Supporting Information

Trifluoromethanesulfonamide vs. Non-Fluorinated Sulfonamides in Oxidative Sulfamidation of the C=C Bond: an *In Silico* Study

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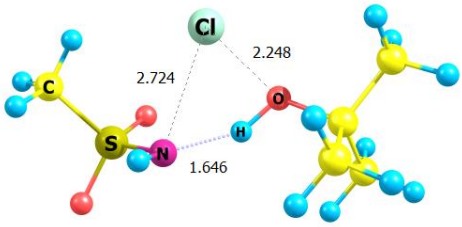
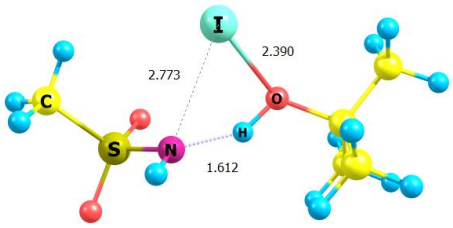


271*i* cm^{-1}

a

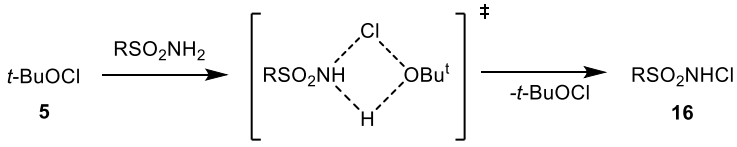


245*i* cm^{-1}

b

Figure 1. Structure of transition states **TS$_{5\text{-}16}$** (**a**) and **TS$_{6\text{-}7}$** (**b**) for R = CH_3.

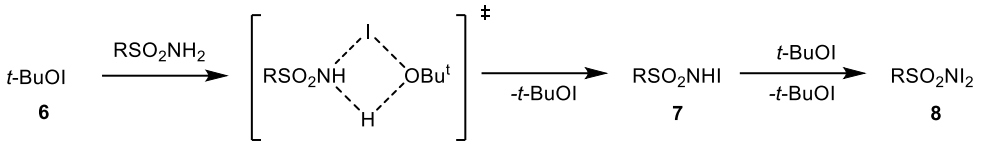
Table 1. Relative energies Δ*E* (ZPVE corrected) and free energies Δ*G* (in kcal/mol) of the intermediates of **5** → **16** transformation.



TS$_{5\text{-}16}$ R = CH_3 (**a**), CF_3 (**b**), *p*-Tol (**c**), *p*-Ns (**d**).

Parameter	5 + [a-d]	TS$_{5\text{-}16}$				16			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**
MP2/B3LYP									
Δ*E*+ZPVE	0.0	64.0	60.4	61.1	59.5	–6.0	–1.8	–6.6	–6.6
Δ*G*	0.0	74.4	71.4	72.7	69.6	–6.4	–1.9	–6.5	–7.6
wB97XD									
Δ*E*+ZPVE	0.0	59.9	59.7	58.2	58.0	–5.9	–1.8	–5.9	–6.0
Δ*G*	0.0	71.3	71.1	70.4	69.2	–6.2	–2.0	–5.8	–6.6

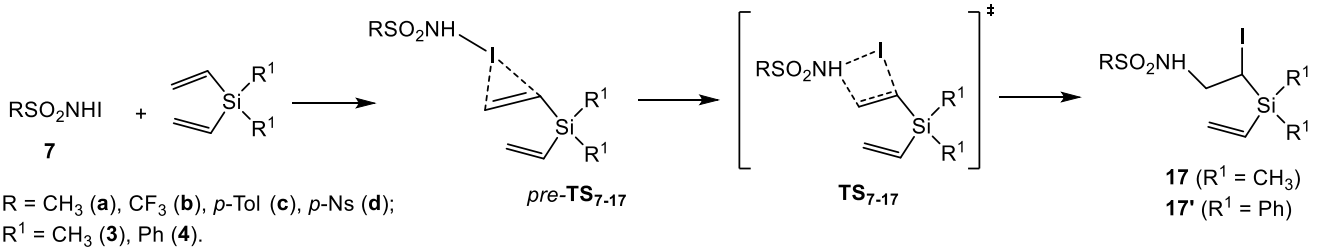
Table 2. Relative energies *ΔE* (ZPVE corrected) and free energies *ΔG* (in kcal/mol) of the intermediates of **6** → **8** transformation.



TS$_{6-7}$ R = CH_3 (**a**), CF_3 (**b**), *p*-Tol (**c**), *p*-Ns (**d**).

Parameter	6 + [a-d]	TS$_{6-7}$				7				TS$_{7-8}$				8			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
MP2/B3LYP																	
Δ*E*+ZPVE	–10.9	28.8	26.1	26.8	26.3	–11.1	–8.7	–13.3	–12.2	21.2	17.7	20.4	18.5	–13.8	–11.6	–15.2	–15.0
Δ*G*	–10.5	40.3	38.5	39.2	38.5	–11.1	–8.2	–13.5	–12.8	33.5	29.8	34.1	31.1	–13.0	–11.3	–13.5	–13.6
wB97XD																	
Δ*E*+ZPVE	–13.0	23.4	–	–	–	–13.8	–12.2	–15.4	–14.5	15.8	–	–	–	–13.4	–12.1	–14.1	–13.7
Δ*G*	–12.8	35.5	–	–	–	–1.1	0.9	–1.6	–2.2	28.3	–	–	–	–12.7	–11.7	–13.4	–12.3

Table 3. Relative energies Δ*E* (ZPVE corrected) and free energies Δ*G* (kcal/mol) of the intermediates of **7** → **17(17′)** transformation.



R = CH_3 (**a**), CF_3 (**b**), *p*-Tol (**c**), *p*-Ns (**d**); R^1 = CH_3 (**3**), Ph (**4**).

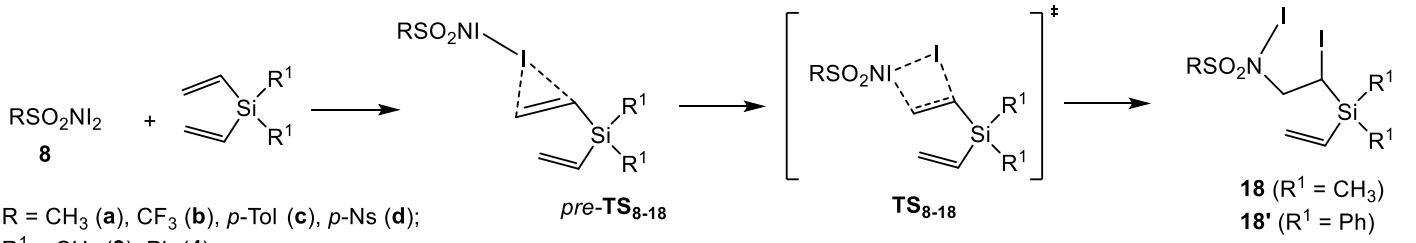
R^1 = CH_3

Parameter	7 + 3	*pre*-TS$_{7-17}$				TS$_{7-17}$				17			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
MP2/B3LYP													
Δ*E*+ZPVE	0.0	–5.8	–8.6	–5.7	–6.3	23.2	23.8	21.9	22.8	–44.4	–48.2	–44.6	–45.1
Δ*G*	0.0	3.8	2.2	5.8	4.2	35.0	35.4	34.3	34.2	–31.3	–35.5	–30.6	–32.0
wB97XD													
Δ*E*+ZPVE	0.0	–5.6	–7.6	–7.4	–5.8	34.2	35.8	33.7	34.0	–44.7	–47.9	–45.3	–45.6
Δ*G*	0.0	4.8	4.6	4.9	5.2	46.7	48.4	44.7	46.8	–31.7	–34.7	–32.2	–32.1

R^1 = Ph

Parameter	7 + 4	*pre*-TS$_{7-17'}$				TS$_{7-17'}$				17′			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
MP2/B3LYP													
Δ*E*+ZPVE	0.0	–6.7	–9.3	–6.7	–7.1	21.4	20.9	18.9	18.4	–43.4	–47.3	–43.5	–44.5
Δ*G*	0.0	3.9	2.1	4.9	3.6	33.0	33.2	33.5	34.2	–29.7	–32.2	–28.6	–30.5
wB97XD													
Δ*E*+ZPVE	0.0	–6.2	–	–	–	31.5	–	–	–	–43.0	–	–	–
Δ*G*	0.0	5.1	–	–	–	45.7	–	–	–	–28.6	–	–	–

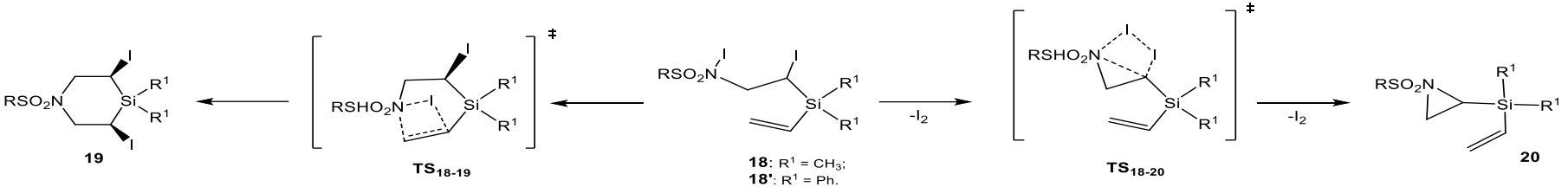
Table S4. Relative energies Δ*E* (ZPVE corrected) and free energies Δ*G* (kcal/mol) of the intermediates of **8 → 18(18′)** transformation.



R = CH_3 (**a**), CF_3 (**b**), *p*-Tol (**c**), *p*-Ns (**d**);
R^1 = CH_3 (**3**), Ph (**4**).

Parameter	**8 + 3**	***pre*-TS$_{8-18}$**				**TS$_{8-18}$**				**18**			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
						R^1 = CH_3							
						MP2/B3LYP							
ΔE+ZPVE	0.0	–8.3	–12.6	–8.2	–9.0	6.0	9.5	4.7	4.8	–44.6	–47.9	–44.8	–45.4
ΔG	0.0	2.3	–1.7	3.2	2.5	18.0	21.9	17.5	17.3	–32.1	–34.9	–31.8	–32.3
						wB97XD							
ΔE+ZPVE	0.0	–7.0	–9.4	–6.9	–7.9	25.2	28.1	25.7	25.9	–45.5	–47.8	–45.8	–46.5
ΔG	0.0	4.0	2.2	4.5	5.0	37.6	41.5	38.9	38.7	–32.9	–34.3	–33.1	–34.2
						R^1 = Ph							
Parameter	**8 + 4**	***pre*-TS$_{8-18'}$**				**TS$_{8-18'}$**				**18′**			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
						MP2/B3LYP							
ΔE+ZPVE	0.0	–9.0	–13.5	–9.4	–10.1	5.6	9.0	4.3	1.6	–44.4	–47.5	–44.8	–45.2
ΔG	0.0	2.3	–1.5	1.1	1.1	18.2	21.7	17.3	14.1	–30.8	–33.8	–30.9	–32.0
						wB97XD							
ΔE+ZPVE	0.0	–8.2	–9.7	–8.5	–9.0	24.1	26.4	24.3	24.3	–44.0	–46.2	–44.6	–45.0
ΔG	0.0	4.3	4.1	4.8	3.8	37.6	42.0	38.5	38.0	–29.8	–31.0	–31.4	–30.6

Table S5. Relative energies *ΔE* (ZPVE corrected) and free energies *ΔG* (kcal/mol) of the intermediates of **18** → **19(20)** and **18′** → **19′(20′)** transformation.



Parameter	18	TS18-19				TS18-20				19*				20			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**D**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
R^1 = CH_3																	
								MP2/B3LYP									
ΔE+ZPVE	0.0	34.2	**	28.3	33.2	7.9	***	10.5	7.8	–41.6	–44.4	–40.7	–40.7	2.7	3.1	4.0	3.9
ΔG	0.0	36.3	**	30.1	34.4	20.9	***	24.0	21.1	–40.0	–42.5	–39.0	–39.7	–7.7	–7.2	–6.9	–6.9
								wB97XD									
ΔE+ZPVE	0.0	46.7	**	47.7	47.6	6.1	***	–	–	–42.4	–44.2	–41.3	–41.3	–2.8	–2.1	–3.3	–3.9
ΔG	0.0	49.1	**	50.7	50.4	19.8	***	–	–	–40.1	–42.8	–38.7	–39.0	–13.0	–12.9	–12.3	–13.4
R^1 = Ph																	
Parameter	**18′**	**TS18′-19′**				**TS18′-20′**				**19′***				**20′**			
		a	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
								MP2/B3LYP									
ΔE+ZPVE	0.0	34.1	50.3	33.6	32.7	6.1	***	10.3	7.5	–41.2	–44.1	–40.5	–40.7	2.4	2.7	4.3	4.1
ΔG	0.0	35.3	52.9	34.8	35.8	19.8	***	23.5	21.2	–38.9	–41.7	–37.8	–37.2	–8.8	–8.1	–7.1	–5.4
								wB97XD									
ΔE+ZPVE	0.0	45.6	57.2	45.7	46.4	5.4	***	–	–	–42.1	–43.5	–41.3	–41.3	–3.3	–2.7	–1.8	–2.3
ΔG	0.0	48.0	59.5	50.4	48.9	18.0	***	–	–	–39.8	–41.5	–37.7	–39.4	–14.3	–14.4	–11.9	–13.1

* *Chair* conformation.

** Spontaneous cyclization with synchronous elimination of CF_3SO_2 occurred.

*** Not located.