Supporting Information

Keteniminium Salts: Reactivity and Propensity towards Electrocyclization Reactions

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Electronic Supporting Information

Table of Contents

Full reference of Gaussian09

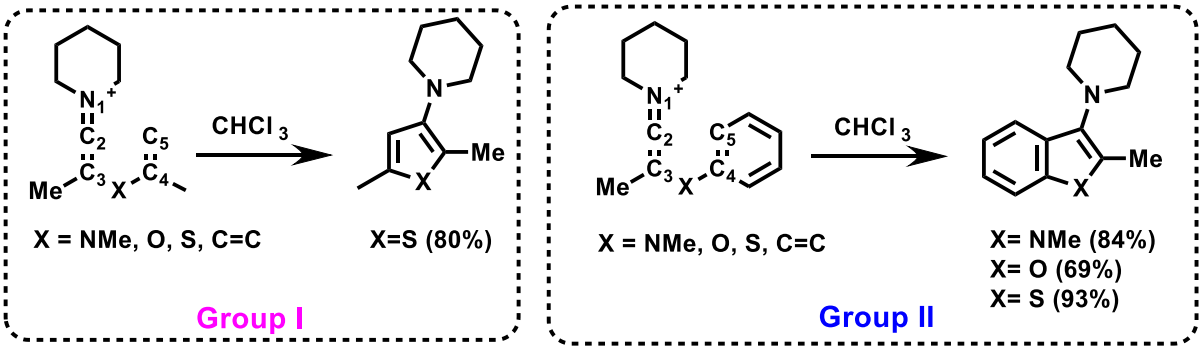
Gaussian 09, Revision E.01,

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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

DFT Survey

Besides M06-2X functional, all calculation in **Table S1** were also performed at the hybrid-GGA B3LYP, hybrid-meta GGA MPWB1K and Second order Møller–Plesset perturbation (MP2). The calculations indicate that even though B3LYP, MPWB1K and MP2 lower the barriers compared to M06-2X optimizations, similar barrier trends were observed regardless of the level of theory.

Table S1. Free energy barriers ($\Delta G^{\ddagger}$), and reaction free energies (ΔG_{rxn}) for 6π-electrocyclization reactions of KIs.[a,b]



		M06-2X/ 6-31+G(d,p)		B3LYP/ 6-31+G(d,p)		MPWB1K/ 6-31+G(d,p)		MP2/ 6-31+G(d,p)	
	Group I	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**
1	pyrrole	**3.0**	**-37.8**	**2.2**	**-36.1**	**1.5**	**-43.0**	*	**-41.9**
2	furan	6.0	-23.8	6.5	-20.5	5.5	-27.2	3.4	-22.9
3	thiophene	11.4	-22.2	10.6	-19.4	10.4	-26.8	8.2	-23.4
4	cyclohexadiene	9.2	-34.8	10.3	-28.6	10.5	-37.1	5.1	-36.6
	Group II	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**
5	indole	**10.8**	**-4.9**	**10.2**	**-3.2**	**8.8**	**-9.1**	**6.1**	**-7.3**
6	benzofuran	17.0	8.0	15.4	8.5	14.8	3.0	13.6	8.7
7	benzothiophene	21.0	9.0	20.4	10.6	18.8	4.3	16.0	9.3
8	naphthalene	14.8	1.7	18.1	8.6	16.2	0.8	6.2	-0.4

[a] M06-2X/6-31+G(d,p) in chloroform (ε=4.7113); free energies in kcal/mol.
[b] 6-311++G(3df,3pd) extra basis set for sulfur atom.
* The TS was not located at the MP2 level of theory.

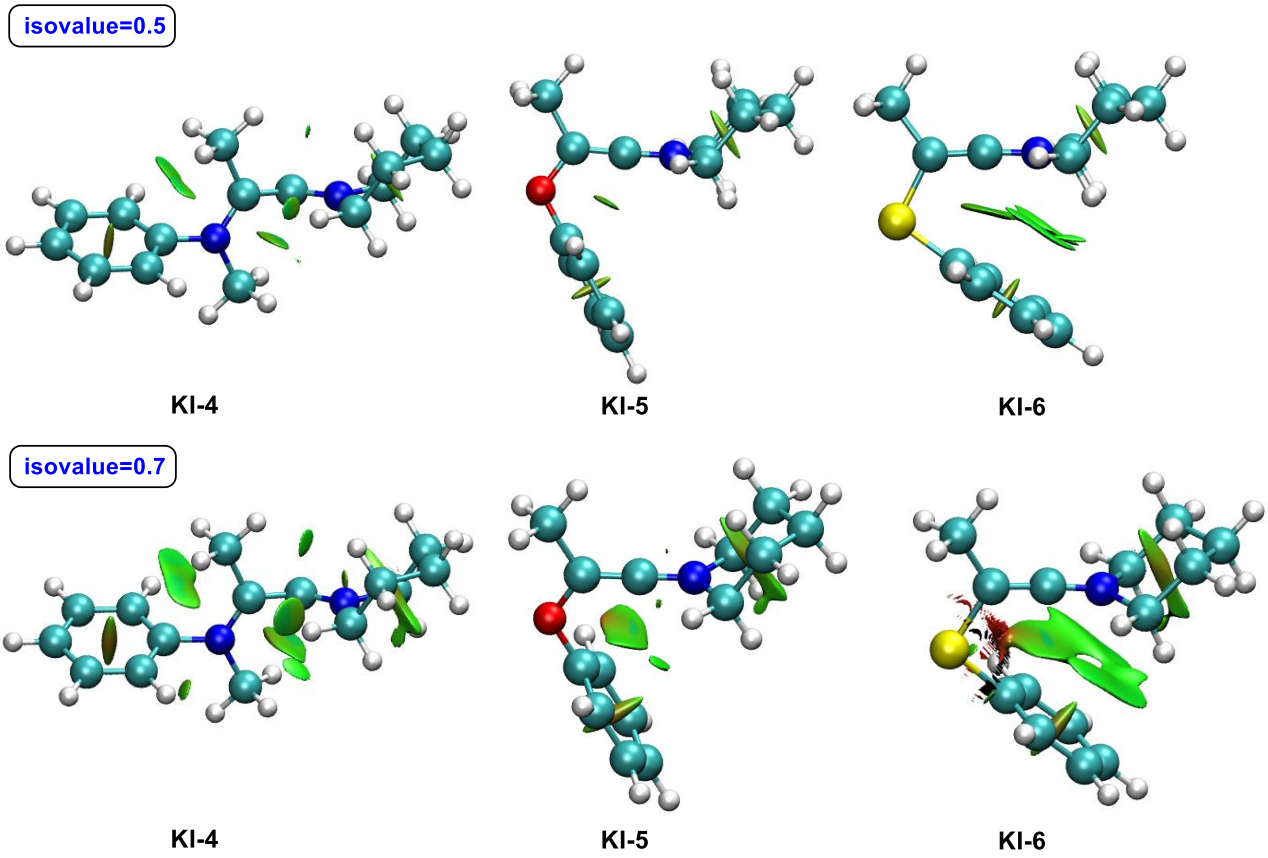
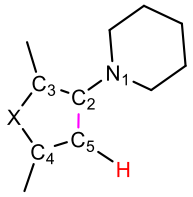
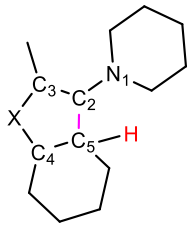


Figure S1. The non-covalent interaction (NCI) plots of the optimized KI structures. NCI isosurface values= 0.5 and 0.7 au using SCF densities. NCI color scale is $-0.04 < \rho < 0.04$ au.

Table S2. Evolution of distances through the electrocyclization reaction (distances in Å).



X= N-Me, O, S



Distance	**KI**[a]	**KI-PRC**	**TS**	**Int**[b]	**Distance**	**KI**[a]	**KI-PRC**	**TS**	**Int**[b]
N_1-C_2	1.25	1.27	1.28	1.36	N_1-C_2	1.25	1.27	1.29	1.37
C_2-C_3	1.31	1.39	1.38	1.37	C_2-C_3	1.31	1.39	1.38	1.37
N-C_3	1.42	1.34	1.35	1.44	**N**-C_3	1.42	1.33	1.36	1.41
N-C_4	1.42	1.43	1.39	1.30	**N**-C_4	1.42	1.44	1.38	1.32
C_4-C_5	1.34	1.33	1.35	1.48	C_4-C_5	1.40	1.39	1.41	1.48
C_2-C_5	3.34	2.88	**2.42**	1.51	C_2-C_5	3.62	4.33	**2.10**	1.53

Distance	**KI**	**TS**	**Int**[b]	**Distance**	**KI**	**TS**	**Int**[b]
N_1-C_2	1.25	1.28	1.36	N_1-C_2	1.25	1.30	1.37
C_2-C_3	1.32	1.34	1.36	C_2-C_3	1.32	1.35	1.36
O-C_3	1.34	1.35	1.43	**O**-C_3	1.35	1.36	1.40
O-C_4	1.41	1.36	1.27	**O**-C_4	1.40	1.35	1.31
C_4-C_5	1.33	1.36	1.48	C_4-C_5	1.39	1.41	1.46
C_2-C_5	3.11	**2.19**	1.51	C_2-C_5	3.22	**1.98**	1.54

Distance	**KI**	**TS**	**Int**[b]	**Distance**	**KI**	**TS**	**Int**[b]
N_1-C_2	1.25	1.28	1.35	N_1-C_2	1.25	1.30	1.36
C_2-C_3	1.30	1.34	1.39	C_2-C_3	1.30	1.35	1.37
S-C_3	1.76	1.73	1.72	**S**-C_3	1.77	1.73	1.73
S-C_4	1.79	1.73	1.62	**S**-C_4	1.78	1.73	1.67
C_4-C_5	1.33	1.36	1.49	C_4-C_5	1.40	1.41	1.47
C_2-C_5	3.54	**2.22**	1.51	C_2-C_5	3.30	**2.01**	1.54

[a] KI (Reactant) unless specified is linear.

[b] Note that the electrocyclization initially leads to an intermediate (Int) where C_5 bears a H atom. Upon deprotonation of C_5, aromaticity is established, and the end product is obtained.

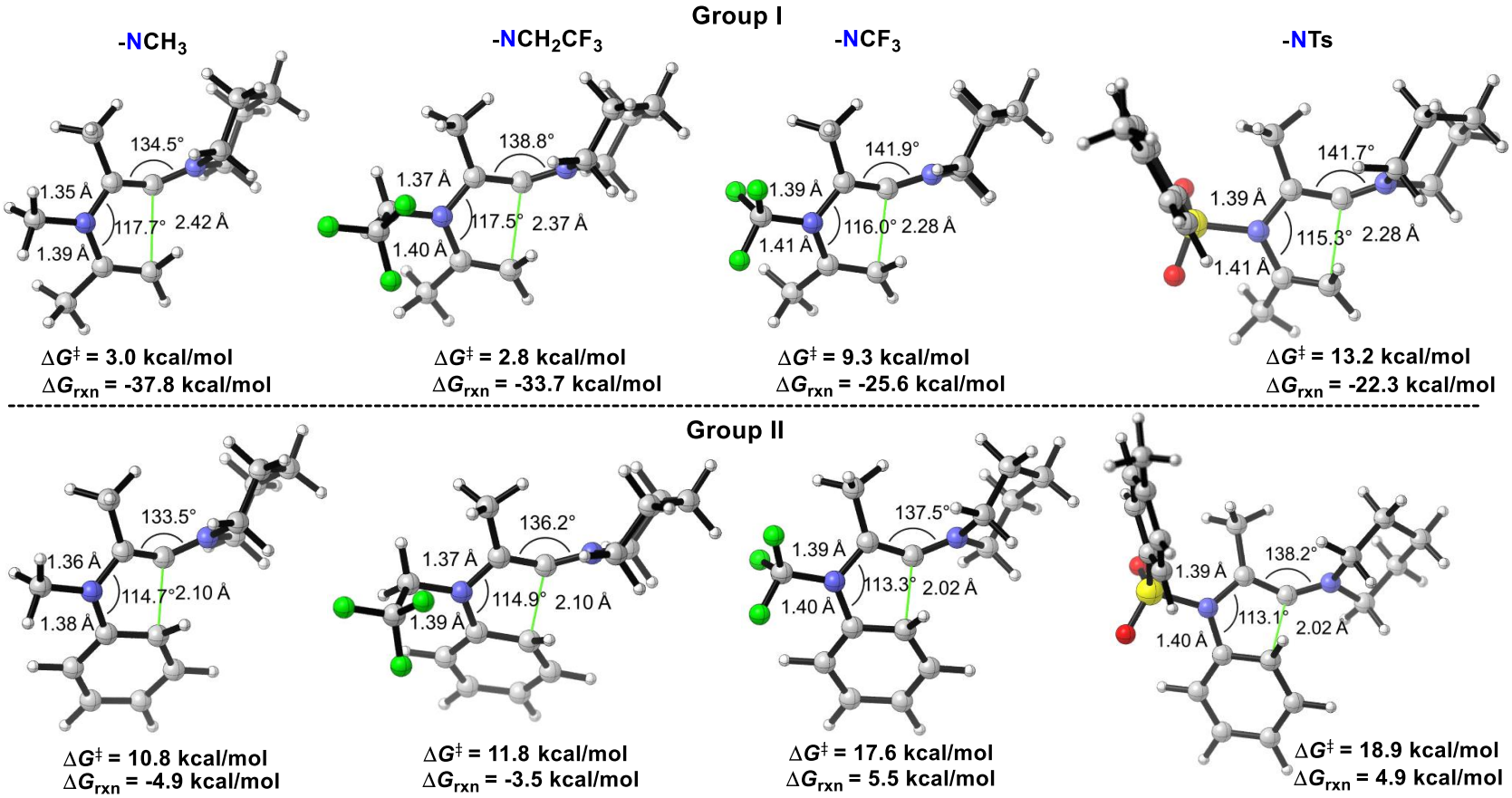


Figure S2. Optimized TS structures (M06-2X/6-31+G(d,p) in $CHCl_3$, 6-311++G(3df,3pd) extra basis set for S atom). All energies for the formation of pyrrole and indole derivatives in **Figure S2** are relative to the pre-reactive conformer (PRC).

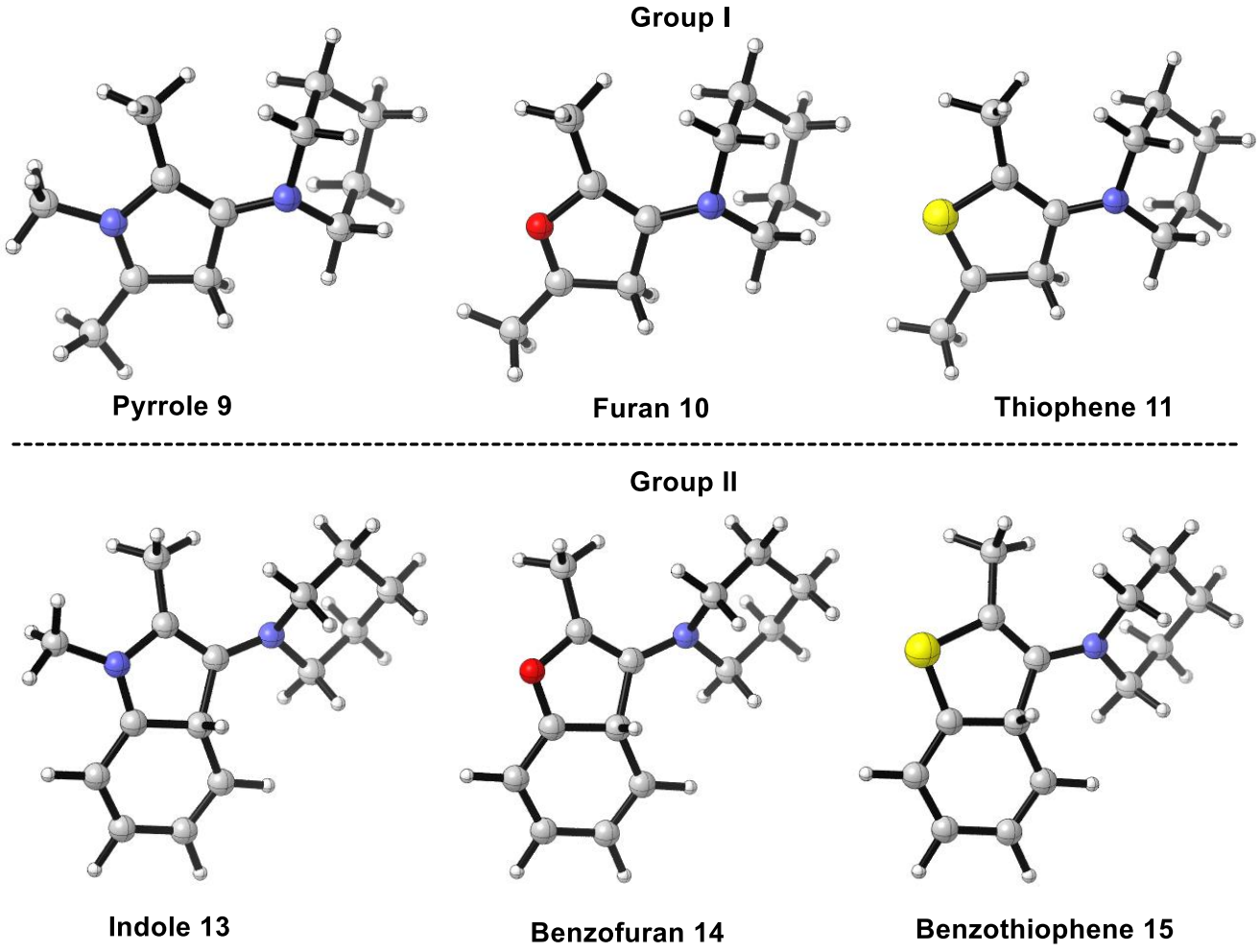


Figure S3. Optimized intermediate structures (M06-2X/6-31+G(d,p) in $CHCl_3$, 6-311++G(3df,3pd) extra basis set for S atom).

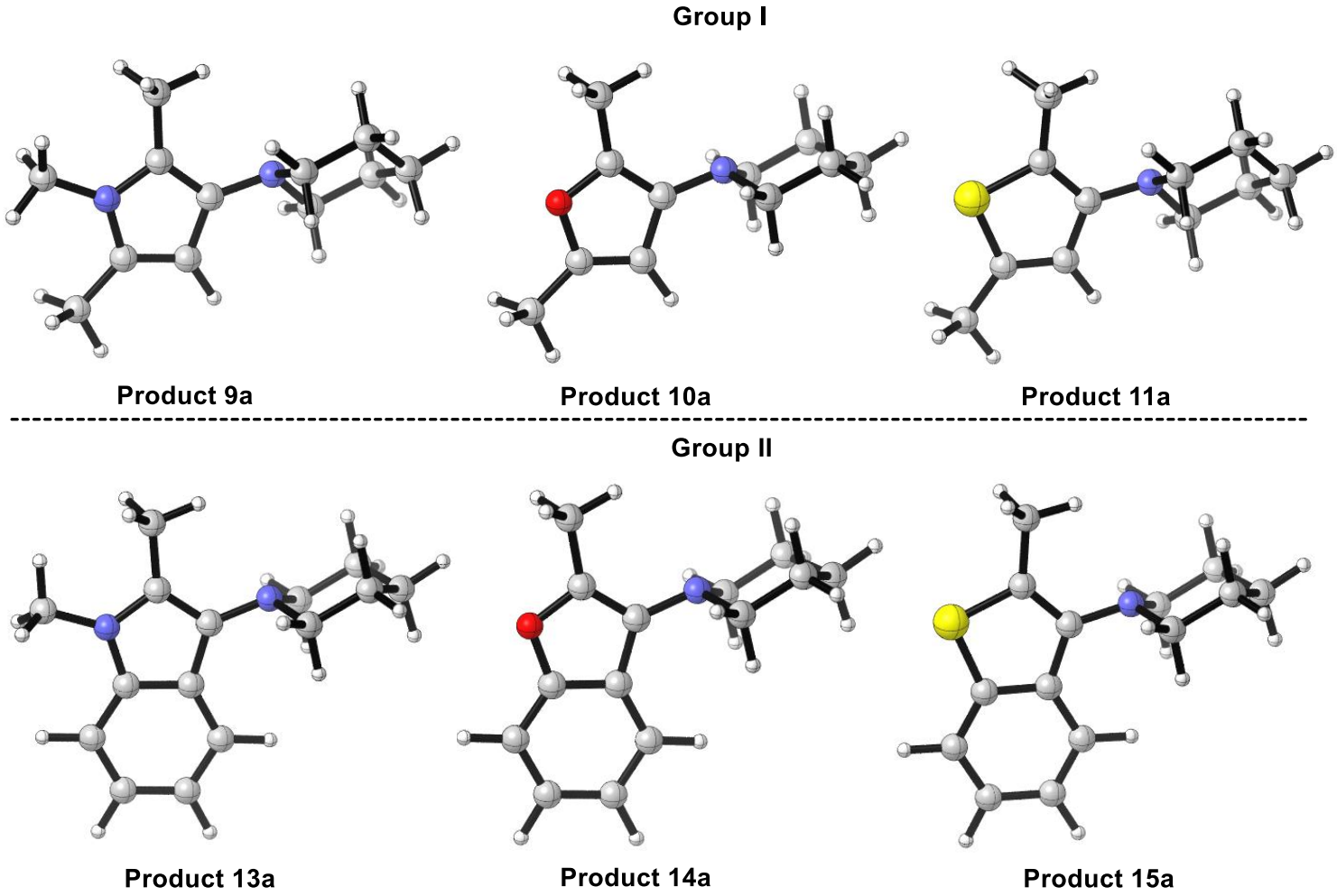


Figure S4. Optimized end product structures (M06-2X/6-31+G(d,p) in $CHCl_3$, 6-311++G(3df,3pd) extra basis set for S atom).

Frontier Molecular Orbitals (FMO) Analysis

According to Woodward-Hoffmann rules,[1] pericyclic ring closure in (4n+2)π systems proceeds through a concerted disrotatory motion. FMO analysis of the keteniminiums in **Groups I** and **II** (**Figure 5**) show HOMOs of keteniminiums primed for a disrotatory closure.

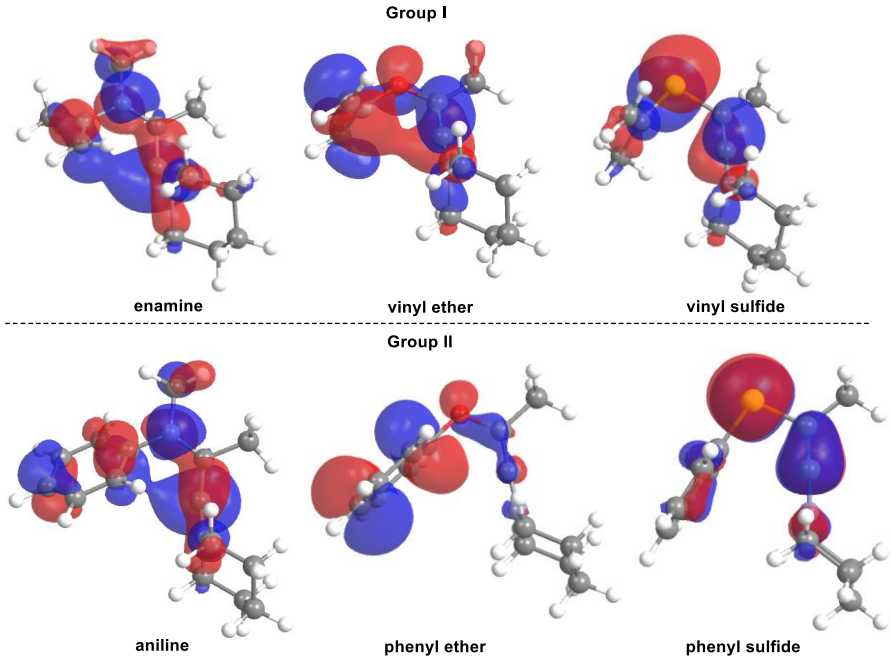


Figure S5. HOMO of keteniminium ions. (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p) in CHCl3, extra basis set for S atom; iso-surface value = 0.03 au).

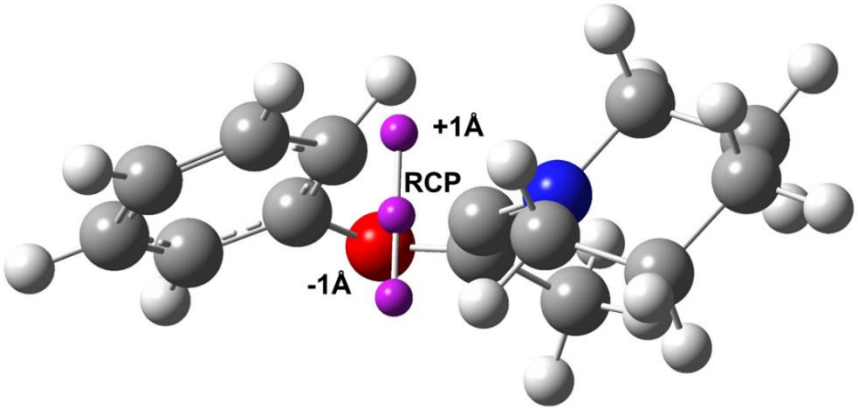


Figure S6. One of the representative image of points (Bq ghost atoms) for NICS calculations

Substituent effect tables of Groups I and II

In general, in case of energy refinements with MPW1K and B2LYP, the activation barriers of phenyl substituent (entry 5, **Group I**) decrease sharply compared to the M06-2X and ωB97XD.

Table S3. Gibbs free energy barriers for the formation of 3-aminopyrrole derivatives in Group I (energies in kcal/mol at 298 K and 1 atm)

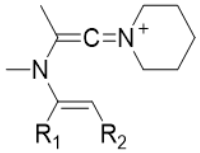
			M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)	
Entry	**R_1**	**R_2**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**
1	CH_3	H	3.0	-37.8	1.9	-42.4	2.9	-39.3	4.8	-34.3
2(E)	H	CH_3 (E)	2.8	-29.8	2.9	-31.2	2.3	-30.9	6.4	-22.3
3(Z)	H	CH_3 (Z)	7.0	-33.0	8.6	-36.0	8.0	-33.5	13.7	-27.2
4	H	H	2.9	-35.1	2.1	-39.0	2.7	-36.3	5.0	-30.9
5	Ph	H	3.8	-35.0	0.6	-42.0	3.7	-36.5	2.7	-34.6
6(E)	H	Ph	2.6	-30.6	1.9	-30.6	2.3	-32.0	4.6	-22.1
7(Z)	H	Ph	5.4	-31.1	5.9	-36.7	6.4	-31.7	10.7	-29.3
8	CO_2Me	H	6.4	-31.8	6.2	-36.7	6.8	-33.6	10.6	-26.3
9(E)	H	CO_2Me	6.0	-24.7	6.7	-25.3	4.7	-26.4	10.0	-16.8
10	CO_2Me	CO_2Me	7.2	-26.7	6.4	-29.1	7.4	-27.5	10.5	-18.7
11	CN	H	5.3	-32.4	5.4	-36.8	5.0	-34.3	9.8	-26.1
12(E)	H	CN (E)	7.0	-19.3	7.6	-19.6	5.9	-20.8	14.3	-11.1
13(Z)	H	CN (Z)	8.0	-22.9	10.7	-24.6	8.3	-24.6	15.5	-16.9

Table S4. Gibbs free energy barriers for the formation of 3-aminofuran derivatives in Group I (energies in kcal/mol at 298 K and 1 atm)

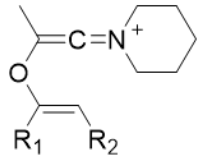
			M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)	
Entry	**R_1**	**R_2**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**
1	CH_3	H	6.0	-23.8	4.8	-27.8	5.5	-26.6	10.1	-19.1
2(E)	H	CH_3 (E)	10.6	-14.0	11.0	-15.7	9.9	-16.0	17.6	-6.8
3(Z)	H	CH_3 (Z)	15.6	-14.1	17.2	-16.0	15.7	-16.1	24.0	-6.9
4	H	H	10.5	-16.1	10.5	-18.6	10.0	-18.4	16.8	-8.9
5	Ph	H	8.3	-23.9	4.1	-31.3	8.0	-26.7	7.5	-24.2
6(E)	H	Ph	9.4	-13.4	10.1	-12.7	8.4	-16.4	16.5	-2.4
7(Z)	H	Ph	15.1	-11.5	15.6	-16.1	14.6	-14.1	22.6	-8.1
8	CO_2Me	H	12.8	-12.7	10.9	-18.3	11.8	-16.3	17.0	-7.7
9(E)	H	CO_2Me	12.6	-8.3	13.3	-8.7	11.9	-9.8	19.7	1.3
10	CO_2Me	CO_2Me	16.9	-6.5	15.1	-9.3	15.1	-9.9	21.5	2.0
11	CN	H	15.9	-9.3	14.3	-14.6	14.7	-12.9	20.4	-3.7
12(E)	H	CN (E)	15.3	-1.7	15.7	-2.8	14.6	-3.5	22.5	6.5
13(Z)	H	CN (Z)	20.1	-1.0	22.5	-2.8	20.3	-2.9	30.5	7.6

Table S5. Gibbs free energy barriers for the formation of 3-aminothiophene derivatives in Group I (energies in kcal/mol at 298 K and 1 atm)

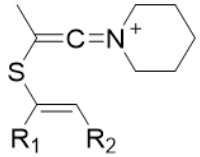
			M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)		Yield%[2]
Entry	**R_1**	**R_2**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	
1	CH_3	H	11.4	-22.2	9.9	-27.4	10.9	-25.0	15.5	**-16.9**	80%
2(E)	H	CH_3 (E)	14.5	-14.5	15.1	-15.8	13.8	-15.9	21.7	-4.8	
3(Z)	H	CH_3 (Z)	20.2	-15.0	22.3	-17.7	20.5	-17.0	29.2	-7.1	
4	H	H	14.3	-18.5	14.4	-22.0	13.9	-20.9	20.6	-10.8	
5	Ph	H	13.5	-22.1	9.4	-30.0	13.4	-24.4	13.3	-20.9	95%
6(E)	H	Ph	13.1	-13.8	14.0	-13.5	12.4	-16.1	20.5	-1.5	72% E/Z:80:20
7(Z)	H	Ph	18.7	-14.0	19.8	-19.2	18.6	-16.5	27.0	-9.8	10% E/Z 13:87
8	CO_2Me	H	15.7	-18.0	13.8	-24.5	14.6	-21.4	19.8	-13.1	47%
9(E)	H	CO_2Me	15.4	-10.7	17.4	-11.0	14.7	-12.3	23.9	0.4	56% E/Z:60:40
10	CO_2Me	CO_2Me	17.0	-13.5	15.6	-17.1	15.9	-15.5	21.5	-5.3	58% E/Z:67:33
11	CN	H	20.0	-14.0	19.4	-19.1	19.5	-16.6	25.7	-7.3	36%
12(E)	H	CN (E)	16.1	-6.7	16.9	-7.9	15.7	-8.2	23.6	3.5	54%
13(Z)	H	CN (Z)	21.1	-7.1	23.5	-9.1	21.4	-9.0	31.4	1.5	E/Z:100:0

Table S6. Gibbs free energy barriers for the formation of 3-aminoindole derivatives in Group II (energies in kcal/mol at 298 K and 1 atm)

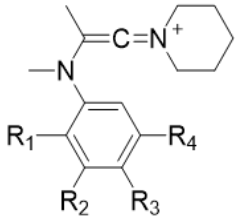
					M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)		Yield%
Entry	**R_1 (*o*-)**	**R_2 (*m*-)**	**R_3 (*p*-)**	**R_4 (*m*-)**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	
1	H	H	H	H	10.8	-4.9	10.1	-8.3	11.6	-5.8	16.4	0.5	84%[3]
2	H	CH_3	H	CH_3	9.2	-4.7	9.2	-7.5	9.7	-6.2	15.1	1.5	
3	CH3	H	H	H	15.2	-1.9	14.1	-5.9	16.0	-2.8	20.5	3.0	
4	H	CH_3	H	H	8.9	-7.5	8.1	-11.0	9.7	-8.4	14.1	-2.5	
5	H	H	CH_3	H	10.4	-4.9	9.7	-8.3	11.1	-5.8	16.0	0.5	
6	H	H	CF_3	H	10.1	-3.8	9.6	-7.1	10.7	-4.9	15.8	1.8	
7	H	CF_3	H	H	9.6	-3.5	9.1	-6.8	10.4	-4.3	15.6	2.7	
8	CF_3	H	H	H	17.2	1.5	15.8	-2.8	18.0	0.6	22.4	6.6	
9	H	H	CN	H	9.9	-3.9	9.2	-7.1	10.4	-5.0	15.6	1.9	
10	H	CN	H	H	10.5	-3.1	10.2	-6.3	11.4	-3.8	16.7	3.6	
11	H	Cl	H	H	10.0	-6.0	9.3	-9.3	10.8	-6.9	15.6	-0.3	
12	H	H	Cl	H	11.0	-4.1	10.4	-7.3	11.7	-5.1	16.8	1.6	
13	Cl	H	Cl	H	17.8	2.8	16.7	-0.9	18.0	1.5	23.2	8.4	

Table S7. Gibbs free energy barriers for the formation of 3-aminobenzofuran derivatives in Group II (energies in kcal/mol at 298 K and 1 atm)

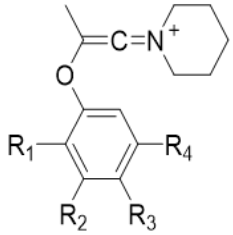
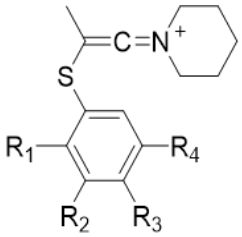
					M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)		Yield%[3]
Entry	**R_1 (*o*-)**	**R_2 (*m*-)**	**R_3 (*p*-)**	**R_4 (*m*-)**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	
1	H	H	H	H	17.0	8.0	15.5	4.2	16.1	5.3	22.4	12.7	69%
2	H	CH_3	H	CH_3	13.6	4.8	12.5	1.2	12.5	1.6	18.9	9.2	93%
3	CH3	H	H	H	16.3	6.3	14.0	1.7	15.4	3.6	20.6	9.9	
4	H	CH_3	H	H	14.6	4.4	12.9	0.4	13.8	1.8	19.4	8.4	
5	H	H	CH_3	H	16.6	7.0	15.0	3.3	15.7	4.3	21.9	11.8	
6	H	H	CF_3	H	18.1	9.6	16.3	5.7	17.0	6.9	23.5	14.5	
7	H	CF_3	H	H	19.6	11.7	18.0	7.9	18.7	9.3	25.5	17.5	
8	CF_3	H	H	H	18.9	11.9	16.0	6.7	17.3	8.6	23.2	15.6	
9	H	H	CN	H	19.3	12.2	17.6	8.7	18.2	9.6	25.1	17.6	
10	H	CN	H	H	19.8	12.0	18.5	8.5	19.0	9.7	26.2	18.5	
11	H	Cl	H	H	18.5	9.3	16.7	5.3	17.7	6.9	23.8	14.2	
12	H	H	Cl	H	17.5	10.1	15.7	6.3	16.4	7.5	23.0	15.1	
13	Cl	H	Cl	H	20.5	13.3	17.9	8.6	19.0	10.3	25.1	17.6	91%

Table S8. Gibbs free energy barriers for the formation of 3-aminobenzothiophene derivatives in Group I (energies in kcal/mol at 298 K and 1 atm)

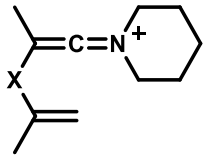
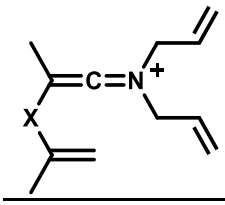
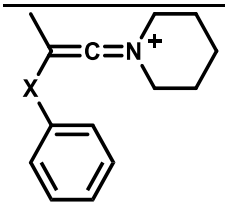
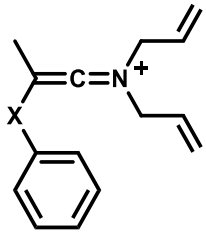


					M06-2X/ 6-31+G(d,p)		MPW1K/ 6-31+G(d,p)		ωB97XD/ 6-31+G(d,p)		B2PLYP/ 6-31+G(d,p)		Yield% [4]
Entry	**R_1 (*o*-)**	**R_2 (*m*-)**	**R_3 (*p*-)**	**R_4 (*m*-)**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	**$\Delta G^{\ddagger}$**	**ΔG_{rxn}**	
1	H	H	H	H	21.0	9.0	18.6	3.9	20.4	6.9	25.5	13.8	93%
2	H	CH_3	H	CH_3	18.8	8.5	16.4	3.7	18.1	6.1	22.7	13.0	78%
3	CH3	H	H	H	19.3	7.6	15.9	1.4	18.9	5.6	22.2	10.7	
4	H	CH_3	H	H	18.9	7.1	15.9	1.2	18.5	4.9	22.2	10.5	
5	H	H	CH_3	H	21.7	10.4	17.2	3.2	21.2	8.3	25.8	14.9	
6	H	H	CF_3	H	22.8	11.5	20.0	6.0	22.3	9.5	26.9	16.0	80%
7	H	CF_3	H	H	20.7	11.5	18.3	6.5	20.5	9.9	25.8	17.2	
8	CF_3	H	H	H	21.5	10.8	18.1	4.6	20.7	8.3	25.2	14.6	88%
9	H	H	CN	H	22.0	12.3	20.1	7.9	21.5	10.3	27.7	18.4	47%
10	H	CN	H	H	22.4	12.0	20.4	7.2	22.2	10.4	27.9	18.1	
11	H	Cl	H	H	21.2	9.3	17.6	3.0	20.7	7.3	25.1	13.7	
12	H	H	Cl	H	22.1	11.7	19.7	6.6	21.6	9.6	26.9	16.7	
13	Cl	H	Cl	H	22.9	13.0	19.8	7.3	21.9	10.5	26.8	17.3	89%

Effect of *N*-substituents on Keteniminium Reactivity

The effect of N-substituents were investigated for the electrocyclization of **Groups I** and **II** keteniminiums with the substitution pattern (**Table S9**).

Table S9. Effect of N-substituents on free energy barriers ($\Delta G^{\ddagger}$), and reaction free energies (ΔG_{rxn}) of *6π*-electrocyclizations of keteniminium salts in Groups I and II.[a,b]

Group I	**Pyrrole**		**Furan**		**Thiophene**	
	$\Delta G^{\ddagger}$	ΔG_{rxn}	$\Delta G^{\ddagger}$	ΔG_{rxn}	$\Delta G^{\ddagger}$	ΔG_{rxn}
	3.0	-37.8	6.0	-23.8	11.4	-22.2
	2.8	-40.8	7.0	-27.0	11.9	-25.8
Group II	**Aniline**		**Phenyl ether**		**Phenyl sulfide**	
	10.8	-4.9	17.0	8.0	21.0	9.0
	10.3	-5.9	16.2	7.1	19.7	8.8

[a] M06-2X/6-31+G(d,p) in $CHCl_3$ (ε=4.7113); free energies in kcal/mol

[b] 6-311++G(3df,3pd) extra basis set for sulfur atom

Cartesian Coordinates for Keteniminiums (KI)

Enamine 1 (reactant, linear)

C	2.570999	0.676045	0.097825
C	2.119135	1.578104	0.982986
H	2.649732	2.513553	1.104794
H	1.236593	1.422882	1.592740
C	0.768103	-0.844280	0.606572
C	-0.383704	-0.453835	0.124117
C	0.902185	-1.574305	1.914404
H	-0.051718	-1.645779	2.437556
H	1.623780	-1.039441	2.538573
H	1.282770	-2.583419	1.733819
N	-1.459188	0.000264	-0.324541
C	-1.943753	1.375045	0.008760
H	-1.193576	1.838267	0.649698
H	-1.990640	1.913521	-0.942641
C	-2.367508	-0.802557	-1.197418
H	-1.896970	-1.772810	-1.353074
H	-2.419630	-0.263459	-2.148532
C	-3.736590	-0.900194	-0.533515
H	-3.648204	-1.497578	0.381200
H	-4.399276	-1.440895	-1.214363
C	-3.315717	1.272827	0.665840
H	-3.208775	0.787898	1.643086
H	-3.676292	2.289546	0.842893
C	-4.293595	0.487273	-0.210170
H	-5.254961	0.392132	0.300276
H	-4.476872	1.035495	-1.142619
N	1.903820	-0.540727	-0.193005
C	2.707647	-1.722778	-0.531534
H	3.314494	-1.509393	-1.410673
H	2.031247	-2.541011	-0.783493
H	3.362647	-2.034633	0.291872
C	3.817343	0.911315	-0.711557
H	4.183283	1.921812	-0.530807
H	4.610739	0.208391	-0.440808
H	3.616352	0.796082	-1.781162

Energy = -578.660765 hartree

Enamine 1 (PRC, KI-1)

H	-4.61329400	-1.06036900	-0.02822600
C	-3.68976700	-1.47587300	-0.44121800
H	-3.64881700	-1.21500200	-1.50337500

H	-3.73603900	-2.56060600	-0.34426300
C	-2.47771800	-0.95596100	0.27685200
C	-1.63535700	-1.70920700	0.98766900
H	-1.78643200	-2.78009900	1.05192700
H	-0.81351100	-1.27911300	1.54954700
C	-1.01076100	0.85400500	-0.27177100
C	-0.00641900	-0.01204400	-0.67450900
C	-0.74237100	2.31441300	-0.52460600
H	0.27214100	2.45025900	-0.89887200
H	-1.44106500	2.72508000	-1.25737700
H	-0.85087000	2.86541400	0.41465400
N	1.12431900	-0.34475900	-0.19403600
C	2.09257500	-1.14538700	-0.98071500
H	1.63368400	-1.34269100	-1.94873800
H	2.22953200	-2.09219800	-0.44563300
C	1.60363200	0.00093500	1.17054600
H	0.82119500	0.58403800	1.66025600
H	1.73649600	-0.94496500	1.70920200
C	2.92515200	0.76125200	1.08227000
H	2.74726400	1.73381200	0.60810500
H	3.27596600	0.95388200	2.09996500
C	3.41326200	-0.39027900	-1.09740000
H	3.25018900	0.51973300	-1.68756800
H	4.11992800	-1.01528200	-1.64998300
C	3.96237900	-0.03024500	0.28375100
H	4.88184400	0.55247600	0.18501500
H	4.21952200	-0.94864900	0.82691900
N	-2.22265400	0.44342800	0.10958400
C	-3.37186700	1.35697700	0.14647500
H	-4.07282200	0.99844200	0.89857300
H	-3.04628400	2.35375400	0.43507100
H	-3.86671700	1.39989000	-0.82810000

Energy = -578.673130 hartree

Enol Ether 2 (KI-2)

H	-3.10562500	-2.47906200	-0.96849400
C	-3.06281400	-1.39505200	-1.07675200
H	-2.34545600	-1.14269300	-1.86506500
H	-4.04466300	-1.02725800	-1.38809000
C	-2.66773300	-0.75738100	0.21317100
C	-2.40382700	-1.32924400	1.38187700
H	-2.45599700	-2.40659900	1.48248800
H	-2.15160000	-0.73392000	2.25321300
C	-1.39362400	1.18749000	-0.04122500
C	-0.28792700	0.46893900	-0.01965300
C	-1.37590700	2.66637200	-0.26580100
H	-1.84862000	3.15253100	0.59093300

H	-1.95389300	2.89296700	-1.16445800
H	-0.35829100	3.03858200	-0.38109300
N	0.80198600	-0.14362500	0.03817900
C	1.44579100	-0.75465900	-1.16156400
H	0.78652000	-0.57212800	-2.00981300
H	1.49753500	-1.82972100	-0.96055400
C	1.56648400	-0.30346800	1.31039200
H	0.98809800	0.17894400	2.09777800
C	2.83745400	-0.15630100	-1.34006300
H	3.31051200	-0.65420500	-2.19058100
H	2.73946800	0.90533100	-1.59478400
H	1.61548400	-1.38112500	1.49779600
C	2.95926000	0.29378100	1.13382900
H	3.51913000	0.11684200	2.05601300
H	2.86940200	1.37903800	1.00838600
C	3.67409400	-0.32233300	-0.07019000
H	3.85140000	-1.38899400	0.11518900
H	4.65127800	0.14778400	-0.20371300
O	-2.61576100	0.65252500	0.12168300

Energy = -559.269379 hartree

Vinyl sulfide 3 (KI-3)

H	-1.33630500	-1.19286400	-1.82778500
C	-2.04801200	-1.78624200	-1.24456400
H	-1.66500300	-2.80481000	-1.15016800
H	-2.98273800	-1.81127800	-1.81240500
C	-2.28236600	-1.18421600	0.11273200
C	-2.22341800	-1.84255300	1.27116700
H	-1.97858300	-2.90160700	1.28598300
H	-2.42964500	-1.35371900	2.21731300
S	-2.77121400	0.53546900	0.13979400
C	-1.21743300	1.33691400	-0.07781400
C	-0.10283900	0.66192100	-0.04600500
C	-1.25656300	2.83195800	-0.28193900
H	-1.77701000	3.29441500	0.55983700
H	-0.25079800	3.24478500	-0.35521300
H	-1.80780500	3.05184700	-1.19862300
N	0.95419100	-0.00721100	0.02766500
C	1.65613400	-0.24325900	1.32555000
H	1.06611500	0.23761200	2.10512300
H	1.64700300	-1.32803500	1.47534300
C	1.62386700	-0.59888600	-1.16864400
H	1.02311700	-0.34136100	-2.04071200
C	3.08023600	0.29286200	1.23214700
H	3.58848900	0.05996000	2.17164000
H	3.04668100	1.38463000	1.13923200
H	1.60835800	-1.68338900	-1.01761200

C	3.05130600	-0.06842400	-1.25791500
H	3.53813300	-0.56080600	-2.10387000
H	3.01899400	1.00478800	-1.47757900
C	3.81837100	-0.31998600	0.04107500
H	3.93201100	-1.39991100	0.19723100
H	4.82337400	0.10219200	-0.03282400

Energy = -882.282789 hartree

Butadiene 4

H	5.24148100	-2.22057300	0.02109100
C	4.23843900	-1.79149000	0.00952400
H	3.71826800	-2.15793800	-0.88175900
H	3.69590600	-2.16358500	0.88500400
C	4.30330100	-0.28794300	0.01443300
C	5.46591500	0.38246200	0.03942200
H	5.49114000	1.46826300	0.04370700
H	6.41816600	-0.13796300	0.05800700
C	0.60278000	0.73693400	-0.03664700
C	-0.57228800	0.15958800	-0.02274000
C	0.65458300	2.24976700	-0.07616400
H	1.19542500	2.56968200	-0.96976200
H	1.18501400	2.61451300	0.80650200
H	-0.34427900	2.68504000	-0.09219200
N	-1.70499200	-0.37211900	0.00525600
C	-2.43732600	-0.62837600	1.28351000
H	-1.77979700	-0.33284600	2.10043400
H	-2.60905700	-1.70845000	1.32212600
C	-2.45880900	-0.72963500	-1.23550200
H	-1.81736500	-0.49786700	-2.08523400
C	-3.75043000	0.14687000	1.26245100
H	-4.29511700	-0.09155200	2.17999600
H	-3.53056100	1.22120100	1.28143700
H	-2.62516200	-1.81021600	-1.18553300
C	-3.77592300	0.03909800	-1.25392100
H	-4.33717400	-0.27980800	-2.13630100
H	-3.56333800	1.10807900	-1.37062300
C	-4.57821900	-0.20623300	0.02528700
H	-4.87826500	-1.26050900	0.07413800
H	-5.49497000	0.38796400	0.00867600
C	1.82458200	-0.07682900	-0.01441800
H	1.69757300	-1.15515900	-0.00238500
C	3.05168600	0.47396900	-0.00791300

H	3.15731200	1.55747400	-0.01804900

Energy = -561.435580 hartree

Aniline 5 (reactant, linear)

H	2.774697	2.510887	-0.653685
C	2.824513	1.457365	-0.407104
C	3.016387	-1.245275	0.249332
C	1.658516	0.714943	-0.184845
C	4.072055	0.840055	-0.307317
C	4.179696	-0.507227	0.024319
C	1.766911	-0.646649	0.138873
H	0.868872	-1.238585	0.293139
C	-0.601266	0.852721	0.617215
C	-0.382541	0.983515	2.100773
H	0.511961	0.425314	2.387781
H	-1.236016	0.612780	2.669064
H	-0.220197	2.039449	2.336909
C	-1.708611	0.365649	0.115397
N	-2.776285	-0.064306	-0.373704
C	-3.018174	-1.520907	-0.608996
H	-3.189628	-1.625652	-1.684682
H	-2.107821	-2.051710	-0.331210
C	-3.926466	0.829747	-0.707644
H	-4.097379	0.707434	-1.781701
H	-3.616566	1.853821	-0.501551
C	-4.236920	-1.955320	0.198702
H	-4.433647	-3.005265	-0.033808
H	-3.997637	-1.895588	1.266933
C	-5.139790	0.394575	0.106713
H	-5.983157	1.024990	-0.187051
H	-4.943184	0.582864	1.168593
C	-5.453524	-1.084880	-0.122355
H	-5.749917	-1.237249	-1.167372
H	-6.300137	-1.386357	0.498954
N	0.373637	1.295448	-0.318789
C	0.277302	2.713608	-0.670586
H	0.721096	3.365876	0.093404
H	0.784759	2.879544	-1.622528
H	-0.774177	2.973335	-0.793136
H	4.965614	1.430137	-0.484696
H	3.079525	-2.298812	0.502658
H	5.153277	-0.978111	0.105022

Energy = -692.943930 hartree

Aniline 5 (PRC, KI-4)

H	1.855709	-2.122386	0.449040
C	2.436653	-1.225240	0.256171
C	3.894562	1.107555	-0.238572
C	1.832462	0.026285	0.354392
C	3.782931	-1.303669	-0.094624
C	4.509526	-0.139752	-0.345783
C	2.550868	1.196736	0.119915
H	5.556826	-0.204547	-0.621203
H	2.064396	2.161891	0.226714
C	-0.499731	0.504903	-0.091701
C	-0.199121	0.774818	-1.539727
H	0.392787	1.685518	-1.654474
H	-1.127846	0.892660	-2.099237
H	0.377037	-0.061308	-1.944244
C	-1.761323	0.866641	0.370767
N	-2.868572	0.240433	0.432432
C	-4.115972	0.914330	0.867533
H	-4.476515	0.378244	1.752579
H	-3.850378	1.933829	1.144480
C	-3.066675	-1.180874	0.038646
H	-3.424441	-1.709510	0.929277
H	-2.093205	-1.582343	-0.248337
C	-5.145992	0.858268	-0.257394
H	-6.066919	1.330021	0.095685
H	-4.777885	1.450420	-1.103860
C	-4.089801	-1.265098	-1.091809
H	-4.250574	-2.320171	-1.330115
H	-3.672095	-0.787066	-1.986044
C	-5.401340	-0.584577	-0.695623
H	-5.867677	-1.140314	0.127766
H	-6.101758	-0.605789	-1.534407
N	0.449339	0.102931	0.745021
C	0.088329	-0.212763	2.129909
H	-0.449144	-1.163087	2.183887
H	0.996564	-0.272888	2.726163
H	-0.551385	0.589867	2.517618
H	4.261150	-2.273956	-0.175647
H	4.461432	2.013594	-0.424130

Energy = -692.959073 hartree

Phenyl Ether 6 (KI-5)

H	2.36304800	0.45905500	2.13054500
C	2.47849700	-0.10118200	1.20823600
C	2.77427900	-1.47739800	-1.21297000

C	2.18376600	0.50120800	-0.00758300
C	2.93061300	-1.42082900	1.20132800
C	3.07534100	-2.10734900	-0.00454400
C	2.32270900	-0.15829700	-1.22276300
H	3.17479500	-1.90809200	2.13927700
H	3.43179300	-3.13183300	-0.00359700
H	2.09131400	0.35953500	-2.14845800
H	2.89834400	-2.00821500	-2.15089400
O	1.72860200	1.82924500	-0.00882100
C	0.38769700	1.96904400	-0.01354800
C	-0.10295700	3.37959600	-0.07169800
H	0.28113700	3.92113600	0.79583400
H	-1.19190600	3.42132100	-0.07447100
H	0.28431300	3.84704400	-0.97987000
C	-0.42504300	0.93266900	0.04710800
N	-1.23108600	-0.02451100	0.04533900
C	-1.79790300	-0.60119000	1.30001800
H	-1.47173000	-1.64577300	1.32589600
H	-1.35484800	-0.05907000	2.13479500
C	-1.72190900	-0.65898200	-1.21427200
H	-1.39257400	-1.70250300	-1.17205900
H	-1.22860600	-0.15332000	-2.04390400
C	-3.31894900	-0.49217300	1.25162000
H	-3.71768100	-0.96513400	2.15290200
H	-3.60160200	0.56657300	1.28509500
C	-3.24275200	-0.55338300	-1.26496400
H	-3.58471000	-1.07156400	-2.16470000
H	-3.52237900	0.50134800	-1.36833800
C	-3.88016400	-1.15168000	-0.00957700
H	-3.68469500	-2.23062200	0.02226600
H	-4.96456300	-1.02260100	-0.04547000

Energy = -673.555742 hartree

Phenyl Sulfide 7 (KI-6)

H	1.50159300	-2.80876900	2.15408900
C	1.62944000	-2.27761000	1.21658200
C	1.97772400	-0.91475000	-1.20162900
C	1.50850300	-2.95632800	0.00313700
C	1.92073100	-0.91429600	1.22820900
C	2.08804400	-0.23892800	0.01649700
C	1.68670700	-2.27804400	-1.20341100
H	1.28475900	-4.01813400	-0.00191900
H	2.01554200	-0.37415000	2.16537700
H	1.60274200	-2.80924900	-2.14580800
H	2.11561400	-0.37451800	-2.13329400
C	-0.26980800	1.21627000	-0.00911600
C	0.69961900	2.08728200	-0.01417800

S	2.37288900	1.51659000	0.02118000
N	-1.14758700	0.32259900	0.00332200
C	-1.68476500	-0.29293200	-1.24610000
H	-1.39510700	-1.34888500	-1.20259600
H	-1.18248400	0.18626200	-2.08647300
C	-1.72765600	-0.21183100	1.27098200
H	-1.44026300	-1.26849800	1.30589300
H	-1.25296800	0.32029300	2.09527300
C	-3.20010500	-0.12756300	-1.27730600
H	-3.57520000	-0.63755000	-2.16852700
H	-3.44070600	0.93635100	-1.38289300
C	-3.24292600	-0.04412600	1.23947600
H	-3.48510400	1.02470100	1.26603000
H	-3.64930700	-0.49409800	2.14916800
C	-3.84321200	-0.69282600	-0.00943700
H	-3.68639200	-1.77807400	0.02887600
H	-4.92262300	-0.52487100	-0.03341200
C	0.49308000	3.57964100	-0.04797300
H	0.97660500	3.98835100	-0.93802200
H	0.95522900	4.02385700	0.83653300
H	-0.56730100	3.82959500	-0.06483900

Energy = -996.571273 hartree

Styrene 8

C	-3.488244	0.695453	-1.081901
C	-4.022026	-0.493922	-0.559522
H	-3.387292	-1.194660	-0.026375
C	0.286978	0.781969	-0.317136
C	1.191531	0.020371	0.245726
C	0.717110	2.126521	-0.863427
H	1.783617	2.294861	-0.716415
H	0.160615	2.918639	-0.357344
H	0.496952	2.168037	-1.932708
N	2.063494	-0.706803	0.772187
C	2.883463	-1.674882	-0.020021
H	2.539078	-1.623842	-1.052439
H	2.663288	-2.664450	0.392150
C	2.399367	-0.635541	2.227967
H	1.738983	0.105050	2.678119
C	4.357992	-1.321898	0.138259
H	4.941485	-2.069689	-0.405515
H	4.546184	-0.351018	-0.334784
H	2.173012	-1.625399	2.636697
C	3.876931	-0.293112	2.383551

H	4.112214	-0.306283	3.451117
H	4.047080	0.727822	2.023354
C	4.757463	-1.279117	1.614090
H	4.655780	-2.280583	2.050617
H	5.807512	-0.992198	1.708072
C	-1.102540	0.317033	-0.399800
H	-1.308966	-0.665958	0.011097
C	-2.072702	1.062933	-0.954837
H	-1.816148	2.039233	-1.362255
C	-4.344827	1.578817	-1.754414
H	-3.943645	2.503588	-2.160521
C	-5.697466	1.284630	-1.908266
H	-6.345224	1.979579	-2.432476
C	-5.371816	-0.786958	-0.712277
H	-5.771380	-1.708759	-0.302060
C	-6.214378	0.100193	-1.387511
H	-7.267917	-0.132624	-1.503306

Energy = -675.718984 hartree

Cartesian Coordinates for TS structures

TS1 - transition state for the parent enamine molecule leading to pyrrole.

H	4.19338400	-0.96210500	1.18162300
C	3.94159200	-1.35465200	0.19281400
H	4.72580100	-1.05027600	-0.50684900
H	3.94247600	-2.44397900	0.23172600
C	2.59418300	-0.88210100	-0.26880800
C	1.62663100	-1.70349100	-0.73896100
H	1.77111500	-2.77682200	-0.71334300
H	0.82120700	-1.33260100	-1.36117300
C	0.05906500	-0.22000200	0.36546300
N	-1.15582300	-0.38408600	-0.00506600
C	-1.76428100	0.26509500	-1.19207400
H	-1.02537000	0.95066700	-1.61010200
H	-1.96416000	-0.52823900	-1.92331600
C	-2.04471300	-1.34643400	0.68116800
H	-1.49156400	-1.75078500	1.52845100
H	-2.25242600	-2.15566500	-0.03011600
C	-3.33723400	-0.65210400	1.10035200
H	-3.10384300	0.10453000	1.85931200
H	-3.99235400	-1.39276900	1.56703800
C	-3.06018900	0.97023300	-0.79865600
H	-2.82444200	1.80853300	-0.13188300
H	-3.51176200	1.38875400	-1.70259900
C	-4.01904600	0.00338800	-0.10151300

H	-4.92017500	0.53386600	0.21689400
H	-4.33470700	-0.77287800	-0.81035600
N	2.28251900	0.46252900	-0.07095000
C	3.34312500	1.46403800	0.09353800
H	4.22495500	1.13674900	-0.45140200
H	3.59110700	1.59639000	1.15035000
H	3.01599600	2.41364800	-0.32682400
C	0.99361500	0.77606900	0.19336600
C	0.61631900	2.18785800	0.55086000
H	0.74404800	2.83307800	-0.32443200
H	1.23706800	2.57601500	1.36188800
H	-0.42762000	2.22740300	0.86192900

Energy = -578.668366 hartree
Imaginary frequency= -218.6951 cm^{-1}

TS2 - transition state for the parent enol ether molecule leading to furan.

H	-4.37611200	-1.99412300	-0.00886000
C	-4.18114000	-0.95425600	-0.26576100
H	-4.22631700	-0.81957800	-1.35007400
H	-4.95734900	-0.32514100	0.18083700
C	-2.85767700	-0.52621900	0.25401700
C	-1.88254700	-1.27203600	0.83162400
H	-1.97920800	-2.35035700	0.86904300
H	-1.23332300	-0.82021000	1.57868700
C	-1.25890000	1.03731200	-0.17891100
C	-0.38568900	0.01876500	-0.11114800
C	-0.93751600	2.42356900	-0.62443500
H	0.10932300	2.49484600	-0.91934500
H	-1.12412400	3.11877000	0.19874200
H	-1.57511600	2.69946500	-1.46712800
N	0.85216900	-0.25366200	0.08578800
C	1.53838600	-1.30255000	-0.70039500
H	0.87746000	-1.58327500	-1.52062000
H	1.66759400	-2.16639900	-0.03557800
C	1.62158900	0.27932800	1.23550800
H	1.01852800	1.05810000	1.70475000
C	2.88916900	-0.78738800	-1.18694500
H	3.39670300	-1.59984500	-1.71398000
H	2.72336500	0.02043400	-1.90940000
H	1.75347700	-0.54833800	1.94440400
C	2.97613800	0.79832600	0.75998200
H	3.54296000	1.12148800	1.63751900
H	2.82167300	1.67942200	0.12575500

C	3.73323000	-0.27975100	-0.01708200
H	3.97045900	-1.11595300	0.65314500
H	4.68289800	0.11918200	-0.38255000
O	-2.57354200	0.77206900	-0.02057200

Energy = -559.259791 hartree
Imaginary frequency= -313.8585cm^{-1}

TS3 - transition state for the parent vinyl sulfide molecule leading to thiophene.

H	-3.90484300	-2.56348400	0.08455500
C	-3.91737800	-1.52529500	-0.24748100
H	-3.94952500	-1.49049500	-1.34030100
H	-4.83166300	-1.05126200	0.12351200
C	-2.71472000	-0.79738400	0.27099200
C	-1.59494100	-1.36812800	0.78573700
H	-1.47114600	-2.44688100	0.76785100
H	-1.01157700	-0.83127200	1.53031900
S	-2.69111300	0.91539900	0.00373300
C	-0.98820600	1.12132400	-0.20393900
C	-0.16314000	0.06758000	-0.11892800
C	-0.49704000	2.47230200	-0.66192200
H	-0.48033000	3.15974700	0.18866700
H	-1.15396400	2.88328500	-1.43129600
H	0.51363300	2.39036600	-1.06482600
N	1.06031100	-0.25156800	0.09719100
C	1.71132600	-1.35807000	-0.63763200
H	1.03937700	-1.65783600	-1.44204700
H	1.81732300	-2.19252000	0.06763100
C	1.84656400	0.31537100	1.22030100
H	1.26553500	1.13290500	1.64983600
C	3.07492500	-0.90562200	-1.15088600
H	3.55849500	-1.75780800	-1.63609600
H	2.92954800	-0.13161800	-1.91359700
H	1.95484200	-0.47916900	1.97016300
C	3.21311500	0.77211900	0.71678900
H	3.79261100	1.12117000	1.57597700
H	3.07929900	1.62630400	0.04237900
C	3.93621000	-0.36338400	-0.00922700
H	4.15252200	-1.17195500	0.70066300
H	4.89519900	-0.00974100	-0.39628400

Energy = -882.264650 hartree
Imaginary frequency= -341.5195 cm^{-1}

TS4 - transition state for the parent butadiene molecule leading to benzene

H	3.16867500	-2.87888600	0.44599300

C	3.58494100	-1.87373800	0.52445600
H	3.62030400	-1.58095600	1.57819100
H	4.61736700	-1.89319000	0.16041800
C	2.78612600	-0.88505700	-0.27653200
C	1.64941500	-1.21026500	-0.94128500
H	1.24374400	-2.21763700	-0.90492600
H	1.26961700	-0.55403300	-1.72059900
C	0.95789700	1.43997500	0.19754100
C	0.20032400	0.35703000	0.04094500
C	0.32491000	2.61629300	0.91886600
H	0.37085800	3.48978500	0.26205800
H	0.88393100	2.84111300	1.83013000
H	-0.71730100	2.42435000	1.17697600
N	-0.94653800	-0.14288000	-0.18948500
C	-1.41829200	-1.38509300	0.46704100
H	-0.66204900	-1.68203200	1.19393700
H	-1.48502300	-2.14973500	-0.31703500
C	-1.86703500	0.41906200	-1.21342200
H	-1.40831200	1.32797700	-1.60380300
C	-2.78142900	-1.13539400	1.10524300
H	-3.13356300	-2.07573600	1.53773500
H	-2.66230500	-0.41941800	1.92694300
H	-1.93556700	-0.32381700	-2.01668900
C	-3.23422000	0.67149500	-0.58424600
H	-3.90796400	1.02488700	-1.36971100
H	-3.14501900	1.47437000	0.15730800
C	-3.77757500	-0.59625600	0.07719100
H	-3.96221600	-1.35985700	-0.68914500
H	-4.73585700	-0.38529500	0.55829300
C	2.37263700	1.53623700	-0.12121200
H	2.78244400	2.54070300	-0.06160400
C	3.22428100	0.49496700	-0.28363000
H	4.29211500	0.70202500	-0.28380200

Energy = -561.420898 hartree
Imaginary frequency= -239.7850 cm^{-1}

TS5 - transition state for the parent aniline molecule leading to indole.

H	-4.22686200	0.66770800	-0.47438100
C	-3.53392400	-0.11221600	-0.18123300
C	-1.72426000	-2.17848800	0.49178600
C	-2.22914300	0.19729700	0.24575600
C	-3.88977000	-1.44203300	-0.29129500

C	-2.97996000	-2.47975000	0.01713100
C	-1.32991100	-0.82284200	0.63111100
H	-4.88294200	-1.69382000	-0.64817400
H	-3.29140700	-3.51291000	-0.08945200
H	-0.61401000	-0.58458700	1.41836500
H	-1.04431600	-2.96363400	0.80509000
N	-1.65972200	1.44502400	0.10039100
C	-0.31606900	1.43509400	-0.12158200
C	0.29778500	0.20706200	-0.21561000
N	1.49581100	-0.21219100	0.03950900
C	2.33229200	0.29420200	1.14816300
H	1.84906000	1.18524800	1.55305800
H	2.34566500	-0.48129900	1.92671100
C	2.02827900	-1.41196100	-0.63263200
H	1.33491000	-1.67431000	-1.43228500
H	2.04080300	-2.22511300	0.10651300
C	3.74944100	0.57776100	0.65605000
H	3.72120200	1.41627800	-0.05041700
H	4.35719100	0.88999900	1.51003500
C	3.43844400	-1.14247400	-1.15087100
H	3.38699200	-0.38679400	-1.94406100
H	3.82724900	-2.06150500	-1.59821600
C	4.34926500	-0.65525500	-0.02272800
H	4.47341500	-1.45542800	0.71864400
H	5.34349700	-0.42240300	-0.41312000
C	0.41244300	2.69730200	-0.47899400
H	0.46301700	3.36000900	0.39118400
H	-0.08300300	3.22980600	-1.29418600
H	1.42971400	2.45749900	-0.78961500
C	-2.47740200	2.63822500	-0.12351000
H	-3.38876600	2.55323100	0.46582800
H	-2.72570000	2.74217300	-1.18375100
H	-1.93339400	3.51846600	0.21368400

Energy = -692.941861 hartree
Imaginary frequency= -247.3606 cm^{-1}

TS6 - transition state for the parent phenyl ether molecule leading to benzofuran.

H	4.21955600	1.19310600	0.65045900
C	3.61223200	0.37545400	0.28016700
C	1.94106100	-1.75556300	-0.57936600
C	2.32850600	0.61200100	-0.19785600
C	4.02983200	-0.94543400	0.33897000
C	3.19013400	-2.01024200	-0.06060100
C	1.48283500	-0.41029800	-0.67911600
H	5.01474800	-1.16829800	0.73580400
H	3.55128200	-3.02941600	0.01581900
H	0.86306700	-0.16578300	-1.54860900

H	1.32244400	-2.55896700	-0.96432000
O	1.73712100	1.81681200	-0.01158500
C	0.39400400	1.69947700	0.13521900
C	-0.32687500	2.94424100	0.51590800
H	-0.33391800	3.63462100	-0.33260500
H	0.17699900	3.42832900	1.35538900
H	-1.35584400	2.71057000	0.79106100
C	-0.12376600	0.45577500	0.07818500
N	-1.29128800	-0.09762800	-0.05855500
C	-1.64253300	-1.30172700	0.71563400
H	-1.54044900	-2.16679600	0.04462800
H	-0.91915000	-1.39886400	1.52630100
C	-2.19060900	0.21254700	-1.18873200
H	-2.09970500	-0.60481000	-1.91851900
H	-1.83816800	1.13662800	-1.65106300
C	-3.07564600	-1.19331100	1.22914000
H	-3.33013400	-2.12219300	1.74705400
H	-3.12913900	-0.38075200	1.96326300
C	-3.62994900	0.32918800	-0.69400200
H	-4.27967800	0.49126400	-1.55864100
H	-3.71371700	1.21177500	-0.04864900
C	-4.04679900	-0.92373600	0.07860500
H	-4.05744600	-1.78588400	-0.60087700
H	-5.06326300	-0.80585800	0.46312900

Energy = -673.528589 hartree
Imaginary frequency= -328.9631 cm^{-1}

TS7 - transition state for the parent phenyl sulfide molecule leading to benzothiophene.

H	-4.61520800	-2.01902400	-0.77277500
C	-3.70769700	-1.59386600	-0.35691300
C	-1.35783400	-0.52130500	0.69920200
C	-2.67565700	-2.45302700	0.07459100
C	-3.57387300	-0.21402800	-0.29849400
C	-2.38398400	0.31698900	0.20371200
C	-1.52116100	-1.93096300	0.61635800
H	-2.80973400	-3.52663300	0.00569500
H	-4.34772000	0.43809500	-0.68935900
H	-0.75582000	-2.58251800	1.02564000
H	-0.78377100	-0.14105100	1.55016300
C	0.22469600	0.46754300	-0.04641300
C	-0.25788500	1.71961300	-0.15438400
S	-1.96237800	1.98826400	0.00968400
N	1.37423900	-0.11774400	0.10015800
C	2.31307600	0.22795600	1.18781700
H	2.24588800	-0.56459300	1.94631400
H	1.97872000	1.16735900	1.63137100
C	1.69417000	-1.34786000	-0.64604800

H	1.62425000	-2.19034700	0.05657400
H	0.93877800	-1.47312500	-1.42328700
C	3.73423800	0.32287500	0.63694300
H	4.41522700	0.50846100	1.47227900
H	3.79863600	1.18477200	-0.03788400
C	3.10635300	-1.25469900	-1.21816800
H	3.13129500	-0.46332300	-1.97661000
H	3.34053400	-2.19844900	-1.71839200
C	4.11944000	-0.95404300	-0.11233400
H	4.15266500	-1.79586700	0.59133500
H	5.12142100	-0.85106100	-0.53692400
C	0.60097500	2.88129700	-0.57724500
H	0.11395200	3.45776300	-1.36663600
H	1.56410100	2.52091900	-0.94260300
H	0.77602200	3.54170400	0.27731600

Energy = -675.695404 hartree
Imaginary frequency= -347.6698 cm^{-1}

TS8 - transition state for the parent styrene molecule leading to naphthalene.

C	-2.58360900	0.40718300	0.15661200
C	-1.50962400	-0.27591200	0.78379900
H	-1.02690200	0.23678600	1.61975000
C	-0.07581000	1.93601900	-0.13169300
C	0.20603300	0.62655300	0.02952300
C	1.00798100	2.81366500	-0.72467300
H	1.36967800	3.50231400	0.04634000
H	0.60572700	3.40630200	-1.54913400
H	1.85081400	2.22689400	-1.09117500
N	1.24072200	-0.12071100	0.22409900
C	1.41138500	-1.41135600	-0.46943800
H	0.56748700	-1.54375600	-1.14780100
H	1.39406700	-2.20659900	0.28660800
C	2.30814000	0.22067900	1.19399500
H	2.07643600	1.20132500	1.61255600
C	2.75282700	-1.41432800	-1.20045400
H	2.87858200	-2.38656400	-1.68485400
H	2.73158100	-0.65199400	-1.98859100
H	2.26500800	-0.52590200	1.99714900
C	3.67145300	0.19053100	0.50492100
H	4.44032800	0.35520500	1.26508800
H	3.73455900	1.02155600	-0.20699300
C	3.89592500	-1.13592900	-0.22316100
H	3.95402000	-1.95162500	0.50902300
H	4.85067000	-1.11274200	-0.75488400
C	-1.37974600	2.53023000	0.04378600

H	-1.41761100	3.61031000	-0.06415500
C	-2.54995200	1.84138600	0.11062900
H	-3.48445800	2.38348100	-0.00342100
C	-3.60236400	-0.33594500	-0.47219100
H	-4.42547000	0.18519300	-0.95089000
C	-3.53152900	-1.71541100	-0.50019200
H	-4.30709900	-2.28331400	-1.00348400
C	-1.48405900	-1.69634400	0.78435500
H	-0.70397200	-2.21794200	1.32910100
C	-2.46835600	-2.40080700	0.12911700
H	-2.45065400	-3.48524100	0.12146100

Energy = -996.537849 hartree
Imaginary frequency= -278.4581 cm^{-1}

Cartesian coordinates for intermediates (Int)

Pyrrole 9

H	3.96161000	-1.52343300	1.22752900
C	3.52256300	-1.72423900	0.24637600
H	4.27972000	-1.51652700	-0.51640800
H	3.26247700	-2.78099700	0.18997300
C	2.30460000	-0.90177300	0.02056600
C	0.94862900	-1.41682100	-0.29769400
H	0.62462600	-2.08446500	0.51173600
H	0.96251000	-2.00957900	-1.21988000
C	0.90478000	0.90509700	-0.12959300
C	0.10756600	-0.16996400	-0.41861500
C	0.69420200	2.38525000	-0.03709200
H	-0.33310400	2.61515500	0.24015900
H	0.91880700	2.90247500	-0.97652800
H	1.32463300	2.81756100	0.74325100
N	-1.18124900	-0.25240900	-0.85849600
C	-2.03426300	0.93535000	-0.91204200
H	-1.44906100	1.78679000	-1.25894900
H	-2.79618200	0.74144200	-1.67623400
C	-1.96434700	-1.45803700	-0.55874000
H	-1.32758600	-2.34212800	-0.61283600
H	-2.71718700	-1.55659500	-1.34915900
C	-2.64925300	-1.32576500	0.80465600
H	-1.87922900	-1.27245900	1.58650400
H	-3.25276000	-2.21756800	1.00074200
C	-2.71380500	1.17672400	0.43801400
H	-1.94860100	1.38298000	1.19866200
H	-3.36150500	2.05691600	0.37564500
C	-3.51855200	-0.06347900	0.84543100

H	-3.94588200	0.07097500	1.84332200
H	-4.36023700	-0.18677800	0.15092200
N	2.23167200	0.39214000	0.09796400
C	3.36033200	1.27060800	0.40423400
H	3.37809800	2.08782200	-0.31626100
H	3.24594800	1.66908900	1.41362100
H	4.28523300	0.70350200	0.33491000

Energy = -578.733434 hartree

Furan 10

H	-4.33202200	-1.52483900	0.54091500
C	-3.95087300	-1.06583500	-0.37742800
H	-3.86144200	-1.86288200	-1.12201300
H	-4.63760700	-0.29580500	-0.72495600
C	-2.62072800	-0.49633000	-0.11427100
C	-1.37173900	-1.17337100	0.29514800
H	-1.11353500	-1.92965800	-0.45851800
H	-1.51382400	-1.70590600	1.24386700
C	-1.05480000	1.10694400	0.02471900
C	-0.39425300	-0.02553500	0.39197700
C	-0.80023600	2.56653300	-0.12427900
H	0.19143100	2.75240500	-0.53898000
H	-0.89028500	3.10427300	0.82453600
H	-1.53091100	2.98216900	-0.82129600
N	0.86463200	-0.20466100	0.87715100
C	1.53868800	-1.49260500	0.66554100
H	0.81959900	-2.30807100	0.75997800
H	2.26490700	-1.60975600	1.47758600
C	1.81061500	0.91452200	0.85732700
H	1.28576700	1.83387000	1.11959800
C	2.25398300	-1.51051000	-0.68824100
H	2.78274700	-2.46099700	-0.80916500
H	1.50629900	-1.44833200	-1.49053700
H	2.54172400	0.72481600	1.65137800
C	2.52315700	0.99735200	-0.49404400
H	3.24048100	1.82375600	-0.48159100
H	1.78684600	1.21301300	-1.28041000
C	3.22708100	-0.33085200	-0.79587700
H	4.04332100	-0.47384800	-0.07555600
H	3.68071700	-0.30416400	-1.79068600
O	-2.41025100	0.74758800	-0.25095600

Energy = -559.307366 hartree

Thiophene 11

H	-3.81192900	-2.25573000	0.67276100
C	-3.62880900	-1.70893300	-0.25784800

H	-3.38489200	-2.44690600	-1.02900200
H	-4.53794800	-1.18006000	-0.54470400
C	-2.48463500	-0.77788700	-0.07714400
C	-1.10567200	-1.19489900	0.29216400
H	-0.74078000	-1.89925600	-0.46936700
H	-1.13234600	-1.75135100	1.23862000
S	-2.55272400	0.83255400	-0.27457100
C	-0.90500600	1.19800400	0.07481800
C	-0.22166000	0.03006900	0.38868600
C	-0.51448000	2.65217000	-0.00213600
H	-0.27856400	3.06831800	0.98099500
H	-1.34445200	3.23642900	-0.40686200
H	0.33842400	2.80975800	-0.66719300
N	1.05809100	-0.12114100	0.78368100
C	1.71897600	-1.43374600	0.75613600
H	0.99743500	-2.23251700	0.92124600
H	2.42022700	-1.45561000	1.59761800
C	2.04344200	0.96496300	0.72762700
H	1.55571600	1.92179300	0.88628300
C	2.47544400	-1.60399500	-0.56488800
H	2.98295300	-2.57332100	-0.56931300
H	1.75305500	-1.60776300	-1.39190600
H	2.73140100	0.81089600	1.56650800
C	2.80814000	0.90416000	-0.59602200
H	3.55060400	1.70742500	-0.62446400
H	2.10411800	1.07592100	-1.42129300
C	3.48096600	-0.46334200	-0.75631000
H	4.27612600	-0.55967400	-0.00552500
H	3.95755000	-0.54061000	-1.73752800

Energy = -882.318104 hartree

Benzene 12

H	-3.36005800	-2.67961300	0.78642300
C	-3.28393600	-2.24332900	-0.21528400
H	-2.75020400	-2.96600200	-0.84166000
H	-4.28986000	-2.10871400	-0.61486900
C	-2.54702900	-0.94227300	-0.16684800
C	-1.18102900	-0.97492600	0.45233400
H	-0.62794600	-1.81916700	0.02841400
H	-1.31513700	-1.21416100	1.52100800
C	-1.03417000	1.53162000	0.08477100
C	-0.34800500	0.27764500	0.33984000
C	-0.47345100	2.89299400	0.43813200
H	0.22369700	2.83669800	1.27724500
H	-1.29934500	3.53988300	0.73936900

H	0.03214400	3.38139900	-0.39958700
N	0.95180800	0.17034300	0.51771500
C	1.59364000	-1.04487600	1.06332100
H	0.84987200	-1.68593800	1.52820800
H	2.26058500	-0.69156900	1.85795400
C	1.95932300	1.14039400	0.03670200
H	1.46764800	2.01426700	-0.37015500
C	2.40609000	-1.76334700	-0.01265300
H	2.86662700	-2.64866900	0.43407800
H	1.73552400	-2.10677400	-0.81006200
H	2.57631600	1.43911500	0.89056000
C	2.80491100	0.47759500	-1.05701100
H	3.55568300	1.20444900	-1.38012200
H	2.15610900	0.27280000	-1.91723500
C	3.46201600	-0.81527500	-0.57973100
H	4.19982900	-0.58727400	0.19988900
H	3.99978000	-1.29078600	-1.40406900
C	-2.31601900	1.44639800	-0.37707900
H	-2.84237700	2.38114900	-0.55739200
C	-3.05202200	0.22645600	-0.59926100
H	-4.04344500	0.28205400	-1.03541200

Energy = -561.490982 hartree

Indole 13

H	-4.41782200	0.21121100	0.09970800
C	-3.53658600	-0.41780000	0.13231500
C	-1.21499300	-2.14168300	0.09242000
C	-2.23057700	0.13852400	0.18163000
C	-3.63003400	-1.77456300	0.02788800
C	-2.46747800	-2.63303100	-0.02195200
C	-1.02109000	-0.69277600	0.36048100
H	-4.61106200	-2.23145000	-0.04873500
H	-2.61895300	-3.69975400	-0.14267600
H	-0.84067800	-0.65094000	1.46315800
H	-0.35709500	-2.80245300	0.11762000
N	-1.85189700	1.38992400	-0.02409200
C	-0.45551400	1.49491300	-0.16866800
C	0.11152300	0.25958100	-0.03649900
N	1.45284600	-0.01031100	-0.02978500
C	2.30309400	0.63728400	0.98083400
H	1.89039300	1.62159500	1.20924400
H	2.27077100	0.03795400	1.90805500
C	1.90758700	-1.34819700	-0.41099100
H	1.23667400	-1.73520800	-1.18137200

H	1.87527800	-2.02584100	0.46078900
C	3.74054400	0.74276200	0.48491200
H	3.76970100	1.42117500	-0.37683300
H	4.35892200	1.18124900	1.27399500
C	3.33756200	-1.28240700	-0.94382300
H	3.33979400	-0.69857100	-1.87192700
H	3.67138800	-2.29553200	-1.18781100
C	4.27089600	-0.63327200	0.07884400
H	4.33601100	-1.27324400	0.96918600
H	5.28210800	-0.54796100	-0.32911300
C	0.20172900	2.79418300	-0.48391800
H	0.28914200	3.44116600	0.39577400
H	-0.34623000	3.33911800	-1.25712100
H	1.20628100	2.59090400	-0.86153700
C	-2.75329700	2.52768000	-0.19896200
H	-2.31331000	3.40274800	0.27724600
H	-2.90115400	2.72051400	-1.26357300
H	-3.70699500	2.30884800	0.27600100

Energy = -692.966902 hartree

Benzofuran 14

H	-4.44802800	1.04905700	-0.06853900
C	-3.69127300	0.28168500	0.03864900
C	-1.65193000	-1.77380300	0.16663100
C	-2.33696600	0.61061000	0.11993500
C	-3.97809700	-1.06403500	-0.00643600
C	-2.96678000	-2.08277700	0.03981100
C	-1.26501300	-0.35885100	0.34523400
H	-5.01306200	-1.37389500	-0.10948300
H	-3.27433600	-3.12008700	-0.02187800
H	-1.11869700	-0.29715700	1.45613300
H	-0.89812700	-2.54575500	0.26528300
O	-1.83955900	1.80092100	-0.09376500
C	-0.45217300	1.72027500	-0.22328600
C	0.25366500	2.98267600	-0.53819500
H	0.37392300	3.61103000	0.34967600
H	-0.30221500	3.54755900	-1.29018200
H	1.24285200	2.74194100	-0.93409200
C	-0.02074000	0.44468500	-0.06766100
N	1.28072400	0.02282400	-0.05504300
C	1.56467200	-1.36716300	-0.41781100
H	1.43362700	-2.02330100	0.46151300
H	0.85902600	-1.67387200	-1.19406700
C	2.18918000	0.57026600	0.96524000
H	2.06572900	-0.00306800	1.90071000
H	1.90477300	1.60475000	1.16809900
C	2.99858500	-1.49169300	-0.92755600

H	3.20311700	-2.54205400	-1.15569500
H	3.09003900	-0.92408400	-1.86104200
C	3.63481700	0.48176600	0.49016900
H	4.29302100	0.84645100	1.28441300
H	3.76257400	1.14089700	-0.37724700
C	3.99009500	-0.95559800	0.10602200
H	3.95874600	-1.58940400	1.00258500
H	5.01019500	-1.00439700	-0.28524800

Energy = -673.542962 hartree

Benzothiophene 15

H	-4.78216100	-1.91760800	-0.26897600
C	-3.79903700	-1.48875800	-0.10530000
C	-1.21227600	-0.44122700	0.40094000
C	-2.68959100	-2.37423400	0.10214300
C	-3.65507300	-0.12269800	-0.12306400
C	-2.36356000	0.40651300	0.04631400
C	-1.43773000	-1.89935900	0.31525800
H	-2.86771200	-3.44348400	0.09883900
H	-4.49553400	0.53189300	-0.32455400
H	-0.61815500	-2.57024000	0.54267500
H	-1.14648200	-0.28171900	1.50954700
C	0.07860000	0.33775300	0.10260100
C	-0.19681300	1.66566300	-0.10338100
S	-1.89448900	1.99770200	-0.18298100
N	1.31628900	-0.20379600	0.22553200
C	2.34178300	0.36525600	1.10665300
H	2.42908800	-0.28938400	1.98860000
H	2.00406100	1.34212100	1.45559500
C	1.64409500	-1.51672500	-0.33306400
H	1.72341600	-2.25897600	0.47730600
H	0.84640000	-1.81911700	-1.01425500
C	3.69396300	0.44951300	0.40363100
H	4.44494800	0.79866700	1.11871400
H	3.63783500	1.18942500	-0.40431300
C	2.97459200	-1.44400900	-1.08366700
H	2.85431100	-0.78304000	-1.95058500
H	3.22248100	-2.44197600	-1.45792000
C	4.08317700	-0.91281700	-0.17381200
H	4.24906700	-1.62260300	0.64783600
H	5.02407000	-0.83686700	-0.72603900
C	0.78089400	2.76496700	-0.38199400
H	0.35852100	3.49926200	-1.07159100
H	1.67619100	2.33713300	-0.84157300
H	1.07932500	3.29083300	0.53011900

Energy = -996.556867 hartree

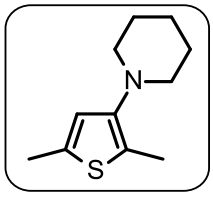
Naphthalene 16

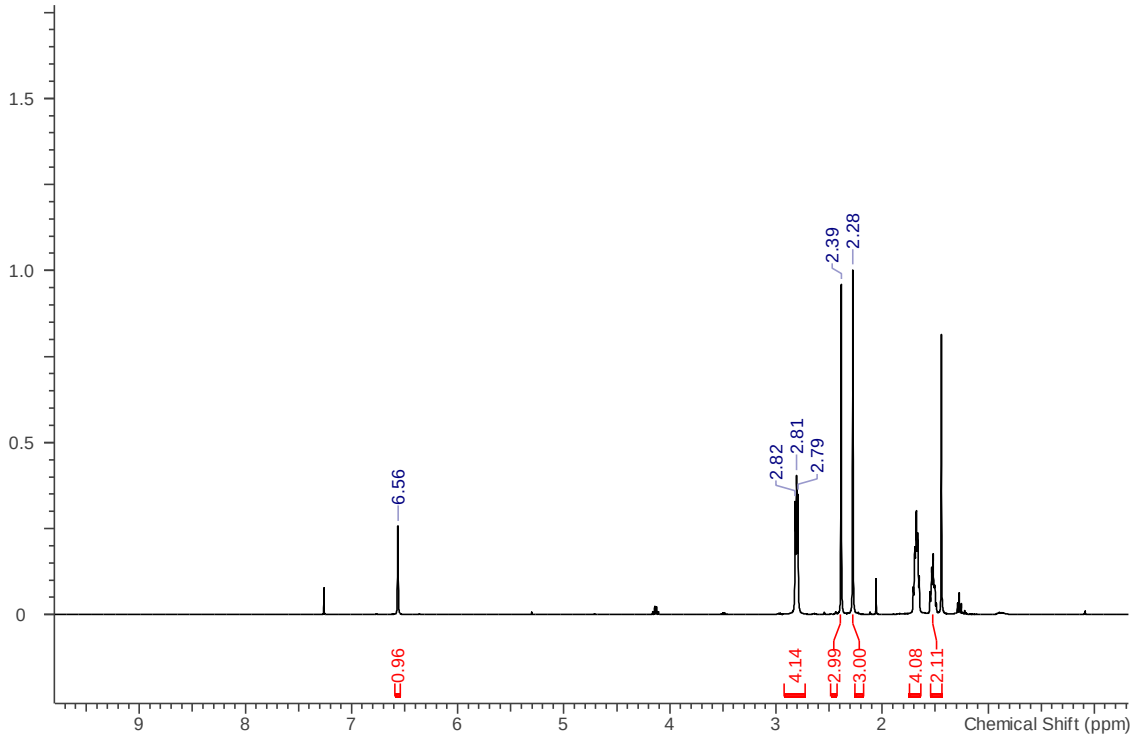
C	2.48899700	0.48378300	-0.32973400
C	1.21593900	-0.29996700	-0.17890900
H	1.09128200	-0.70430700	-1.20843100
C	-0.00038100	1.92068300	0.08926900
C	-0.05509600	0.47901100	0.09782400
C	-1.20249400	2.83527600	0.16498400
H	-2.05629900	2.43100000	-0.38064000
H	-0.94446700	3.78926400	-0.29662100
H	-1.51407800	3.04878100	1.19087400
N	-1.16758700	-0.22443300	0.28547000
C	-2.35213500	0.23174900	1.04678600
H	-2.14251700	1.18787500	1.51064800
H	-2.45659100	-0.49894200	1.85894300
C	-1.37401600	-1.59540900	-0.23676900
H	-0.50032200	-1.93049800	-0.78846800
C	-3.62447800	0.23276300	0.20444200
H	-4.45971100	0.52499700	0.84717600
H	-3.54601200	0.98169800	-0.59138000
H	-1.52575700	-2.27091700	0.61335800
C	-2.60394000	-1.60715700	-1.14851800
H	-2.72340200	-2.62553600	-1.52938500
H	-2.41103000	-0.95519000	-2.00895600
C	-3.85723000	-1.14802900	-0.40723300
H	-4.09429400	-1.86594100	0.38804600
H	-4.71312900	-1.12486400	-1.08658100
C	1.21641400	2.51033400	-0.16746400
H	1.22742100	3.59434300	-0.24729100
C	2.45469000	1.83683800	-0.37327300
H	3.35366200	2.41312000	-0.56366200
C	3.70603200	-0.29257100	-0.46542800
H	4.58485000	0.19461400	-0.87602800
C	3.76321600	-1.55142700	0.02372400
H	4.68606700	-2.11900500	-0.03001400
C	1.42677000	-1.51539200	0.70842700
H	0.59050800	-1.90451300	1.27648000
C	2.62412900	-2.11730100	0.73740200
H	2.76842500	-3.01406800	1.33045600

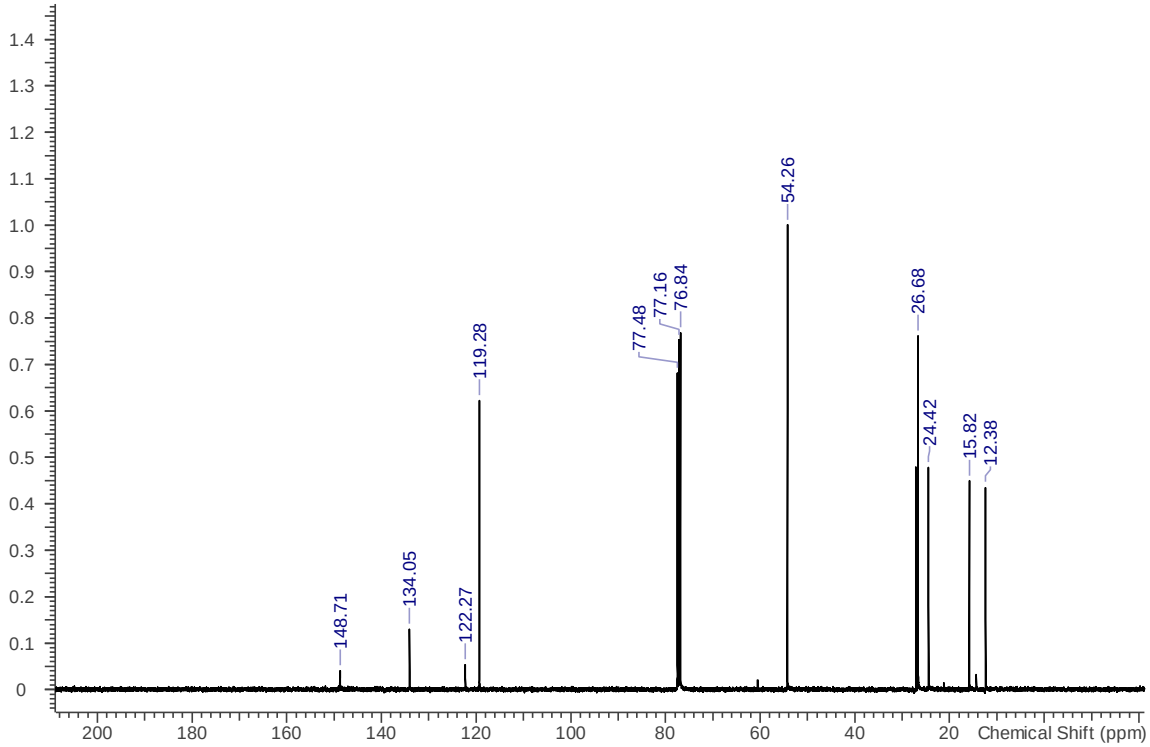
Energy = -675.716234 hartree

Characterization of Compounds 11a, 13a, 14a and 15a - ^{1}H and ^{13}C NMR Spectra

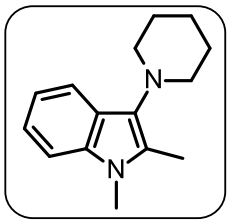
Compound **11a**[2]

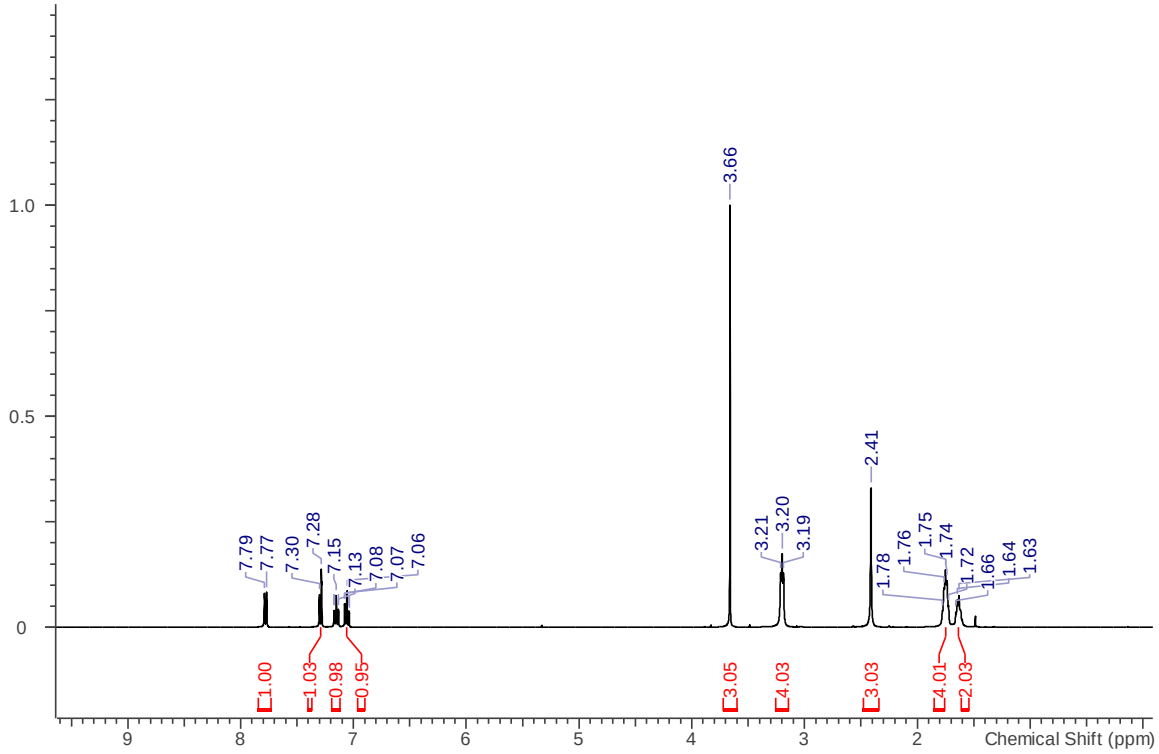


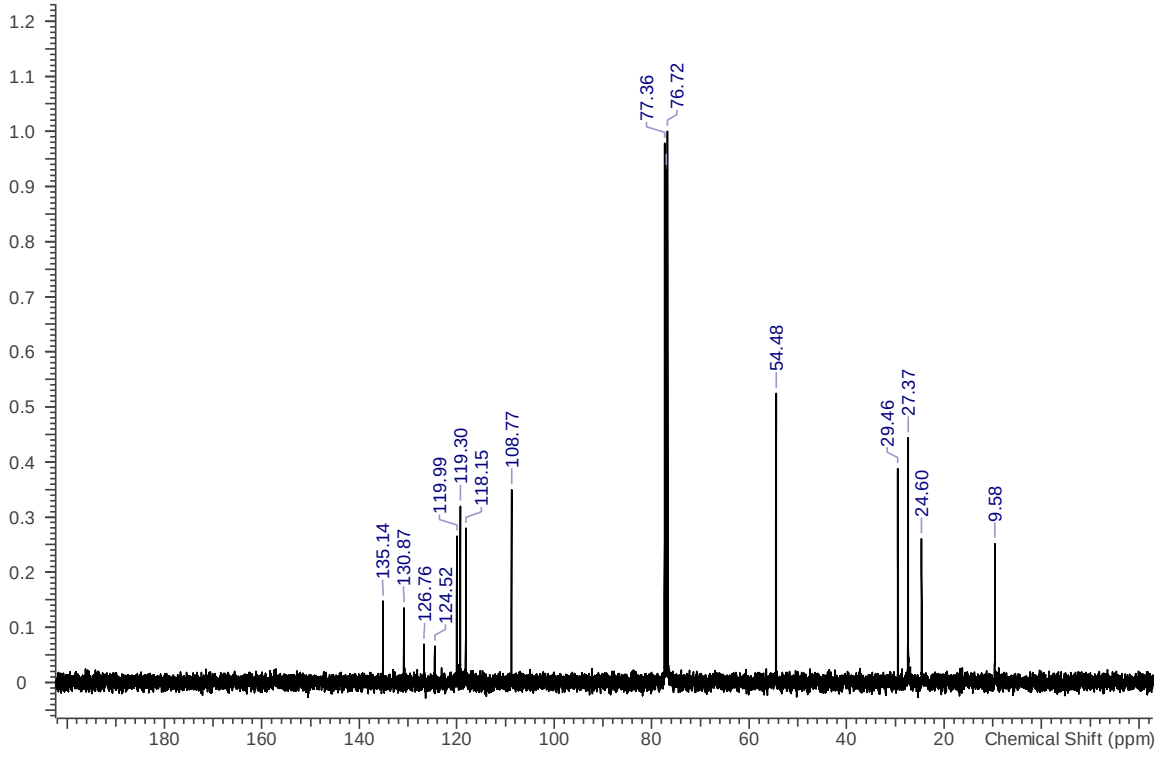




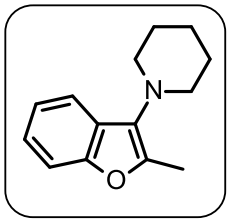
Compound **13a**[3]

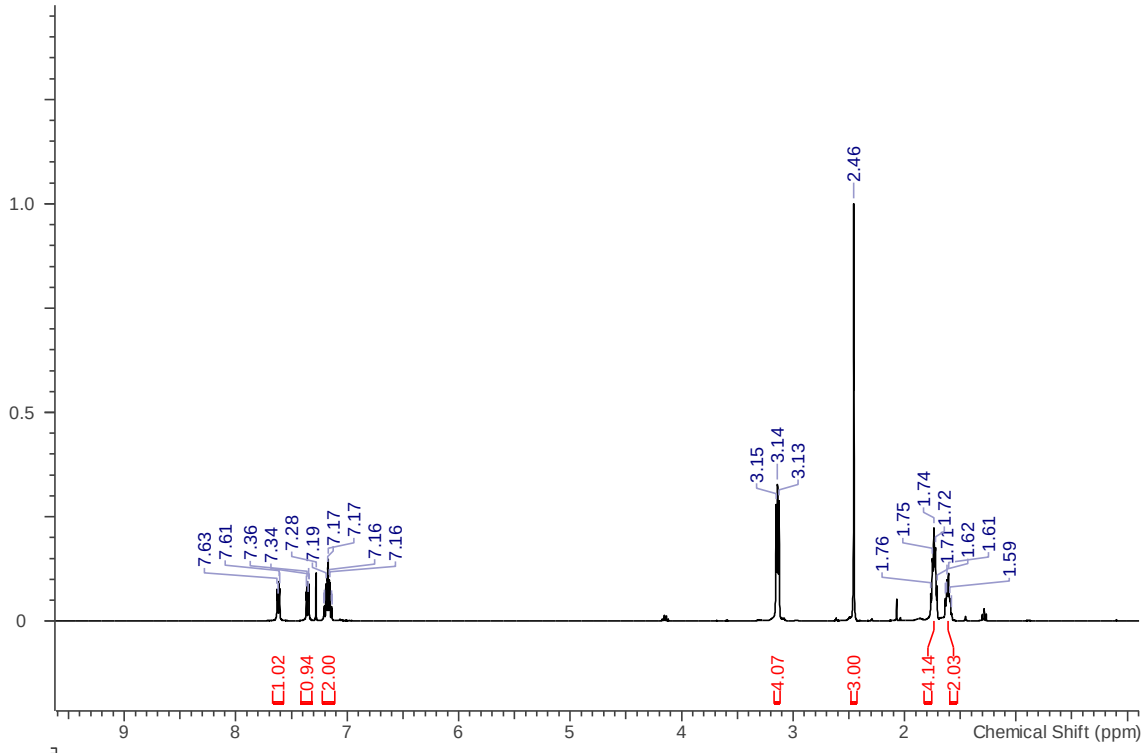


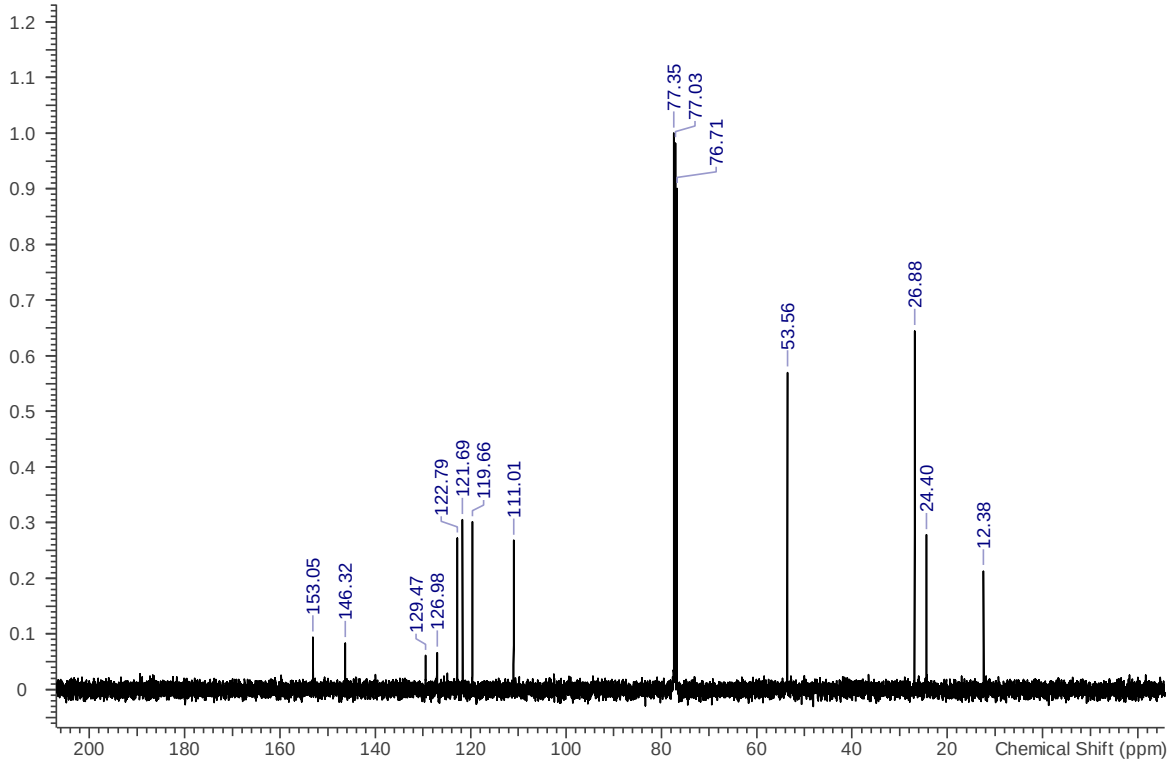




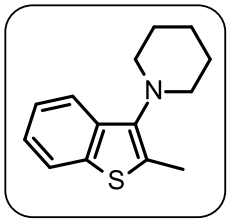
Compound **14a**[3]

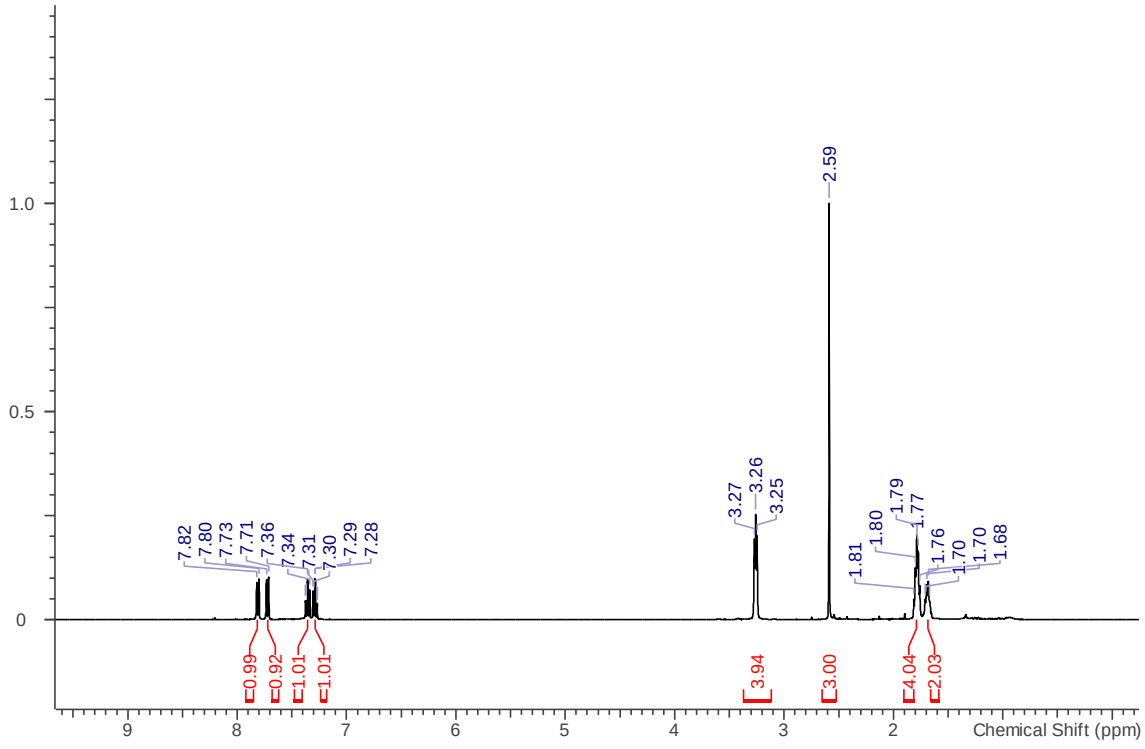


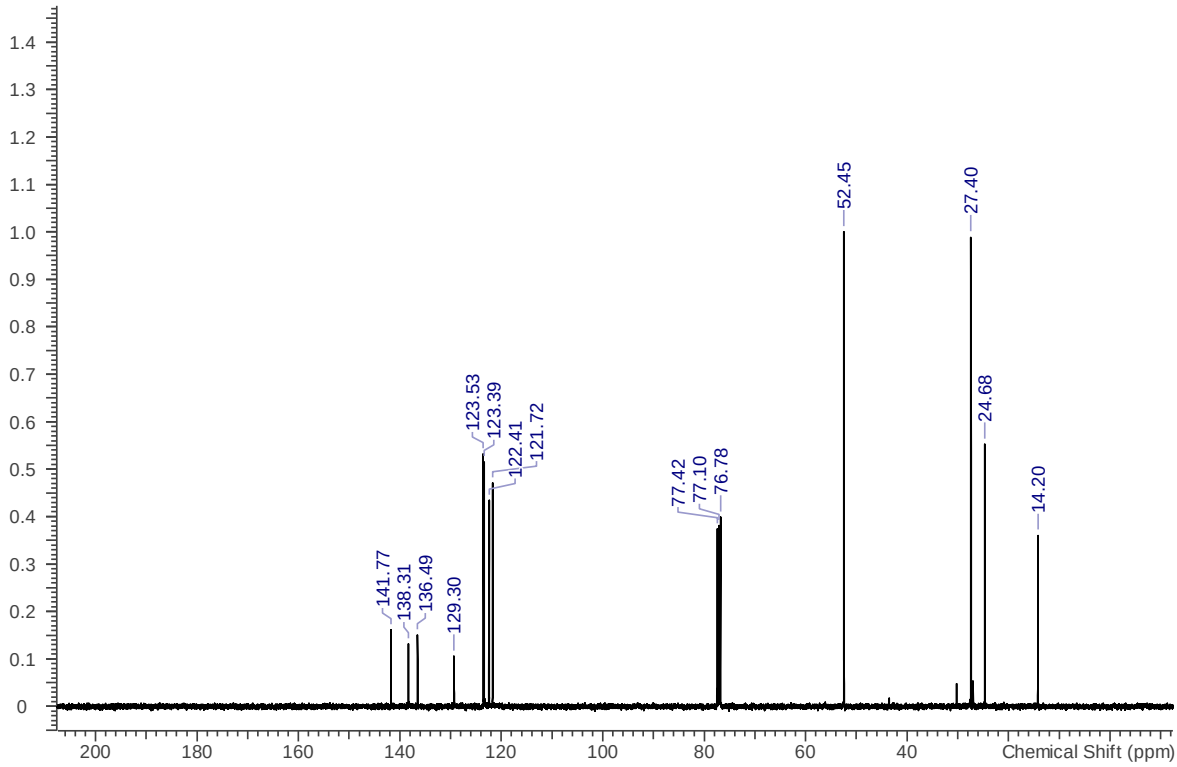




Compound **15a**[4]







References

(1) Hoffmann, R.; Woodward, R. B. The Conservation of Orbital Symmetry. *Acc. Chem. Res.* **1968**, *1* (1), 17–22.

(2) Dagoneau, D.; Kolleth, A.; Lumbroso, A.; Tanriver, G.; Catak, S.; Sulzer-Mossé, S.; De Mesmaeker, A. Straightforward Synthesis of 3-Aminothiophenes Using Activated Amides. *Helv. Chim. Acta* **2019**, *102* (4), e1900031.

(3) Dagoneau, D.; Kolleth, A.; Quinodoz, P.; Tanriver, G.; Catak, S.; Lumbroso, A.; Sulzer-Mossé, S.; De Mesmaeker, A. Keteniminium Salts as Key Intermediate for the Efficient Synthesis of 3-Amino-Indoles and -Benzofurans. *Helv. Chim. Acta* **2019**, 102, No. e1900217.

(4) Lumbroso, A.; Behra, J.; Kolleth, A.; Dakas, P. Y.; Karadeniz, U.; Catak, S.; Sulzer-Mossé, S.; De Mesmaeker, A. Access to Functionalized 3-Amino-Benzothiophenes Using Keteniminium Intermediates. *Tetrahedron Lett.* **2015**, *56* (47), 6541–6545.