Supporting Information

Activation of Lewis acid catalyst in the presence of an organic salt containing non-coordinating anion: its origin and application potential

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1. Experimental Procedure

1.1 General remarks

All reactions were performed in argon atmosphere using standard Schlenk techniques. Chromatographic purification of products were carried out by flash chromatography using Merck silica gel 60 (230-400 mesh). Thin layer chromatography was carried out on Merck silica gel 60F plates. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz and 125 MHz) and ^{19}F NMR (282 MHz) spectra were recorded on Varian 300 spectrometers using TMS as an internal standard for ^{1}H and ^{13}C NMR or using $CFCl_3$ as external standard for ^{19}F NMR. Solid state ^{19}F-NMR spectra were obtained on a DSX Bruker 400 (376 MHz) spectrometer using external solid $LiAsF_6$. FAB-MS and ICP analysis were performed using JMS-700 (Jeol, Japan) and IRIS Interpid 1 (Duo type), respectively.

$Sc(OTf)_3$, $InCl_3$ and TMS-OTf were purchased from Aldrich and used without further purification. The IL **1a** was purchased from C-Tri Co., Ltd., Korea, www.c-tri.co.kr and used without further purification. They were spectrometrically pure, nearly chloride-free (<5 ppm) and their water content was <100 ppm (determined by Karl-Fisher titration). Other organic solvents were dried (CaH_2 or Na) and distilled under argon atmosphere prior to use. All other chemicals were obtained from commercial sources and used without further purification.

1.2 Preparation of $[NBu_4][SbF_6]$

$[NBu_4]Cl$ (5.0 g, 0.018 mol) and $KSbF_6$ (6.0 g, 0.022 mol) were stirred in 12 mL acetone at room temperature for 24h. After filtration of the formed KCl salt, the solution was concentrated. The resulted solid was again dissolved in CH_2Cl_2. Finally, the organic solution was washed with water, dried over anhydrous Na_2SO_4, concentrated, and dried in vacuo to afford 7.9 g (92% yield) of $[NBu_4][SbF_6]$. ^{19}F NMR (282 MHz, $CFCl_3$ as external standard): δ -119.9 ppm (sextet, $J_{(F\text{-}Sb(I=5/2)}$ = 1945 Hz, octet, $J_{(F\text{-}Sb(I=7/2)}$ = 1071 Hz).

1.3 Preparation of resin 3

Water (3 mL) and MeOH (1 mL) were added to a flask containing Merrifield's resin-bound imidazolium chloride (1 g, 1.75 mmol; 1.75 mmol N/g) and $NaSbF_6$ (2.26 g, 8.75 mmol). The mixture was stirred for 24 h at RT. The resultant suspension was filtered, washed successively with H_2O, MeOH, CH_2Cl_2 and ether, and dried in vacuo to afford 1.9 g of **3**. (See solid state ^{19}F NMR spectrum data in section 2)

1.4 Preparation of the resin-bound imidazolium triflate

Water (3 mL) and MeOH (1 mL) were added to a flask containing Merrifield's resin-bound imidazolium chloride (0.51 g, 0.86 mmol; 1.75 mmol N/g) and KOTf (0.84 g, 4.46 mmol). The mixture was stirred for 24 h at RT. The resultant suspension was filtered, washed successively with H_2O, MeOH, CH_2Cl_2 and ether, and dried in vacuo to afford 1.2 g of resin-bound imidazolium triflate. (See solid state ^{19}F NMR spectrum data in section 2)

1.5 Anion exchange experiment between resin 3 and $Sc(OTf)_3$

Under Ar atmosphere, the flask was charged with resin **3** (300 mg, 0.39 mmol; 1.3 mmol N/g) and $Sc(OTf)_3$ (37.9 mg, 0.08mmol). After the solid mixture was evacuated and the flask was recharged with argon, 2 mL of distilled THF was added to the flask. The mixture was then stirred for 24 h at RT. The suspension was filtered, washed successively with THF, MeOH, H_2O and MeOH, and dried in vacuo to afford resin **4**. (See solid state ^{19}F NMR spectrum data in section 2)

1.6 Experimental procedure for ^{19}F NMR study of 2 in the filtrate of the anion exchange experiment

The highly acidic species **2** was shown to be unstable in CH_2Cl_2 but stable in the presence of electron donor molecules such as DMSO. Therefore, to detect the existence of **2** in the filtrate, the following anion exchange experiment was performed in d_6-DMSO/d_8-THF (1:1, v/v). A mixture of resin **3** (300 mg, 0.39 mmol; 1.3 mmol N/g) and $Sc(OTf)_3$ (38 mg, 0.08 mmol) was stirred in a mixture of dried d_6-DMSO (1 mL) and d_8-THF (1 mL) for 4 h at RT. Using cannula equipped with membrane filter and Ar-gas pressure, the clear filtrate was then transferred from the suspension into a second flask and concentrated in vacuo to distill off THF, thereby affording d_6-DMSO solution of Sc-species.

1.7 Typical Procedure for Diels-Alder reactions in the presence of $Sc(OTf)_3$ and NBu_4SbF_6

Under Ar atmosphere, 1,3-cyclohexadiene (0.24 g, 3.0 mmol) was added to a mixture of 1,4-naphthoquinone (0.16 g, 1.0 mmol), $Sc(OTf)_3$ (0.98 mg, 0.002 mmol), and $[NBu_4][SbF_6]$ (0.48 g, 1.0 mmol) in dichloromethane (1 mL). The mixture was stirred at 20 ^{0}C for 5 min. Water was added to the mixture, which was extracted with ethyl acetate. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The obtained crude product was purified by flash column chromatography (hexane) to give 95% yield (226 mg) of the corresponding product.

1.8 Typical Procedure for Intermolecular Friedel-Crafts Alkylations in the presence of $Sc(OTf)_3$ and NBu_4SbF_6

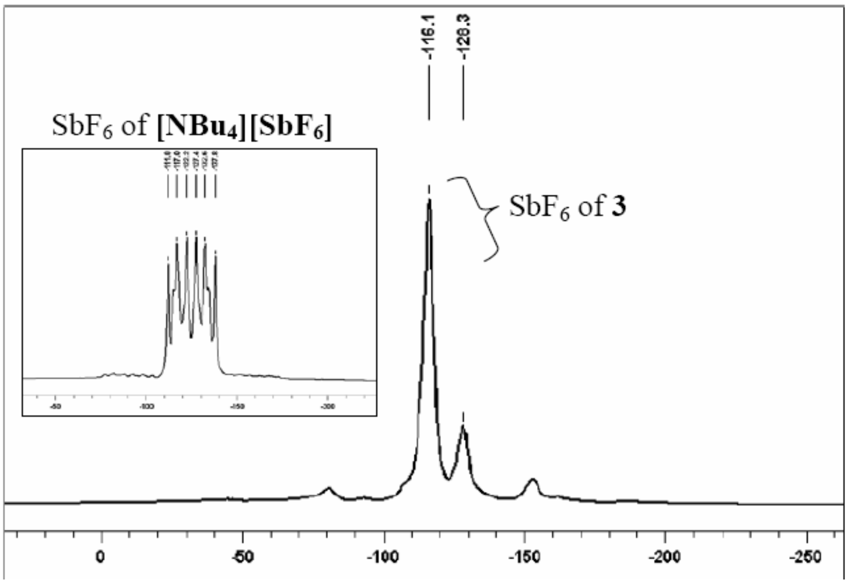
Under Ar atmosphere, cyclohexene (41.0 mg, 0.5 mmol) was added to a mixture of $Sc(OTf)_3$ (49.2 mg, 0.1 mmol), benzene (2 mL), 1,2-dichloroethane (2 mL) and $[NBu_4][SbF_6]$ (1.19 g, 2.5 mmol). The mixture was stirred at 20 ^{0}C for 24 h. Water was added to the mixture, which was extracted with ethyl acetate. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The obtained crude product was purified by flash column chromatography (hexane) to give 98% yield (79 mg) of cyclohexylbenzene.

1.9 Typical Procedure for Friedel-Crafts Alkenylations in the presence of $InCl_3$ and NBu_4SbF_6

Under Ar atmosphere, 1-phenyl-1-propyne (34.8 mg, 0.3 mmol) was added to a mixture of $InCl_3$ (13.3 mg, 0.06 mmol), *p*-xylene (1 mL), 1,2-dichloroethane (2 mL) and $[NBu_4][SbF_6]$ (0.72 g, 1.5 mmol). The mixture was refluxed for 3 h and upon reaction completion was cooled to RT. Water was added to the mixture, which was extracted with ethyl acetate. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The obtained crude product was purified by flash column chromatography (hexane) to give 88% yield (58.9 mg) of 1-Phenyl-1-(*p*-xylyl)-1-propene.

2. Spectroscopic data

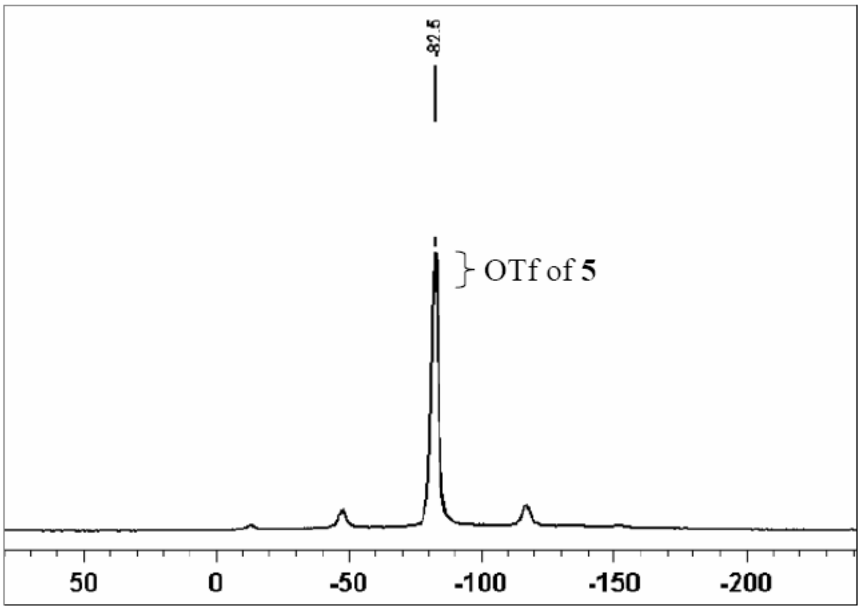
2.1 Solid state ^{19}F NMR spectrum for polymeric imidazolium-SbF_6 3



Inset : Solid state NMR spectrum for NBu_4SbF_6

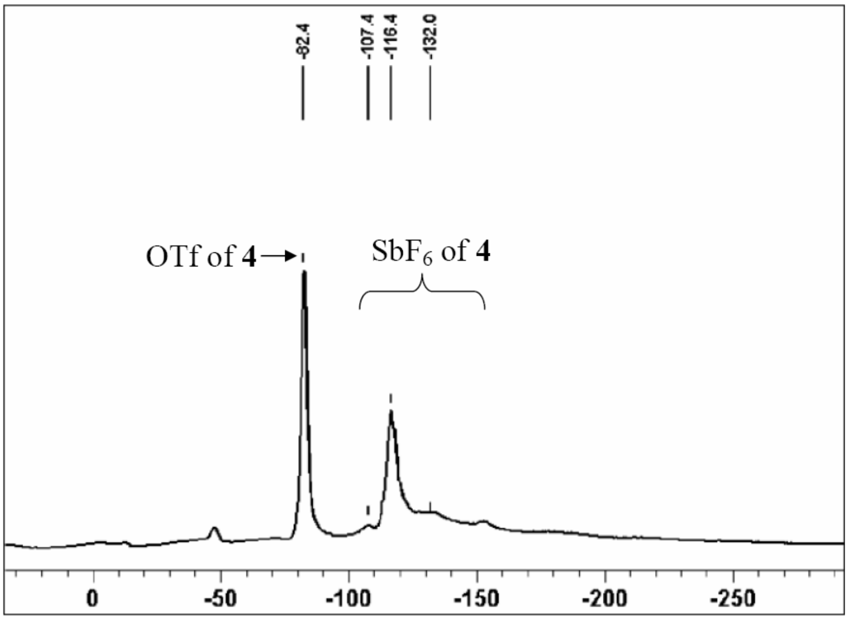
Solid state ^{19}F NMR of **3** (376 MHz, solid $LiAsF_6$ as external standard): δ -100 ~ -140 ppm (br m). (Note that the solid ^{19}F NMR of **3** did not show a fine coupling pattern between ^{19}F and two NMR-active Sb-nuclides (I=5/2 and 7/2), whereas the solid state ^{19}F NMR of $[NBu_4][SbF_6]$ did show all coupling patterns).

2.2 Solid state ^{19}F NMR spectrum for polymer-bound imidazolium triflate



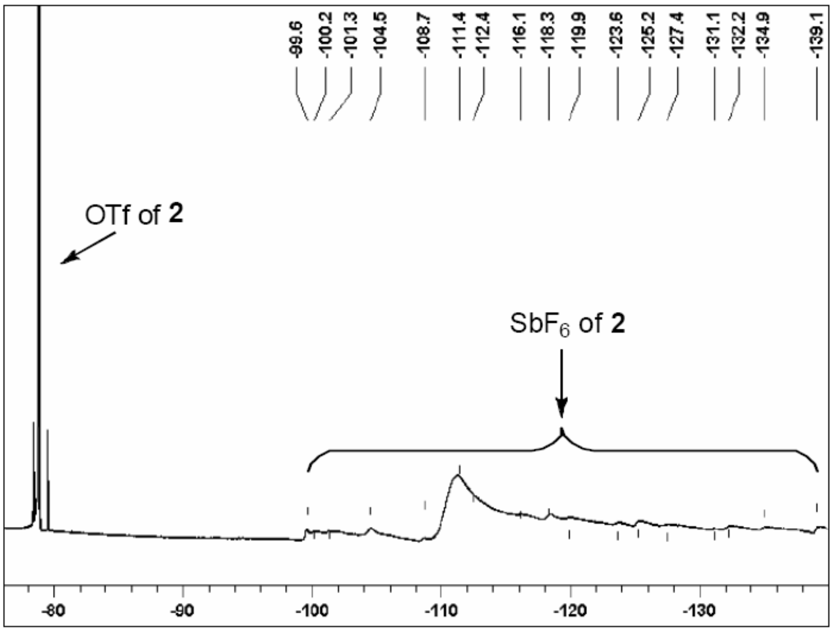
Solid state ^{19}F NMR (376 MHz, solid $LiAsF_6$ as external standard): δ -82.54 (br s).

2.3 Solid state ^{19}F NMR spectrum of resin 4

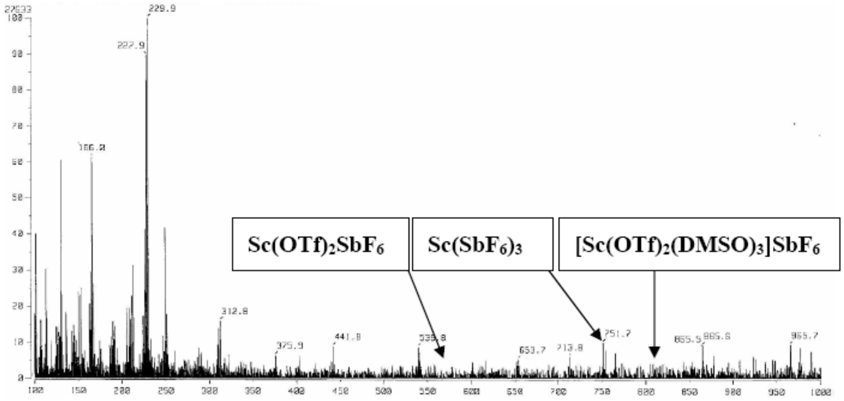


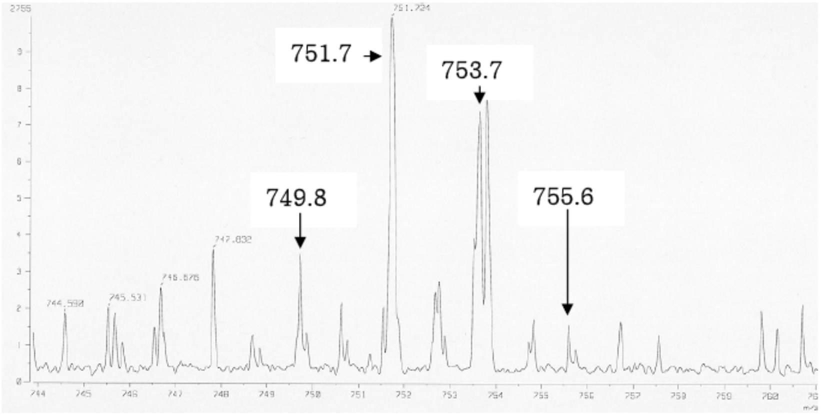
Solid state ^{19}F NMR of **4** (376 MHz, solid $LiAsF_6$ as external standard): δ -82.5 ppm (br s), -100 ~ -140 ppm (br m).

2.4 ^{19}F NMR spectrum and FAB-MS spectra of 2 from the filtrate

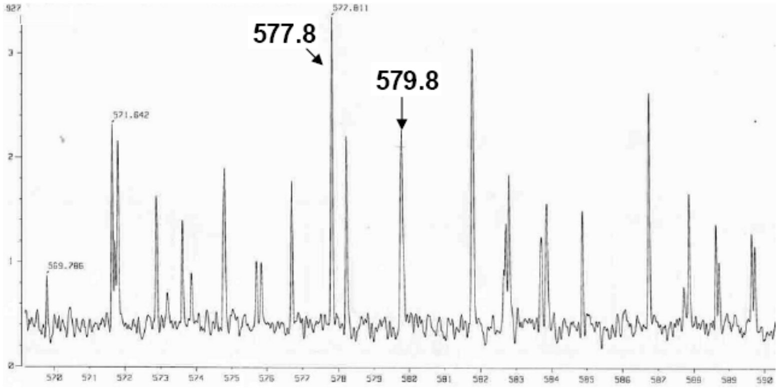


^{19}F NMR of **2** from the filtrate (282 MHz, $CFCl_3$ as external standard): δ -121.8 ppm (sextet, $J_{(F\text{-}Sb(I=5/2))}$ = 1945 Hz, octet, $J_{(F\text{-}Sb(I=7/2))}$ = 1071 Hz).

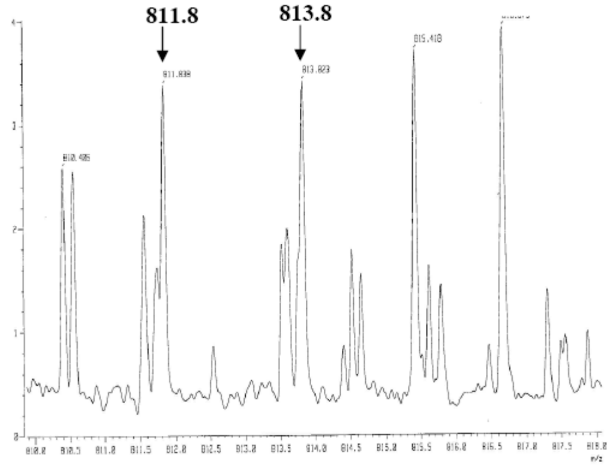




Molecular ion peaks for $Sc(SbF_6)_3$: Calc. m/z: 751.6 (100 %), 753.6 (74.3 %), 749.6 (44.8 %), 755.6 (18.4 %); Obsd. m/z: 751. 7 (100 %), 753.7 (73.7 %), 749.6 (34.8 %), 755.6 (15.7 %).



Molecular peaks for $Sc(OTf)_2SbF_6$: Calc. m/z: 577.75 (100 %), 579.75 (83.8 %); Obsd. m/z: 577.8 (100 %), 579.8 (65.6 %).



Molecular Peaks for $Sc(OTf)_2SbF_6(DMSO)_3$: Calc. m/z: 811.8 (100 %), 813.8 (100 %); Obsd. m/z: 811.8 (100 %), 813.8 (101 %).

3. The theoretical calculation of the atomic charges at Si of TMS-SbF_6 and TMS-OTf

To explain our experimental results that the Lewis acid catalyst could be strongly activated in the presence of organic salt bearing non-coordinating anion, we have carried out ab initio calculations for the TMS-OTf catalyst in the presence of $[NMe_4][SbF_6]$ salt. The geometry optimization have been performed for all the separated ionic species (TMS^+, OTf^-, NMe_4^+, SbF_6^-), organic salts ($[NMe_4][SbF_6]$ and $[NMe_4][OTf]$) and possible catalytic species (TMS-OTf and TMS-SbF_6), and they were confirmed to be minima from the vibrational frequencies. To include solvent effect, we used polarizable continuum model (PCM) method where the solvent is treated as the continuum medium, while the solute molecule can be polarized due to the medium field. At the optimized geometries, the natural bond orbital (NBO) charges were calculated to compare the electronic properties of silicon atoms in various species. For the gas phase and PCM calculations, the density functional theory with three-parameterized Lee-Yang-Parr exchange correlation functional (B3LYP) was employed using 3-21G* basis sets. These calculations were performed using a suite of Gaussian 03 programs (M. J. Frisch, et al. Gaussian 03, Rev. C.02; Gaussian, Inc.: Wallingford, CT, 2004).

$$\text{TMS-OTf} \; + \; [NMe_4][SbF_6] \; \rightleftarrows \; \text{TMS-}SbF_6 \; + \; [NMe_4][OTf] \quad (1)$$

The optimized structures were shown in Figure 3, and the energies were represented in Table 2. We first obtained the reaction enthalpy for the postulated reaction (Eq. 1) of TMS-OTf in the presence of [NMe_4][SbF_6] using the calculated energies. The reaction enthalpy was calculated to be 16.7, 13.9, and 13.7 kcal/mol for the gas phase, dichloromethane (DCM) solvent, and DMSO solvent, respectively. Basically, the endothermic reaction seems to be due to the fact that the spherically shaped NMe_4^+ prefers likely-shaped (spherically shaped) SbF_6^- to the non-spherically shaped OTf^-. Thus, apparently, it seems that the TMS-OTf may not turn into the TMS-SbF_6 via anion exchange. However, more important factor to determine the direction of the reaction (1) is the reactivity of TMS-OTf and TMS-SbF_6 because the above reaction is an equilibrium reaction and the reaction enthalpy value is not that large. Thus, if the TMS-SbF_6 is more activated than the TMS-OTf, the reaction (1) must proceed from the left-hand-side to the right-hand-side.

Table 2. Energies calculated at B3LYP/3-21G* level in gas/dichloromethane/DMSO.

Species	gas	DCM	DMSO
TMS-OTf	-1363.6436755	-1363.643354	-1363.6443324
[TMS][SbF_6]	-7291.6090472	-7291.616266	-7291.6173268
[NMe_4][OTf]	-1169.6751215	-1169.7007078	-1169.7046636
[NMe_4][SbF_6]	-7098.1525489	-7097.6957141	-7097.6994718
NMe_4^+	-213.0163982	-213.0855734	-213.0928636
TMS^+	-406.8561864	-406.9291526	-406.9371629
OTf^-	-956.4969296	-956.5778672	-956.5864083
SbF_6^-	-6884.4914967	-6884.5671769	-6884.5749181

Energies are in Hartree. 1 Hartree = 627.51 kcal/mol.

Table 3. Atomic charges at Si of TMS+, TMS-OTf, and [TMS][SbF_6].

Species	gas	DCM	DMSO
TMS^+	2.102	2.138	2.145
TMS-OTf	1.991	1.974	1.974
[TMS][SbF_6]	2.007	2.009	2.009

Charges were obtained from the natural bond orbital populations.

Charges are in e^+.

It is expected that the more positive atomic charge at the silicon atom of the TMS makes the TMS more Lewis-acidic. The NBO charges at Si in gas/DCM/DMSO are 2.102/2.138/2.145, 1.991/1.974/1.974, and 2.007/2.009/2.009 for naked TMS^+, TMS-OTf, and TMS-SbF_6, respectively (See Table 3). As clearly seen, the charge at Si of TMS-SbF_6 is more positive than that of TMS-OTf and close to the charge of naked TMS^+ cation. Therefore, TMS-SbF_6 is expected to be more activated than TMS-OTf, which drives the reaction (1) to the right. This result definitely supports the experimental result that the Lewis acid catalyst comes to be more activated in the presence of organic salt bearing non-coordinating anion.

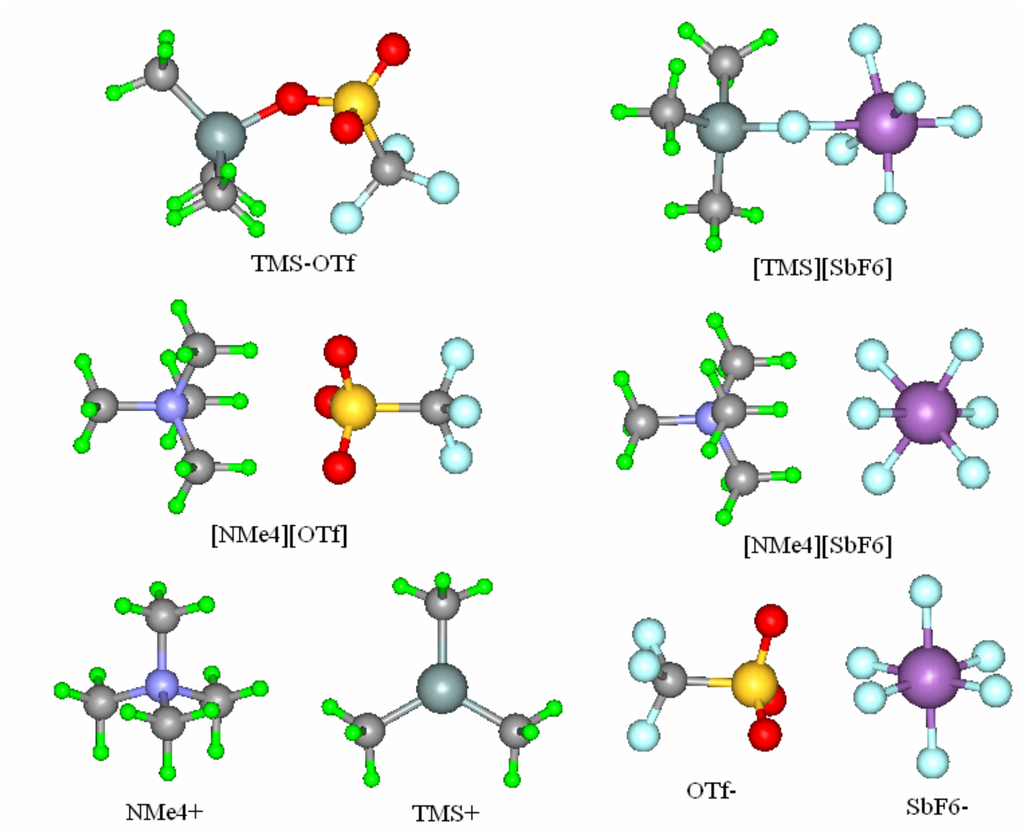


Figure 3. B3LYP/3-21G* optimized structures of TMS-OTf, TMS-SbF_6, $[NMe_4][OTf]$, $[NMe_4][SbF_6]$, NMe_4^+, TMS^+, OTf^-, and SbF_6^-.