5.187949  -1.464576   0.775043
  33   8   0   6.044646   0.348419  -0.085478
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```

10e-IM

```
Zero-point correction=  0.230516 (Hartree/Particle)
HF=-2230.396992 NIMAG=0
---------------------------------------
 Center  Atomic  Atomic  Coordinates (Angstroms)
 Number  Number  Type  X  Y  Z
 ---------------------------------------
  1   6   0   3.668136   1.638065   0.264587
  2   6   0   3.748561   0.245889   0.159905
  3   6   0   2.628822  -0.575367  -0.057223
  4   6   0   1.393734   0.100049  -0.130836
  5   6   0   1.308215   1.490406   0.001911
  6   6   0   2.436351   2.279159   0.196093
  7   1   0   4.580972   2.204455   0.405127
  8   1   0   2.358731   3.355731   0.293256
  9   6   0   0.106038  -0.607668  -0.317504
  10   6   0   0.139003  -2.136065  -0.438930
  11   1   0   0.005318  -2.520399   0.580343
  12   1   0  -0.720921  -2.457168  -1.020521
  13   6   0   1.469126  -2.587682  -1.038721
  14   1   0   1.483086  -3.682649  -1.055468
  15   1   0   1.537928  -2.254935  -2.081709
  16   6   0   2.673559  -2.077506  -0.244321
  17   1   0   2.708642  -2.551756   0.745128
  18   1   0   3.604463  -2.365904  -0.736004
```

19	7	0	-0.983847	0.037617	-0.346585
20	8	0	-2.649584	-1.624193	-0.443005
21	16	0	-3.745452	-0.974929	0.344894
22	8	0	-3.447538	-0.695221	1.751622
23	8	0	-4.321385	0.265685	-0.423650
24	6	0	-5.155592	-2.077894	0.208767
25	1	0	-4.872104	-3.019940	0.679884
26	1	0	-5.992068	-1.614578	0.733255
27	1	0	-5.381028	-2.218393	-0.848311
28	1	0	-3.801193	1.190920	-0.324046
29	17	0	-3.079021	2.822207	-0.311163
30	17	0	-0.301530	2.161685	-0.094904
31	7	0	5.098197	-0.333696	0.294458
32	8	0	5.192406	-1.468069	0.765110
33	8	0	6.049674	0.363244	-0.055524

10f-Ms-TS-S

Zero-point correction= 0.255146 (Hartree/Particle)
HF=-2140.4206926 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.207075	0.497753	0.361533
2	6	0	-3.655739	1.781667	0.302230
3	6	0	-2.297373	1.999554	0.060383
4	6	0	-1.486645	0.864837	-0.133781
5	6	0	-2.041173	-0.416364	-0.065997
6	6	0	-3.399430	-0.632741	0.176207
7	1	0	-5.268260	0.384732	0.549457
8	1	0	-4.308941	2.637061	0.450032
9	6	0	-0.033619	0.963011	-0.400046
10	6	0	0.576198	2.364324	-0.487962
11	1	0	0.993036	2.562543	0.508828
12	1	0	1.423383	2.320289	-1.168793
13	6	0	-0.460434	3.415022	-0.893118
14	1	0	0.019499	4.398650	-0.847186
15	1	0	-0.765946	3.257471	-1.935204
16	6	0	-1.691763	3.383764	0.016287
17	1	0	-1.401274	3.684142	1.033680
18	1	0	-2.444952	4.104584	-0.319170
19	7	0	0.697266	-0.076897	-0.535689
20	8	0	2.803077	0.630417	-0.903956
21	16	0	3.444325	0.291955	0.434323
22	8	0	2.936754	1.127936	1.544324
23	8	0	3.423931	-1.189062	0.717565
24	6	0	5.189196	0.687879	0.195242
25	1	0	5.273533	1.756267	-0.006768
26	1	0	5.708097	0.425395	1.118586
27	1	0	5.563605	0.097965	-0.641780
28	1	0	2.650364	-2.250847	0.025314
29	17	0	1.983561	-3.335290	-0.520948
30	8	0	-3.815170	-1.922326	0.211893
31	6	0	-5.191523	-2.196173	0.477536
32	1	0	-5.835062	-1.769640	-0.300570
33	1	0	-5.278683	-3.282232	0.468050
34	1	0	-5.486718	-1.812728	1.460965
35	17	0	-0.890867	-1.729274	-0.291080

10f-IM

Zero-point correction= 0.260685 (Hartree/Particle)
HF=-2140.4270671 NIMAG=0

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	-4.178299	0.472945	0.408395
2	6	0	-3.663301	1.774095	0.347394
3	6	0	-2.316619	2.022487	0.074303
4	6	0	-1.510454	0.896411	-0.143380
5	6	0	-2.014040	-0.400003	-0.082899
6	6	0	-3.359552	-0.649519	0.196905
7	1	0	-5.231623	0.335392	0.622170
8	1	0	-4.336584	2.609279	0.518794
9	6	0	-0.079680	0.973492	-0.444970
10	6	0	0.577004	2.354671	-0.491090
11	1	0	0.982597	2.513751	0.516836
12	1	0	1.429346	2.316871	-1.167522
13	6	0	-0.451361	3.428633	-0.874297
14	1	0	0.038876	4.405507	-0.803416
15	1	0	-0.749761	3.297653	-1.921734
16	6	0	-1.696837	3.401917	0.024567
17	1	0	-1.417370	3.706439	1.043648
18	1	0	-2.437955	4.128547	-0.325002
19	7	0	0.596277	-0.086841	-0.632748
20	8	0	2.995301	0.629038	-0.947562
21	16	0	3.473069	0.253964	0.405578
22	8	0	2.844337	0.964846	1.534009
23	8	0	3.460187	-1.295860	0.635105
24	6	0	5.242398	0.559952	0.442817
25	1	0	5.386712	1.635957	0.334913
26	1	0	5.631514	0.209106	1.399136
27	1	0	5.695300	0.018583	-0.387949
28	1	0	2.754781	-1.920368	0.117353
29	17	0	1.738455	-3.189138	-0.565531
30	8	0	-3.753699	-1.942032	0.236235
31	6	0	-5.118192	-2.237525	0.542441
32	1	0	-5.790474	-1.817727	-0.214418
33	1	0	-5.188267	-3.324584	0.531034
34	1	0	-5.387622	-1.861632	1.535875
35	17	0	-0.801862	-1.642720	-0.347594

10g-Ms-TS-S

Zero-point correction= 0.255225 (Hartree/Particle)
HF=-2140.4223487 NIMAG=1

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	3.899159	1.353203	0.349129
2	6	0	3.861421	-0.040792	0.206095
3	6	0	2.649158	-0.704020	-0.084968
4	6	0	1.500174	0.083829	-0.204796
5	6	0	1.545551	1.477001	-0.053794
6	6	0	2.737114	2.124505	0.221580
7	1	0	4.832565	1.858062	0.565117
8	1	0	2.776434	3.201142	0.340942
9	6	0	0.169333	-0.495000	-0.472167

10	6	0	0.054084	-2.020272	-0.567865
11	1	0	-0.183273	-2.349939	0.452297
12	1	0	-0.807201	-2.261958	-1.187227
13	6	0	1.362121	-2.625049	-1.083026
14	1	0	1.260115	-3.715648	-1.065314
15	1	0	1.512293	-2.338429	-2.131165
16	6	0	2.579612	-2.203605	-0.252541
17	1	0	2.538140	-2.670285	0.742563
18	1	0	3.505807	-2.558853	-0.712449
19	7	0	-0.855301	0.243354	-0.577317
20	8	0	-2.751393	-1.157297	-0.948147
21	16	0	-3.405554	-1.001278	0.394924
22	8	0	-2.591462	-1.482701	1.527399
23	8	0	-3.960306	0.419918	0.609272
24	6	0	-4.921625	-1.970129	0.330140
25	1	0	-4.640599	-3.016543	0.204155
26	1	0	-5.448172	-1.819472	1.273417
27	1	0	-5.517700	-1.617111	-0.511440
28	1	0	-3.461230	1.408148	0.177567
29	17	0	-2.975138	2.840184	-0.303366
30	8	0	4.949973	-0.848615	0.330796
31	6	0	6.219732	-0.263443	0.617136
32	1	0	6.206235	0.258875	1.580846
33	1	0	6.921602	-1.095887	0.665216
34	1	0	6.525856	0.427505	-0.177149
35	17	0	-0.004532	2.269203	-0.207166

10g-IM

Zero-point correction= 0.260626 (Hartree/Particle)
HF=-2140.4285207 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.899176	1.353175	0.349123
2	6	0	3.861448	-0.040828	0.206093
3	6	0	2.649205	-0.704055	-0.084965
4	6	0	1.500275	0.083820	-0.204781
5	6	0	1.545586	1.476952	-0.053809
6	6	0	2.737131	2.124491	0.221569
7	1	0	4.832585	1.858030	0.565113
8	1	0	2.776466	3.201130	0.340928
9	6	0	0.169448	-0.494885	-0.472153
10	6	0	0.054051	-2.020170	-0.567890
11	1	0	-0.183279	-2.349897	0.452255
12	1	0	-0.807190	-2.261856	-1.187308
13	6	0	1.362081	-2.625034	-1.083034
14	1	0	1.260036	-3.715629	-1.065320
15	1	0	1.512269	-2.338418	-2.131170
16	6	0	2.579592	-2.203632	-0.252543
17	1	0	2.538110	-2.670328	0.742554
18	1	0	3.505765	-2.558922	-0.712464
19	7	0	-0.854944	0.243778	-0.577242
20	8	0	-2.751720	-1.157265	-0.948142
21	16	0	-3.405429	-1.001564	0.394744
22	8	0	-2.591550	-1.482515	1.527441
23	8	0	-3.960631	0.420112	0.609431
24	6	0	-4.921752	-1.969860	0.330295
25	1	0	-4.640623	-3.016250	0.204305

26	1	0	-5.448357	-1.819280	1.273545
27	1	0	-5.517741	-1.616892	-0.511363
28	1	0	-3.462513	1.403397	0.178988
29	17	0	-2.974874	2.840359	-0.303431
30	8	0	4.949986	-0.848666	0.330796
31	6	0	6.219745	-0.263509	0.617133
32	1	0	6.206254	0.258813	1.580842
33	1	0	6.921612	-1.095957	0.665214
34	1	0	6.525875	0.427437	-0.177152
35	17	0	-0.004679	2.269117	-0.207195

Structures of *peri*-OMe compounds in TSs and IMs for substitution reactions

13a-Ms-TS-S

Zero-point correction= 0.266773 (Hartree/Particle)
HF=-1680.84314 NIMAG=1

Center Number	Atomic Number	Atom Type	X	Y	Z
1	6	0	-3.948000	1.783467	-0.980755
2	6	0	-4.191581	0.411101	-0.837317
3	6	0	-3.255126	-0.424718	-0.214099
4	6	0	-2.095887	0.194345	0.252113
5	6	0	-1.861693	1.559057	0.120549
6	6	0	-2.775015	2.392936	-0.507242
7	1	0	-4.693353	2.403052	-1.469919
8	1	0	-5.114357	-0.010570	-1.224918
9	1	0	-2.606511	3.457890	-0.615514
10	6	0	-0.957317	-0.491294	0.857099
11	6	0	-1.024116	-2.007104	0.960456
12	1	0	-0.548326	-2.368335	0.038020
13	1	0	-0.404254	-2.344229	1.790737
14	6	0	-2.490875	-2.458378	1.079489
15	1	0	-2.507121	-3.553132	1.072295
16	1	0	-2.901526	-2.141799	2.046530
17	6	0	-3.382214	-1.923614	-0.057724
18	1	0	-3.088297	-2.396447	-1.005604
19	1	0	-4.429196	-2.194794	0.115217
20	7	0	0.036581	0.219429	1.210714
21	8	0	1.883521	-1.410040	0.958712
22	16	0	2.166687	-1.259026	-0.509602
23	8	0	1.152887	-1.912324	-1.379673
24	8	0	2.398236	0.185638	-0.910677
25	6	0	3.741622	-2.093491	-0.790702
26	1	0	3.621708	-3.143765	-0.521720
27	1	0	3.988152	-1.988825	-1.848326
28	1	0	4.498243	-1.616702	-0.165951
29	1	0	3.264776	1.173375	-0.143947
30	17	0	3.969748	2.190365	0.451561
31	8	0	-0.674030	1.901798	0.733897
32	6	0	0.351487	2.647625	-0.014604
33	1	0	1.190745	2.746193	0.669788
34	1	0	0.642731	2.069519	-0.891674
35	1	0	-0.074806	3.620597	-0.264578

13a-IM

Zero-point correction= 0.270505 (Hartree/Particle)
HF=- 1680.8617409 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.335622	-1.748540	2.336051
2	6	0	-1.284784	-0.718630	2.439689
3	6	0	-1.863150	-0.159797	1.296650
4	6	0	-1.445925	-0.721298	0.095599
5	6	0	-0.511859	-1.729131	0.007039
6	6	0	0.094841	-2.289716	1.110807
7	1	0	0.113859	-2.136902	3.244652
8	1	0	-1.547184	-0.339498	3.423131
9	1	0	0.877197	-3.034535	1.058722
10	6	0	-1.859282	-0.361498	-1.228326
11	6	0	-2.796748	0.801420	-1.393594
12	1	0	-2.152581	1.680274	-1.533515
13	1	0	-3.418836	0.695047	-2.286555
14	6	0	-3.649356	0.961690	-0.108621
15	1	0	-4.233670	1.883079	-0.197424
16	1	0	-4.367291	0.133416	-0.051351
17	6	0	-2.816640	1.009066	1.196459
18	1	0	-2.215581	1.929521	1.215778
19	1	0	-3.486313	1.043600	2.062934
20	7	0	-1.337112	-1.064278	-2.174318
21	8	0	0.800205	1.099011	-1.311073
22	16	0	1.178381	1.847615	-0.095553
23	8	0	0.237941	2.865658	0.384300
24	8	0	1.464365	0.861995	1.107477
25	6	0	2.788055	2.585719	-0.393723
26	1	0	2.699529	3.260842	-1.247221
27	1	0	3.089753	3.131068	0.501923
28	1	0	3.488479	1.774217	-0.606412
29	1	0	2.122674	0.070999	0.831626
30	17	0	3.242741	-1.290284	0.370330
31	8	0	-0.385334	-2.045563	-1.376133
32	6	0	0.972402	-2.033080	-2.021378
33	1	0	0.809611	-2.517320	-2.981275
34	1	0	1.283156	-0.993408	-2.089599
35	1	0	1.627284	-2.583504	-1.348433

13c-Ms-TS-S

Zero-point correction= 0.269252 (Hartree/Particle)
HF=-1885.3365637 NIMAG=1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.893613	-0.216008	0.766391
2	6	0	3.545043	-1.563617	0.725199
3	6	0	2.327679	-1.970225	0.160514
4	6	0	1.499865	-0.958838	-0.327646
5	6	0	1.819376	0.399614	-0.293171
6	6	0	3.052765	0.781158	0.248326

7	1	0	4.842091	0.099429	1.184961
8	1	0	4.229887	-2.303059	1.128063
9	6	0	0.169678	-1.179156	-0.893889
10	6	0	-0.360601	-2.602525	-0.937422
11	1	0	-0.925502	-2.715174	-0.000906
12	1	0	-1.075795	-2.698334	-1.753769
13	6	0	0.809455	-3.595728	-1.036628
14	1	0	0.397770	-4.608288	-0.978994
15	1	0	1.300073	-3.507797	-2.013999
16	6	0	1.848721	-3.400015	0.081551
17	1	0	1.399622	-3.662449	1.050356
18	1	0	2.703473	-4.069981	-0.058470
19	7	0	-0.473868	-0.151261	-1.275655
20	8	0	-2.792798	-0.949457	-0.889013
21	16	0	-2.939815	-0.678187	0.583701
22	8	0	-2.182867	-1.637254	1.435216
23	8	0	-2.625101	0.757547	0.943539
24	6	0	-4.693115	-0.898136	0.945952
25	1	0	-4.962353	-1.928449	0.710109
26	1	0	-4.840701	-0.690548	2.006823
27	1	0	-5.259580	-0.198113	0.330197
28	1	0	-3.136018	2.010976	0.157051
29	17	0	-3.448794	3.184744	-0.452789
30	8	0	0.826961	1.135258	-0.886138
31	6	0	0.089672	2.212458	-0.160285
32	1	0	-0.696524	2.502660	-0.851994
33	1	0	-0.338572	1.781389	0.743865
34	1	0	0.796910	3.018387	0.013029
35	7	0	3.546311	2.161844	0.234430
36	8	0	2.958758	2.966188	-0.490465
37	8	0	4.529013	2.421682	0.925248

13c-IM

Zero-point correction= 0.270374 (Hartree/Particle)

HF=-1885.3547528 NIMAG=0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.292842	1.738333	1.395553
2	6	0	0.169719	1.220856	2.044124
3	6	0	-0.214885	-0.110844	1.844269
4	6	0	0.576738	-0.837734	0.957579
5	6	0	1.680462	-0.342311	0.294278
6	6	0	2.087177	0.970842	0.525614
7	1	0	1.592704	2.767367	1.556371
8	1	0	-0.416926	1.867279	2.686793
9	6	0	0.403374	-2.219844	0.594314
10	6	0	-0.763719	-2.984321	1.151285
11	1	0	-1.560238	-2.863014	0.406409
12	1	0	-0.528354	-4.046542	1.252482
13	6	0	-1.194667	-2.351199	2.498282
14	1	0	-2.128395	-2.826597	2.812224
15	1	0	-0.445670	-2.583952	3.266045
16	6	0	-1.405708	-0.820255	2.430325
17	1	0	-2.261553	-0.585527	1.782669
18	1	0	-1.637984	-0.421410	3.422254
19	7	0	1.292512	-2.676748	-0.215134
20	8	0	-0.479569	-0.376112	-2.556896

21	16	0	-1.660165	0.029424	-1.744934
22	8	0	-2.169286	-1.030419	-0.829532
23	8	0	-1.382838	1.333184	-1.007650
24	6	0	-2.986683	0.404419	-2.905357
25	1	0	-3.211396	-0.505630	-3.463461
26	1	0	-3.855610	0.733346	-2.333316
27	1	0	-2.639560	1.193851	-3.573113
28	1	0	-2.275861	1.820597	0.027531
29	17	0	-3.063419	2.339316	1.063358
30	8	0	2.223886	-1.401845	-0.465044
31	6	0	2.411511	-1.273712	-1.967961
32	1	0	2.696359	-2.280253	-2.261029
33	1	0	1.450351	-0.952136	-2.373233
34	1	0	3.220448	-0.560048	-2.081745
35	7	0	3.302423	1.553396	-0.032004
36	8	0	4.078758	0.784646	-0.612234
37	8	0	3.496666	2.753244	0.130244

Table S12 Calculated Activation Energies (ZPE corrected) of Substitution reaction of *peri*-Cl Compounds.

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Es	Es2
10a-Ms (8-Cl)	-2025.97246500	-2025.93843150	-2025.94098410	21.35634457	1.60178075
10d-Ms (7-nitro)	-2230.52257250	-2230.48537920	-2230.49253440	23.33914909	4.48995597
10e-Ms (5-nitro)	-2230.52858710	-2230.48949710	-2230.49240350	24.52934635	1.82379361
10b-Ms (7-ester)	-2253.86850970	-2253.83844350	-2253.84841030	18.86682613	6.25426168
10c-Ms (5-ester)	-2253.87250350	-2253.83683550	-2253.84038520	22.38200885	2.22747047
10f-Ms (7-OMe)	-2140.49437600	-2140.46129550	-2140.46441590	20.75832801	1.95808064
10g-Ms (5-OMe)	-2140.49553400	-2140.46288330	-2140.46651870	20.48862443	2.28124804

Table S13. Calculated Activation Energies (ZPE corrected) of Alkyl migration of *peri*-Cl Compounds

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Eb	Eb2
10a-Ms (8-Cl)	-901.13880250	-901.13382940	-901.17445230	3.12066749	25.49125567
10d-Ms (7-nitro)	-1105.68878220	-1105.67987020	-1105.71927040	5.59236466	24.72399980
10e-Ms (5-nitro)	-1105.68869210	-1105.68323290	-1105.72096000	3.42569986	23.67411366
10b-Ms (7-ester)	-1129.04334800	-1129.03158530	-1129.07016830	7.38120600	24.21119904
10c-Ms (5-ester)	-1129.03712760	-1129.03208690	-1129.06974030	3.16308714	23.62786621
10f-Ms (7-OMe)	-1015.66178360	-1015.65714740	-1015.69773480	2.90925954	25.46897908
10g-Ms (5-OMe)	-1015.66445680	-1015.65925160	-1015.69781210	3.26631245	24.19708007

Table S14 Calculated Activation Energies (zero point energy (ZPE) corrected) of Benzene Migration of *peri*- Br Compounds.

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Activation Energy (kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Eb	Eb2
				R->TS	TS->P
3a-Ms (8-Br)	-4139.88931870	-4139.85199920	-4139.92945640	23.41834079	48.60512884
3d-Ms (7-nitro)	-4344.44235040	-4344.39479650	-4344.44951280	29.84052401	34.33499805
3f-Ms (5-nitro)	-4344.44504730	-4344.39429080	-4344.44916980	31.85018594	34.43709385
3b-Ms (7-COOMe)	-4367.78529510	-4367.74659900	-4367.83166280	24.28217036	53.37834261
3e-Ms (5-COOMe)	-4367.78918850	-4367.74953700	-4367.79259070	24.88169294	27.01660576
3g-Ms (7-OMe)	-4254.41199100	-4254.37543020	-4254.45740720	22.94224933	51.44134628
3h-Ms (5-OMe)	-4254.41338230	-4254.37655800	-4254.41713850	23.10759808	25.46464926

Table S15. Calculated Activation Energies (ZPE corrected) of Substitution Reaction of *peri*-Br Compounds.

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Activation Energy (kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Es	Es2
				R->TS	TS->P
3a-Ms (8-Br)	-4139.889844	-4139.860588	-4139.877744	18.35791592	10.76555298
3d-Ms (7-nitro)	-4344.439533	-4344.409294	-4344.434083	18.97507152	15.55514474
3f-Ms (5-nitro)	-4344.446033	-4344.412724	-4344.430857	20.90121193	11.37831601
3b-Ms(7-CO_2Me)	-4367.787019	-4367.759191	-4367.785129	17.46258537	16.27634141
3e-Ms (5-CO_2Me)	-4367.79066	-4367.758888	-4367.777523	19.93704358	11.69389054
3g-Ms (7-OMe)	-4254.412072	-4254.384364	-4254.40199	17.38659397	11.0604197
3h-Ms (5-OMe)	-4254.413934	-4254.385318	-4254.402907	17.95656085	11.0373901

Table S16. Calculated Activation Energies (ZPE corrected) of Alkyl migration of *peri*-Br Compounds.

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Es	Es2
				R->TS	TS->P
3a-Ms (8-Br)	-3475.48838650	-3475.46599460	-3475.47844750	14.05	7.81
3d-Ms (7-nitro)	-3680.04518300	-3680.01151550	-3680.03382960	21.13	14.00
3f-Ms (5-nitro)	-3680.04213610	-3680.01668450	-3680.03076800	15.97	8.84
3b-Ms (7-ester)	-3703.39528530	-3703.36038710	-3703.38184950	21.90	13.47
3e-Ms (5-ester)	-3703.38845820	-3703.36488660	-3703.37746300	14.79	7.89
3g-Ms (7-OMe)	-3590.01236370	-3589.98935780	-3590.00157340	14.44	7.67
3i-Ms (5-OMe)	-3590.01347870	-3589.99149100	-3590.00199370	13.80	6.59

Table S17 Calculated Activation Energies (ZPE corrected) of Beckmann rearrangement of *peri*-Cl Compounds.

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)

	E /Hartree	E /Hartree	E/Hartree	Eb	Eb2
10a-Ms (8-Br)	-2025.97132970	-2025.93444140	-2026.01148150	23.14775869	48.34339463
10d-Ms (7-nitro)	-2230.52285940	-2230.47772240	-2230.56319310	28.32389630	53.63367622
10e-Ms (5-nitro)	-2230.52635910	-2230.48070160	-2230.56574980	28.65051500	53.36855346
10b-Ms (7-ester)	-2253.86872220	-2253.82958810	-2253.87311820	24.55701952	27.31555129
10c-Ms (5-ester)	-2253.87160540	-2253.82906010	-2253.90957270	26.69757993	50.52242137
10f-Ms (7-OMe)	-2140.49356120	-2140.45740370	-2140.53364210	22.68917475	47.84032026
10g-Ms (5-OMe)	-2140.49553300	-2140.45855200	-2140.53426040	23.20592882	47.50774023

Table S18. Calculated Activation Energies (ZPE corrected) of Substitution reaction of *peri*-OMe Compounds

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Es	Es2
13a-Ms (8-OMe)	-1680.8682712	-1680.8378025	-1680.8505986	19.1193987	8.02967431
13c-Ms (7-nitro)	-1885.4191193	-1885.3859010	-1885.3959117	20.84479882	6.28180935

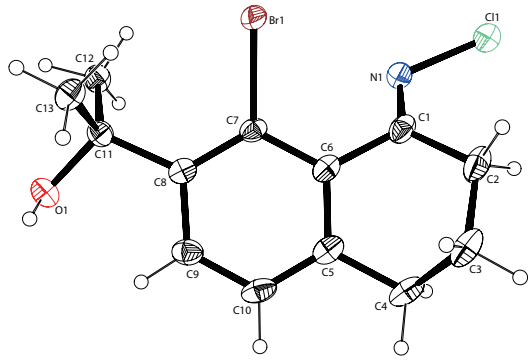
Table S19. Calculated Activation Energies (ZPE corrected) of Alkyl migration of *peri*-OMe Compounds

IEFPCM-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p)

cmp.Name	Reactant	TS	Product	Energy(kcal/mol)	
	E /Hartree	E /Hartree	E/Hartree	Es	Es2
13a-Ms (8-OMe)	-1016.4592795	-1016.4532295	-1016.4863266	3.79643247	20.76623463
13c-Ms (7-nitro)	-760.59161670	-760.57912410	-760.61894950	7.83922518	24.99081684

XI. X-ray Crystallographic Structure Determinations:

7

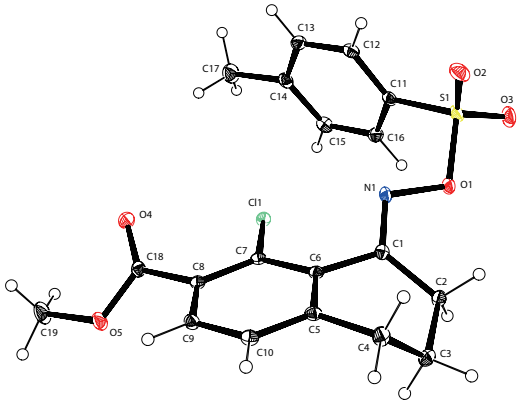


Crystal data and structure refinement for compound **7**.

CCDC number	CCDC 1470724	
Empirical formula	$C_{13}H_{15}BrClNO$	
Formula weight	316.62	
Temperature	100(2)K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.5871(9) Å	a= 90°.
	b = 17.4471(15) Å	b= 107.844(3)°.
	c = 7.3732(6) Å	g = 90°.
Volume	1296.42(19) Å^3	
Z	4	
Density (calculated)	1.622 Mg/m^3	
Absorption coefficient	6.077 mm^{-1}	
F(000)	640	
Crystal size	0.130 x 0.120 x 0.020 mm	
Theta range for data collection	4.387 to 79.217°.	
Index ranges	-12<=h<=13, -22<=k<=20, -9<=l<=8	
Reflections collected	15100	
Independent reflections	2713 [R(int) = 0.0581]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.6858 and 0.5395	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2713 / 0 / 156	

Goodness-of-fit on F^2	1.092
Final R indices [I>2sigma(I)]	$R_1 = 0.0522$, $wR_2 = 0.1254$
R indices (all data)	$R_1 = 0.0601$, $wR_2 = 0.1306$
Extinction coefficient	n/a
Largest diff. peak and hole	1.442 and -0.659 e.Å^{-3}

10b

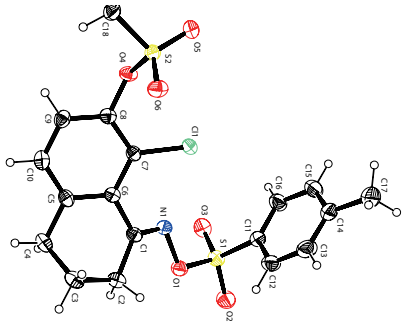


Crystal data and structure refinement for compound **10b**.

CCDC number	CCDC 1470722	
Empirical formula	$C_{19}H_{18}ClNO_5S$	
Formula weight	407.85	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0351(11) Å	α= 72.0480(10)°.
	b = 10.0395(11) Å	β= 81.2720(10)°.
	c = 10.3718(11) Å	γ = 66.1780(10)°.
Volume	908.92(17) Å^3	
Z	2	
Density (calculated)	1.490 Mg/m^3	
Absorption coefficient	0.357 mm^{-1}	
F(000)	424	
Crystal size	0.500 x 0.500 x 0.400 mm	
Theta range for data collection	2.065 to 25.678°.	
Index ranges	-11<=h<=11, -12<=k<=11, -11<=l<=11	
Reflections collected	7866	
Independent reflections	3105 [R(int) = 0.0226]	
Completeness to theta = 25.000°	95.3 %	

Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3105 / 0 / 246
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R_1 = 0.0275, wR_2 = 0.0716
R indices (all data)	R_1 = 0.0297, wR_2 = 0.0731
Extinction coefficient	n/a
Largest diff. peak and hole	0.221 and -0.405 e.Å^{-3}

10i

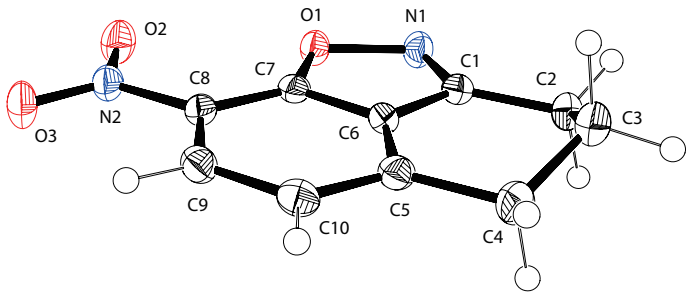


Crystal data and structure refinement for compound **10i**.

CCDC number	CCDC 1470723	
Empirical formula	$C_{18}H_{18}ClNO_6S_2$	
Formula weight	443.90	
Temperature	100(2)K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.5262(12) Å	a= 90°.
	b = 9.5955(9) Å	b= 93.049(3)°.
	c = 16.6342(15) Å	g = 90°.
Volume	1996.5(3) Å^3	
Z	4	
Density (calculated)	1.477 Mg/m^3	
Absorption coefficient	3.968 mm^{-1}	
F(000)	920	
Crystal size	0.200 x 0.150 x 0.100 mm	
Theta range for data collection	3.533 to 79.102°.	
Index ranges	-15<=h<=15, -11<=k<=11, -20<=l<=20	
Reflections collected	22548	

Independent reflections	4166 [*R*(int) = 0.0475]
Completeness to theta = 67.679°	99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.6653 and 0.5516
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4166 / 0 / 255
Goodness-of-fit on F^2	1.179
Final *R* indices [*I*>2sigma(*I*)]	$R_1 = 0.0636$, $wR_2 = 0.1779$
R indices (all data)	$R_1 = 0.0730$, $wR_2 = 0.1923$
Extinction coefficient	n/a
Largest diff. peak and hole	1.040 and -0.826 e.Å^{-3}

16c.



Crystal data and structure refinement for compound:**16c**

CCDC number	CCDC 1470721	
Empirical ßformula	$C_{10}H_8N_2O_3$	
Formula weight	204.18	
Temperature	100K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	*a* = 19.170(3) Å	*a*= 90°.
	b = 5.9569(10) Å	*b*= 90°.
	c = 7.7612(14) Å	*g* = 90°.
Volume	886.3(3) Å^3	
Z	4	
Density (calculated)	1.530 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	424	
Crystal size	0.400 x 0.090 x 0.080 mm	

Theta range for data collection	2.125 to 27.187°.
Index ranges	-24<=*h*<=24, -7<=*k*<=7, -9<=*l*<=9
Reflections collected	8519
Independent reflections	1865 [*R*(int) = 0.0251]
Completeness to theta = 25.000°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1865 / 1 / 168
Goodness-of-fit on F^2	1.054
Final *R* indices [*I*>2sigma(*I*)]	$R_1 = 0.0310$, $wR_2 = 0.0796$
R indices (all data)	$R_1 = 0.0344$, $wR_2 = 0.0818$
Absolute structure parameter	0.2(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.412 and -0.180 e.Å^{-3}

X. References in supporting information:

1. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian, Inc., Wallingford CT,* **2009**.

2. NBO Version 3.1, Glendening ED, Reed AE, Carpenter JE, Weinhold F.

3. Breneman C. M., Wiberg K.B. Determining atom-centered monopoles from molecular electrostatic potentials - the need for high sampling density in formamide conformational-analysis. *J. Comp. Chem.* **1990**, 11(3): 361-373.

4. Hirshfeld, F. L. *Theor. Chem. Acc.* **1977**, 44(2), 129-138.

5. Johnson, E. R., *et al* Revealing noncovalent interactions. *J. Am. Chem. Soc.* **2010**, 132(18), 6498-6506

6. Lu, T., Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comp. Chem.* **2011**, 33(5): 580-592.

7. Humphrey, W., Dalke, A., Schulten, K. VMD - Visual Molecular Dynamics, *J. Molec. Graphics* **1996**, 14(1): 33-38.

8. teVelde. G., *et al*, Chemistry with ADF. *J. Comp. Chem. Soc.* **2001**, 22(9), 931-967.

9. ADF2016, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, E.J. Baerends, T. Ziegler, A.J. Atkins, J. Autschbach, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, D.P. Chong, D.V. Chulhai, L. Deng, R.M. Dickson, J.M. Dieterich, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J.W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, M. Pavanello, C.A. Peeples, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, J.I. Rodríguez, P. Ros, R. Rüger, P.R.T. Schipper, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev, **2016**.