# Computational and Experimental Evidence for Sb(V) Metal Mediated C-H Activation and Oxidative Functionalization of Arenes

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### 1. General Considerations

All air and water sensitive procedures were carried out using standard Schlenk techniques under argon or MBraun inert atmosphere glovebox. For handling air sensitive acid solution of Sb<sup>V</sup>, we developed an acid box by making a few appropriate modifications to the commercially available benchtop glovebox to handle acid solutions and by connecting to the argon and vacuum lines. The deuterated solvents purchased from Cambridge Isotope Laboratories, Inc. were dried and distilled using established procedures prior to use and stored under argon atmosphere. Toluene, Trifluoroacetic anhydride [CF<sub>3</sub>CO)<sub>2</sub>O, TFAA] and trifluoroacetic acid [(CF<sub>3</sub>COOH or TFAH; CF<sub>3</sub>COOD or TFAD) were purchased from commercial sources and were distilled and stored under argon atmosphere prior to use. Trifluoromethanesulfonic acid (TfOH) and Trifluoromethanesulfonic anhydride (TfAA) were purchased from commercial sources and used as received. Compounds Sb(TFA)<sub>3</sub>[or Sb(OOCCF<sub>3</sub>)<sub>3</sub>],<sup>[1]</sup>  $[Sb(OMe)_5]_2$ ,<sup>[2]</sup>  $[Sb(OCD_3)_5]_2$ ,<sup>[3]</sup>  $Sb(OOCCF_3)_5$ ,<sup>[4]</sup> p-Toluenestibonic acid (pSA) <sup>[5]</sup> and m-Toluenestibonic acid (mSA)<sup>[6]</sup> were synthesized according to the previously published procedures. The cresol esters of trifluoroacetate and trifluoromethanesulfonate (p-Tolyl trifluoroacetate, m-Tolyl trifluoroacetate, p-Tolyl triflate and m-Tolyl triflate) were synthesized by using established methods from the corresponding acid anhydrides. NMR spectra were obtained on Bruker Digital Avance III 400 (400.132 MHz for <sup>1</sup>H, 376.461 MHz for <sup>19</sup>F and 100.623 MHz for <sup>13</sup>C, 61.423 MHz for <sup>2</sup>H), Varian NMR System 500 (499.722 MHz for 1H, 470.263 MHz for 19F, 202.332 MHz for 31P, 125.696 MHz for 13C, 76.728 MHz for 2H), Bruker Avance Neo 500 ( 500.170 MHz for 1H, 470.630 MHz for 19F, 202.473 MHz for 31P, 125.768 MHz for 13C, 76.779 MHz for 2H). All chemical shifts are reported in units of ppm and <sup>1</sup>H-NMR spectra are referenced to an internal reference (MeTFA, CH<sub>3</sub>OOCCF<sub>3</sub>, 3.75 ppm in TFAH medium and MeOTf, CF<sub>3</sub>SO<sub>2</sub>OCH<sub>3</sub>, 3.75 ppm in TfOH).

## 2. General Protocol for Reaction of Sb(TFA)<sub>5</sub> with Toluene

### a. Reactions below 120 °C in TFAH medium:

The compound [Sb(OMe)<sub>5</sub>]<sub>2</sub>, 42 mg, 0.076 mmol {or [Sb(OCD<sub>3</sub>)<sub>5</sub>]<sub>2</sub>, 44mg, 0.075 mmol}, was weighed out into a 2 mL Schlenk bomb flask containing a stir bar in a glovebox under argon atmosphere. The flask was then removed from the glovebox and 0.2 mL of TFAA was added at room temperature under a steady flow of argon while stirring the contents. After 5 mins, 0.8 mL of TFAH was added and the solution stirred at room temperature under argon for another 15 mins, generating a 152 mM solution of Sb(TFA)5. Under an inert atmosphere of argon, ~0.04 mmol of toluene was added, the flask was sealed under 1 atm of argon and heated in an oil bath with stirring. Post reaction (after 4hrs at 60°C or 80 °C) the Schlenk bomb was removed from the oil bath and allowed to reach room temperature. An aliquot of the reaction solution (400-500 µL) was transferred into a 5 mm NMR tube and a sealed capillary of deuterated solvent (DMSO or D<sub>2</sub>O or C<sub>6</sub>D<sub>6</sub>) was placed into the tube as an external solvent for locking and shimming. <sup>1</sup>H-NMR spectra were taken with 20 second relaxation delays, and the spectra were referenced to the methyl protons in MeTFA (CF<sub>3</sub>COOCH<sub>3</sub>) (3.75 ppm), (generated from reaction of Sb(OMe)<sub>5</sub> and TFAA), Figure S1. <sup>1</sup>H NMR analysis did not indicate the formation of any cresol (Ar-OMe) products. Only C-H activation of the paraaromatic C-H bonds were observed; no products from C-H activation of the ortho-, meta-aromatic C-H bonds nor the methyl C-H bonds were generated. Based on analysis of the <sup>1</sup>H-NMR spectra, the main initial major product is the mono-tolyl, (TFA)<sub>4</sub>Sb<sup>V</sup>(para-tolyl), labelled as \*. The proposed bis-tolyl, (TFA)<sub>3</sub>Sb<sup>V</sup>(para-tolyl)<sub>2</sub>, labelled as \$, is generated at longer reaction times or higher temperatures (Figure S2). Attempts to isolate and characterize the bis-tolyl, (TFA)<sub>3</sub>Sb<sup>V</sup>(para-tolyl)<sub>2</sub> were unsuccessful due to the incomplete conversion and the high air/moisture sensitive nature of the product resulted in isolation of insoluble polymer residues.



**Figure S1:** Overlay of <sup>1</sup>H NMR spectra of reaction mixtures of Sb(TFA)<sub>5</sub> and toluene taken at room temperature after heating at different temperatures and time intervals in TFAH+TFAA (4:1) medium.

### b. Reactions at and above 120°C in TFAH medium:

The compound [Sb(OMe)<sub>5</sub>]<sub>2</sub>, 91 mg, ~ 0.164 mmol {or [Sb(OCD<sub>3</sub>)<sub>5</sub>]<sub>2</sub>, 96mg, 0.164 mmol}, was weighed out into a 5 mL Schlenk flask in a glovebox under argon atmosphere, the flask was removed from the glovebox and under argon atmosphere the solid was dissolved in 0.8 mL of TFAA and stirred at room temperature for 10 mins after which added 1.4 mL of TFAH and stirred for another 15 mins, making a ~ 150 mM solution of Sb(TFA)5. To this solution 9 mg of toluene, ~0.1 mmol was added under an inert atmosphere. In an inert atmosphere acid box, 1 mL aliquot of the mixture of Sb(TFA)<sub>5</sub> and toluene was transferred to a separate 2 mL glass vial with a stir bar. A tapered 6.35 mm diameter PTFE plug containing a small through hole was used to stopper the vial in order to reduce low due to bumping/boiling. The vial was placed into a 3 mL, stainless steel pressure reactor. The reactor was hand tightened, brought out of the acid box and sealed. The reactor was connected to a high-pressure gas manifold and, with the inlet valve of the reactor opened, degassed by slowly pressurizing to 500 psig argon followed by slow pressure release (3x) with constant stirring at 400 rpm. The reactor was then pressurized with 500 psig of argon, the inlet valve to the reactor was closed, and the reactor was disconnected from the manifold and placed into preheated aluminum block with stirring at 1000 rpm. The reaction was run for a few hours as specified below in the NMR spectrum. The reactor was then removed from the heating block and quickly cooled in a dry ice/acetone bath. The reactor was removed from the dry ice/acetone bath and allowed to reach room temperature. Then the pressure was slowly released and a 0.017 mmol of C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> standard in TFAH was added to the reaction mixture and stirred well. An aliquot of the solution (400-500 µL) was transferred into a 5 mm NMR tube and a sealed capillary of deuterated solvent (DMSO or D<sub>2</sub>O or C<sub>6</sub>D<sub>6</sub>) was introduced into the NMR tube as an external solvent for locking and shimming. <sup>1</sup>H-NMR spectra were taken with 20 second relaxation delays, and the spectrum was referenced to the methyl protons in MeTFA (CF<sub>3</sub>COOCH<sub>3</sub>) (3.75 ppm). <sup>1</sup>H NMR analysis showed primarily the bis-tolyl product, (TFA)<sub>3</sub>Sb<sup>V</sup>(tolyl)<sub>2</sub> along with low yields of oxy-functionalized products, the trifluoroacetate esters of ortho- and meta-cresol in ~11% and 6%, respectively, along with traces of para-cresol TFA ester and other unidentified products, see Figure S2. These cresol esters were identified by spiking with pure esters in TFAH/TFAA solvent.



**Figure S2:** *Top:* Outline of reductive functionalization selectivity for  $(TFA)_4Sb^{\vee}(para-tolyl)$  in TFAH. *Bottom:* Overlay of <sup>1</sup>H NMR spectra of reaction mixtures of Sb(TFA)<sub>5</sub> and toluene taken at room temperature after heating at different temperatures and time intervals( spectrum 1 to 3) with neat *m*-cresol (spectrum 4) and *o*-cresol (spectrum 5) in TFAH+TFAA (4:1) medium.

#### c. Reactions in TfOH medium:

The compound [Sb(OMe)<sub>5</sub>]<sub>2</sub>, 55 mg, ~ 0.1 mmol was weighed out into a 5 mL Schlenk flask in a glovebox under argon atmosphere, the flask was removed from the glovebox the flask was placed in an ice bath. Under a steady stream of argon atmosphere 1.9 mL of TfOH was carefully transferred into the flask while stirring the contents. Solids in the flask were quickly dissolve to make a homogeneous solution of Sb(OTf)<sub>5</sub>. After stirring the contents for 10 minutes at 0°C, a 100 uL stock solution of toluene (2.1M) was added to the flask under argon atmosphere to make a final test concentration of toluene, ~104 mM, and that of Sb(OTf)<sub>5</sub> ~ 100 mM. After stirring the contents at 0°C for 40 mins, under an atmosphere of argon 0.7 mL aliguots of the reaction mixture were transferred into two separate J-Young NMR tubes (one for monitoring reaction at 0 °C and another at 70 °C) and then sealed capillary tube containing DMSO was inserted into the NMR tubes for NMR signal locking. Then an appropriate volume of standard, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> (343 mM) prepared in HTFA+TFAA (9:1, 1.35mL), was added to the J-Young NMR tube and then sealed under argon. For reactions carried out above room temperature, C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> was used as an external standard prepared in the sealed capillary tube. <sup>1</sup>H-NMR spectrum were taken (on 500 mHz Varian) with 10 second relaxation delays, and the spectrum were referenced to the CF<sub>3</sub>SO<sub>2</sub>OCH<sub>3</sub>, 3.75 ppm. <sup>1</sup>H NMR analysis showed only traces of oxyfunctionalized products at room temperature after 24 hrs. But after 90 mins at 70 °C, an ~23% conversion (based on added toluene) to the triflate esters of para- and meta-cresols in 2:1 ratio was observed, and an ~ 40% conversion to para- and metatolyl triflates were observed in 2:1 ratio after 5 hr (see Figure S3.) These cresol esters were identified by spiking the test solutions with neat triflate esters of cresols.



**Figure S3:** *Top:* Outline of reductive functionalization selectivity for  $(OTf)_4Sb^{\vee}(para-tolyl)$  in TfOH. *Bottom:* Overlay of <sup>1</sup>H NMR spectra of crude reaction mixtures of  $Sb^{\vee}(OMe)_5$  and toluene in TfOH taken after 24 hr at room temperature (bottom spectrum 1), after 90min at 70 °C (spectrum 2), after 5hr at 70 °C (spectrum 3), with neat *p*-tolyl triflate (spectrum 4) and neat *m*-tolyl triflate (top spectrum 5).

# 3. Isolation of the mono-tolyl product, generated from C-H activation of toluene by Sb(TFA)<sub>5</sub>, and comparison to *p*-toluenestibonic acid made following the reported method<sup>[5]</sup>

Following the procedure described under section 2.a a reaction mixture of Sb(TFA)<sub>5</sub>, 0.45 M and toluene, 0.46 M in TFAH+TFAA (4:1) was prepared in a Schlenk flask and heated at 65 °C for 4 hrs at which point clear colorless solution turned yellow. After which reaction mixture was cooled to RT and added 1:1 mixture of pyridine:conc HCI while stirring. No apparent precipitate was observed. After stirring the contents for 30 mins reaction mixture was pumped dry and then added 2mL each of hexane and methanol to give insoluble layers. Contents were stirred at RT overlight which gave off white colored residue and a yellow colored viscous layer. Then the residue was carefully separted from the yellow colored viscous layer washed with hexane to remove any traces of yellow viscous layer. The resultant white residue was transferred to a 20 mL vial and dissolved in 0.5 M aq KOH solution and placed at 0 °C. An amorphous white solid crashed to the bottom of the vial overnight. <sup>1</sup>H NMR (Figure S4) matches with the NMR data of independently synthesized *p*-Toluenestibonic acid following the known literature procedure.<sup>[5]</sup> See Scheme S1 and Figure S4. Note: <sup>1</sup>H data is not available for *p*-Toluenestibonic acid in literature. Similarly, <sup>1</sup>H NMR of *p*SA (made following the literature procedure) taken in TFAH+TFAA (4:1) matches with <sup>1</sup>H NMR of crude reaction product from the reaction of Sb(TFA)<sub>5</sub> with toluene in TFAH+TFAA (4:1) after 1hr at 80°C. See Scheme S2, Figure S5 and Figure S6.



TFAH= CF<sub>3</sub>COOH; TFA=CF<sub>3</sub>COO<sup>-</sup>





**Figure S4:** Overlay of <sup>1</sup>H NMR spectra of *p*SA made by using published literature procedure<sup>[5]</sup> (top) and *via* reaction of Sb(TFA)<sub>5</sub> with toluene (bottom). <sup>1</sup>H NMR spectra was taken by dissolving *p*SA in ~ 0.5M KOD in D<sub>2</sub>O.



Scheme S2: Schematic diagram showing two different pathways to make p-Tolylantimony tetrakis(trifluoroacetate).



**Figure S5:** <sup>1</sup>H NMR spectra of *p*-Toluenestibonic acid (*p*SA) (made following reported method<sup>[5]</sup>) dissolved in a mixture of TFAH+TFAA (4:1) after 12hrs at room temperature showing formation of *p*-Tolylantimony tetrakis(trifluoroacetate).



**Figure S6:** <sup>1</sup>H NMR spectra of *p*-Tolylantimony tetrakis(trifluoroacetate) made by C-H activation of toluene by Sb(TFA)<sub>5</sub> in a mixture of TFAH+TFAA (4:1) after 1hr at 80 °C.

## 4. Disproportionation of *p*-Toluenestibonic acid(*p*SA)<sup>[5]</sup> in TFAH+TFAA medium

### a Time and temperature dependent studies:

A 95 mM solution of *p*-Toluenestibonic acid in HTFA+TFAA medium was prepared in a J-young NMR tube by dissolving ~15mg in 0.6 mL of 4:1 mixture of TFAH: TFAA. A 0.03 mmol MeTFA in TFAH+TFAA is added as an internal standard to these NMR solutions. A sealed capillary containing  $D_2O$  was inserted into the J-young NMR tube as an external lock. <sup>1</sup>H NMR data was collected (d1 = 20 seconds) at regular intervals at 60 °C as shown in the Figure S7. Oil baths were used to heat the solutions in NMR tube. <sup>1</sup>H NMR data indicated formation of additional product, possibly a bis(*p*-Tolyl)stibonic acid labelled as '\$' in the <sup>1</sup>H NMR spectrum and matches exactly with the product generated in the reaction of toluene with Sb(TFA)<sub>5</sub> as described in Section 2. Attempts to isolate and characterize this product failed due to the incomplete conversion and simultaneous generation of other unidentified products coupled with poor solubility in non-aqueous solvents. <sup>1</sup>H NMR data also indicated protonation of *p*-tolyl ligand in trace quantities to generate toluene-H<sub>8</sub>. At higher temperatures cresol esters (labelled with @) were also observed in minor yields. See Figure S8.



Figure S7: Overlay of time dependent <sup>1</sup>H NMR spectra of *p*-Toluenestibonic acid (*p*SA) taken in TFAH+TFAA (4:1) at 60 °C.



**Figure S8:** Overlay of time and temperature dependent <sup>1</sup>H NMR spectra of *p*-Toluenestibonic acid (*p*SA) in TFAH+TFAA (4:1).

# 5. Functionalization of *p*-Toluenestibonic acid (*p*SA) and *m*-Toluenestibonic acid (*m*SA) in TfOH medium

A 88 mM solution of *p*-Toluenestibonic acid was prepared in a J-young NMR tube by dissolving ~18.4 mg in 0.8 mL of 5:1 mixture of TfOH:TfAA. A 0.035 mmol MeTFA in TFAH+TFAA is added as an internal standard to these NMR solutions. A sealed capillary containing DMSO was inserted into the J-young NMR tube as an external lock. <sup>1</sup>H NMR data was collected (d1=10 seconds) at room temperature after heating the sample at 70 °C (see Figure S9). Oil baths were used to heat the solutions in NMR tube Similarly, a 88 M solution of *m*-Toluenestibonic acid in TfOH+TfAA medium was prepared in a J-young NMR tube and studied functionalization reaction at 70 °C (see Figure S10).



**Figure S9:** Overlay of <sup>1</sup>H NMR spectra of crude reaction mixture of *para*-toluenestibonic acid in TfOH after 60 min at 70 °C (bottom) with neat *p*-tolyl triflate (top) in TfOH medium.



**Figure S10**: Overlay of <sup>1</sup>H NMR spectra of crude reaction mixture of *meta*-toluenestibonic acid in TfOH after 30 min at 70 °C (bottom) with neat *p*-tolyl triflate (top) in TfOH medium.

## 6. Stability of products under Reaction Conditions in TFAH medium

Following the procedure described under the section "Reactions below 120°C" a reaction mixture of Sb(TFA)<sub>5</sub>, 34 mM and cresol, 31 mM in 1.8mL of TFHA+TFAA (4:1) was prepared in a Schlenk flask and 1 mL of this reaction mixture was transferred to a separate 2 mL glass vial containing stir bar. A tapered 6.35 mm diameter PTFE plug containing a small through hole was used to stopper the vial in order to reduce bumping. The vial was placed into a 3 mL stainless steel pressure reactor. The reactor was hand tightened, brought out of the acid box and sealed. The reactor was connected to a high-pressure gas manifold and, with the inlet valve of the reactor opened, degassed by slowly pressurizing to 500 psig argon followed by slow pressure release (3x) with constant stirring at 400 rpm. The reactor was then pressurized with 500 psig of argon, the inlet valve to the reactor was closed. The reaction was run for 4 hours. The reactor was then removed from the heating block and quickly cooled in a dry ice/acetone bath. The reactor was removed from the dry ice / acetone bath and allowed to reach room temperature. Then the pressure was slowly released. The reactor was opened, and an aliquot of the reaction solution (400-500  $\mu$ L) was transferred into a 5 mm NMR tube and a sealed capillary of deuterated solvent (DMSO or D<sub>2</sub>O or C<sub>6</sub>D<sub>6</sub>) was placed into the tube as an external solvent for locking and shimming. <sup>1</sup>H-NMR spectra were taken with 20 second relaxation delays, and the spectrum were referenced to the methyl protons in MeTFA (CF<sub>3</sub>COOCH<sub>3</sub>) (3.75 ppm), <sup>1</sup>H NMR analysis indicated complete decomposition of products and no apparent conversion to other cresol-TFA esters was observed.

Stability studies at 80 °C were conducted in a J-Young NMR tube by transferring an aliquot (0.4 - 0.5mL) of the reaction mixture of  $Sb(TFA)_5$  and toluene. Then a sealed capillary tube containing deuterated solvent (DMSO or  $D_2O$  or  $C_6D_6$ ) was placed into the NMR tube and the tube was sealed under inert atmosphere. <sup>1</sup>H NMR analysis of the reaction mixture at regular intervals indicated slow conversion of cresols to unknown products, but not interconversion to other cresol products. Approximately 75% of cresol products were observed after 22 hrs at 80°C (Figure S11, and Figure S12). MeTFA ester in the reaction mixture was used as internal standard to monitor the cresol stability.



**Figure S11:** Overlay of <sup>1</sup>H NMR spectra of reaction mixture of *p*-cresol + Sb(TFA)<sub>5</sub> in TFAH+TFAA medium at RT after 15 min (bottom) and at 80 °C after 22 hr (top).



**Figure S12:** Overlay of <sup>1</sup>H NMR spectra of reaction mixture of *m*-cresol + Sb(TFA)<sub>5</sub> in TFAH+TFAA medium at RT after 30min (bottom) and at 80 °C after 22 hr (top).

## 7. Computational Methodology

General methods: MN15/def2-SVP density functional and basis set was used to all structures using the Gaussian 16 program. All density functional theory (DFT) energy evaluations (even within optimizations) used the ultrafine integration grid. Frequency calculations and intrinsic reaction coordinate (IRC) calculations were used to establish potential-energy surface connections. Typically, this was done by running both forward and reverse IRC directions and then optimizing a structure at about step 10. All intermediates have all positive vibrational frequencies while transition-state structures have a single imaginary frequency. In addition to IRCs, for transition-state structures we often checked structure connections by distorting the structure only along the negative vibrational mode and then optimizing the structure. This method and IRCs always provided the same connections. Continuum solvent effects were included in all calculations using the SMD method with a modification for the dielectric and radius for TFAH. Additionally, in nearly all calculated structures there was inclusion of at least one explicit solvent of TFAH. The explicit solvent either coordinates directly to the Sb metal center or is involved in hydrogen bonding with ligands or the substrate. Because of the flexibility of the explicit solvent and the ligands surrounding the Sb center, for every reported structure we performed both manual and automated conformational search. For manual search the structure was changed followed by a MN15/def2-SVP structure optimization. The automated search was done using CREST/GFN2-xTB. Because of the uncertainty in xTB energies, we then fully optimized the 15 lowest energy xTB structures using MN15/def2-SVP. The manual and automated search structures were then combined and only the lowest energy MN15/def2-SVP structure was reported in the manuscript. MN15/def2-TZVPD single point energies were then performed on the lowest energy MN15/def2-SVP structures. Final energies in the manuscript correspond to MN15/def2-TZVPD//MN15/def2-SVP.

**Xyz coordinates:** Xyz coordinates for key intermediate and transition-state structures are given in a separate Supporting Information file.

**Comparison of density functionals:** Below is a comparison of enthalpy and Gibbs energies for key intermediates and transition states.



Structure energies:

Energies of computed structu	res (absolute energ	ies in a.u and relativ	e energies in kcal/n	nol)	
	SCF	SCF+ΔZPE	Н	G	
	MN15/def2-SVP				
	-3392.174819	-3391.984057	-3391.940348	-3392.069334	
(TFAH)SD*(TFA)5	MN15/def2-TZVPD//MN15/def2-SVP				
	-3396.172637	-3395.981875	-3395.938166	-3396.067152	
	MN15/def2-SVP				
Taluana	-270.977682	-270.849377	-270.842192	-270.880114	
Toldene	MN15/def2-TZVPD//MN15/def2-SVP				
	-271.305841	-271.177536	-271.170351	-271.208273	
	MN15/def2-SVP				
	-3663.188538	-3662.868735	-3662.817416	-3662.960129	
l l		MN15/def2-TZVPI	D//MN15/def2-SVP		
	-3667.507525	-3667.187722	-3667.136403	-3667.279116	
Relative energy	-18.2	-17.8	-17.5	-2.3	
	MN15/def2-SVP				
4*	-3663.181795	-3662.868141	-3662.817014	-3662.95963	
1.	MN15/def2-TZVPD//MN15/def2-SVP				
	-3667.485940	-3667.172286	-3667.121159	-3667.263775	
Relative energy	-4.7	-8.1	-7.9	7.3	
	MN15/def2-SVP				
2	-3663.212945	-3662.893241	-3662.842073	-3662.984363	
Z	MN15/def2-TZVPD//MN15/def2-SVP				
	-3667.521182	-3667.201478	-3667.150310	-3667.292600	
Relative energy	-26.8	-26.4	-26.2	-10.8	
	MN15/def2-SVP				
2‡	-3663.171581	-3662.856941	-3662.804633	-3662.949986	
2.	MN15/def2-TZVPD//MN15/def2-SVP				
	-3667.47307	-3667.158430	-3667.106122	-3667.251475	
Relative energy	3.4	0.6	1.5	15.0	
3	MN15/def2-SVP				

	-3408.294946	-3407.886652	-3407.834604	-3407.980521
	MN15/def2-TZVPD//MN15/def2-SVP			
	-3412.264535	-3411.856241	-3411.804193	-3411.950110
Relative energy	-8.0	-8.0	-7.5	-9.9
	MN15/def2-SVP			
ТЕЛН	-525.908214	-525.868376	-525.861271	-525.899427
	MN15/def2-TZVPD//MN15/def2-SVP			
	-526.575293	-526.535455	-526.528350	-526.566506
		MN15/d	ef2-SVP	
3‡	-3408.235053	-3407.831082	-3407.778583	-3407.925535
5	MN15/def2-TZVPD//MN15/def2-SVP			
	-3412.196437	-3411.792466	-3411.739967	-3411.886919
Relative energy	34.7	32.1	32.8	29.8
	MN15/def2-SVP			
ortho1	-3663.175228	-3662.860691	-3662.809739	-3662.953693
0000	MN15/def2-TZVPD//MN15/def2-SVP			
	-3667.480594	-3667.166057	-3667.115105	-3667.259059
Relative energy compared to 1 <sup>‡</sup>	3.4	3.9	3.8	3.0
	MN15/def2-SVP			
meta-1‡	-3663.176892	-3662.862573	-3662.811650	-3662.952935
	MN15/def2-TZVPD//MN15/def2-SVP			
	-3667.480045	-3667.165726	-3667.114803	-3667.256088
Relative energy compared to 1 <sup>‡</sup>	3.7	4.1	4.0	4.8
	MN15/def2-SVP			
Transition State for 2 to 3	-3408.262375	-3407.860976	-3407.809272	-3407.952628
	MN15/def2-TZVPD//MN15/def2-SVP			
	-3412.224846	-3411.823447	-3411.771743	-3411.915099
Relative energy	16.9	12.6	12.9	12.1
	MN15/def2-SVP			
[(TFAH)Sb <sup>∨</sup> (TFA)₅] <sup></sup>	-3392.379411	-3392.192194	-3392.146947	-3392.282230
		MN15/def2-TZVPI	D//MN15/def2-SVP	

	-3396.371809	-3396.184592	-3396.139345	-3396.274628
	MN15/def2-SVP			
**	-270.735012	-270.608574	-270.601050	-270.639674
C <sub>7</sub> H₀	MN15/def2-TZVPD//MN15/def2-SVP			
	-271.063016	-270.936578	-270.929054	-270.967678
	MN15/def2-SVP			
	-270.329007	-270.213593	-270.20699	-270.243269
C <sub>7</sub> H <sub>7</sub>	MN15/def2-TZVPD//MN15/def2-SVP			
	-270.655763	-270.540349	-270.533746	-270.570025
	MN15/def2-SVP			
	-2866.873255	-2866.714341	-2866.676769	-2866.792383
[(1FAH)Sb"(1FA)4]"	MN15/def2-TZVPD//MN15/def2-SVP			
	-2870.201407	-2870.042493	-2870.004921	-2870.120535
	MN15/def2-SVP			
	-3663.082918	-3662.772719	-3662.720384	-3662.868984
$[(IFAH)SB^{T}(H)(IFA)S] + CFH$	MN15/def2-TZVPD//MN15/def2-SVP			
	-3667.396929	-3667.086730	-3667.034395	-3667.182995
	MN15/def2-SVP			
- · · *	-270.145484	-270.027552	-270.020907	-270.056803
C <sub>7</sub> H <sub>7</sub>	MN15/def2-TZVPD//MN15/def2-SVP			
	-270.471360	-270.353428	-270.346783	-270.382679
PECT		MN15/def2-TZVP	D//MN15/def2-SVP	
Relative energy				
([(TFAH)Sb <sup>Ⅳ</sup> (TFA)₄] +TFAH+ C <sub>7</sub> H <sub>7</sub> - (TFAH)Sb <sup>V</sup> (TFA)₅-Toluene)	51.6	48.4	49.0	33.0
ET	ET MN15/def2-TZVPD//MN15/def2-SVP			
Relative energy				
(C <sub>7</sub> H <sub>☉</sub> +[(TFAH)Sb <sup>∨</sup> (TFA) <sub>5</sub> ] <sup></sup> (TFAH)Sb <sup>∨</sup> (TFA) <sub>5</sub> -Toluene)	27.4	24.0	25.2	20.8
Hydride	MN15/def2-TZVPD//MN15/def2-SVP			
Relative energy	51.2	45.6	46.5	58.0

[(TFAH)SB <sup>∨</sup> (H)(TFA)₅] <sup>-</sup> +C <sub>7</sub> H <sub>7</sub> <sup>-</sup> - (TFAH)Sb <sup>∨</sup> (TFA)₅-Toluene		

## 8. References

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