Supporting Information

Non-Radical Pathways Control Methane Sulfonation versus Oxygenation C-H Functionalization Selectivity with Hg(II) and Au(III) Catalysis

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Table of Contents

1. General Considerations.

All air and water sensitive procedures were carried out either in an MBraun inert atmosphere glovebox or using standard Schlenk line techniques under argon. The deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were dried and distilled prior to use and stored under argon atmosphere. Chemicals, mercury(II)sulfate ($HgSO_4$), gold(III)oxide (Au_2O_3), tetramethyltin (Me_4Sn), sulfuric acid-D_2 (D,99%) 96-98% in D_2O, sulfuric acid (95-98%), oleum (sulfuric acid, fuming, 20% as free SO_3), methanesulfonic acid or MSA (CH_3SO_3H), methanedisulphonic acid or MDA [$CH_2(SO_3H)_2$], acetic acid or AcOH (glacial, >99% pure), methanol or MeOH, and methane (99.999 % purity) were purchased from commercial suppliers. Deuterated NMR solvents were dried if required following appropriate drying methods, distilled and stored under an atmosphere of argon prior to use. Deuterated NMR solvents were dried if required following appropriate drying methods, distilled and stored under an atmosphere of argon prior to use. Methyl bisulfate or MBS, (CH_3OSO_3H) was prepared according to the published procedure by treating methanol with concentrated sulfuric acid. Methylenedisulfuric acid (MDS), $CH_2(OSO_3H)_2$ was prepared in situ according to the published procedure (*J. Geophysical Research*, **1993**, *98*, 2957-2962). Methane C-H activation intermediate, CH_3-Hg-OSO_3H (or Me-Hg-OSO_3H) was prepared according to the previously reported method (See the following reference: *Science* **1993**, *259*, 340-343). NMR spectra were obtained on Bruker Digital Avance III 400 (400.132 MHz for 1H, 376.461 MHz for 19F and 100.623 MHz for 13C, 61.423 MHz for 2H), 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 reported in units of ppm and ^{1}H-NMR spectra were referenced to an internal standard, acetic acid (or AcOH), 2.0 ppm in sulfuric acid and D_2O solvent mixture. *Caution: Oleum is a super acid. Wear appropriate protective gear and well-ventilated fume hood when handling oleum solutions.*

Use similar caution for all acidic solutions discussed in this report. Gas phase analysis was performed on the Agilent 8890 GC paired with Agilent 7000D GC/TQ (gas chromatography/triple quadrupole mass spectrometry), using helium as carrier gas and Agilent 190915S-433UI: 3355534H, HP-5MS UI (30 m x 250 μm x 0.25 μm) column for separating the components in the gas phase. Following GC program is used for separating the components in the gas phase: oven initial temperature 30 °C (hold time 5 min); ramp: 2 °C/min (final temperature 100 °C, hold time 1min), carrier gas flow (constant flow): 1.3mL/min. CO_2 peak at rt 0.872 min. SO_2 mass spectra at rt 0.908 min.

2. Methane functionalization reactions.

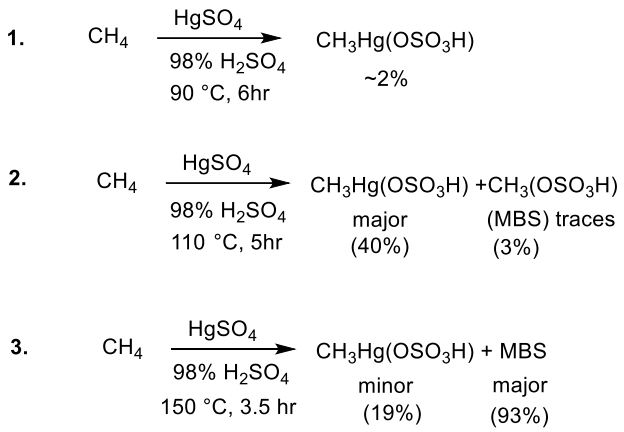
2.1. General procedure for methane functionalization with $HgSO_4$ and Au_2O_3.

A 2 mL glass insert equipped with a stir bar was charged with either $HgSO_4$ (30 mg, 0.1 mmol) or Au_2O_3 (22 mg, 0.1 mmol). To this, 1.5 mL of 98% H_2SO_4, (or D_2SO_4) or oleum was added. The insert containing the reaction mixture was placed into a stainless-steel pressure reactor, which was promptly sealed and leak tested. The reactor was then connected to a high-pressure gas manifold equipped with argon and methane gas lines. With the inlet valve open, the reactor contents were degassed by pressurizing to 500 psig with argon, followed by slow venting. This purge cycle was repeated three times under continuous stirring at 500 rpm. The same procedure was then performed using methane at 500 psig. After the final purge, the reactor was repressurized to 500 psig with methane, the inlet valve was closed, and the reactor was disconnected from the manifold. The sealed reactor was placed into a preheated aluminum heating block, and the contents were stirred at 1000 rpm. The reaction was allowed to proceed for a predetermined duration. Upon completion, the reactor was removed from the heating block and rapidly cooled in a dry ice/acetone bath, then gradually brought to room temperature before depressurization and collecting the gas phase into a separate vessel for GC-MS analysis. The reactor was opened, and the reaction mixture was cooled to 0 °C. Approximately 0.5 mL of D_2O was added dropwise under vigorous stirring, followed by the addition of an internal standard, acetic acid prepared in D_2O. An aliquot (400–500 μL) of the reaction solution was transferred to a Wilmad NMR tube fitted with J. Young Teflon vacuum/pressure valves, and ^1H NMR spectra were recorded. GC–MS analysis of extended-duration reactions revealed a decline in functionalized products accompanied by elevated CO_2 levels in the headspace.

Both $HgSO_4$ and Au_2O_3 were found to react with methane in 98% H_2SO_4 to yield methyl bisulfate (MBS) as the primary methane-functionalized product. In reactions involving $HgSO_4$, the methane C–H activation product CH_3-Hg-OSO_3H (δ = 1.056 ppm, $^2J_{^{199}Hg,^1H}$ = 264 Hz; see Scheme S1and Figure S1) was observed in both 98% H_2SO_4 and oleum at lower temperatures. In oleum, $HgSO_4$ also produced methanesulfonic acid (MSA) at 90 °C, which subsequently converted to MBS at elevated temperatures (>120 °C). At temperatures exceeding 150 °C, significant formation of methanedisulfonic acid (MDA, δ = 4.276 ppm; see Scheme S2 and Figure S2) was detected. In contrast, Au_2O_3 consistently generated only MBS across all tested temperatures (RT to 150 °C), even in oleum. Only trace amounts of MSA were observed, attributed to background oleum reactivity with methane. For additional data, refer to Scheme S3, Figure S3, Figure S4 and Table S1.

Following the same procedure described above, methane functionalization using $HgSO_4$ was conducted in a 1:1 mixture of 98% H_2SO_4 and oleum (20wt% as free SO_3) to generate ~ 5.8wt% of free SO_3 in H_2SO_4. Interestingly, MSA (methanesulfonic acid) was consistently observed as the initial product when the reaction was carried out at 90 °C for 3 hours (see Figure S5 and Table S1). A similar product profile was obtained at 110 °C, with MSA remaining the dominant product and only trace amounts of MBS (methyl bisulfate) detected (see Figure S6 and Table S1). No functionalization reactions with Au_2O_3 were conducted

in 1:1 mixture of 98% H_2SO_4 and oleum since Au(III) generated only MBS both in pure 98% H_2SO_4 and in oleum (20wt% as free SO_3 in H_2SO_4).



Scheme S1: The temperature dependent product selectivity of methane functionalization with $HgSO_4$ in 98% H_2SO_4. *Note: reactions are not balanced.*

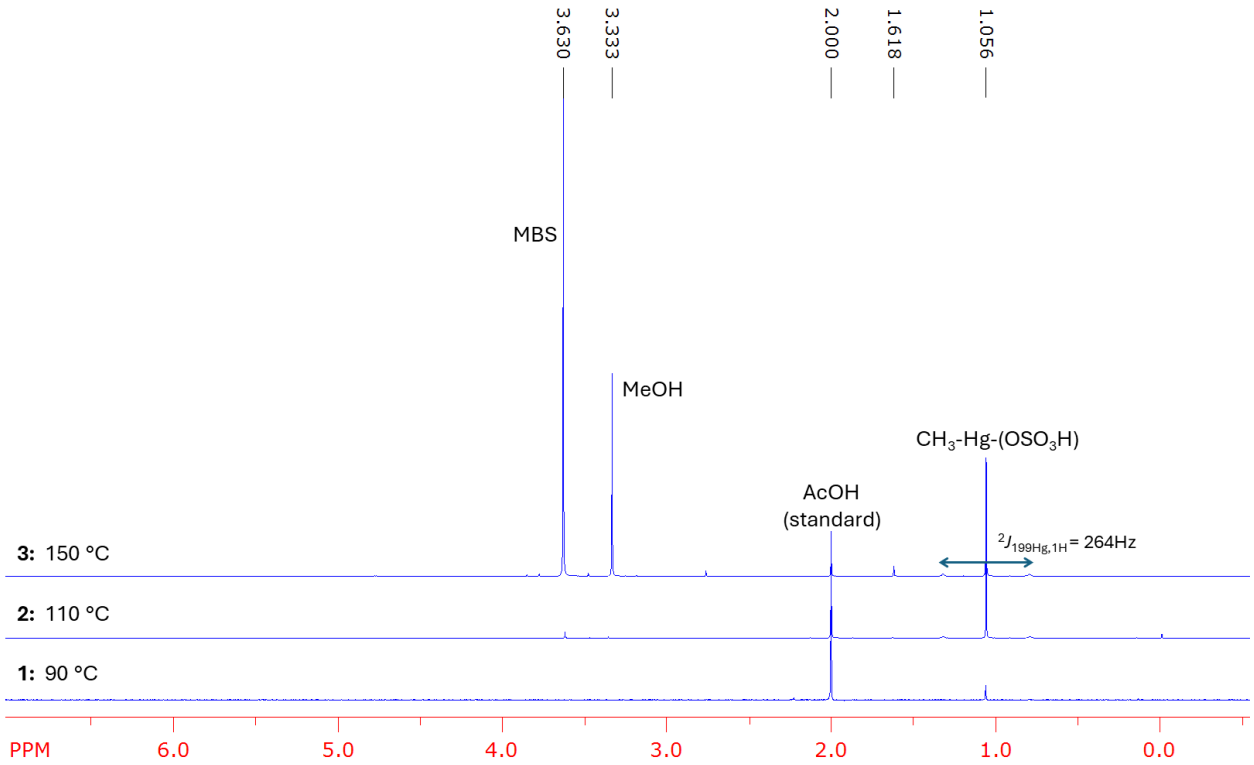
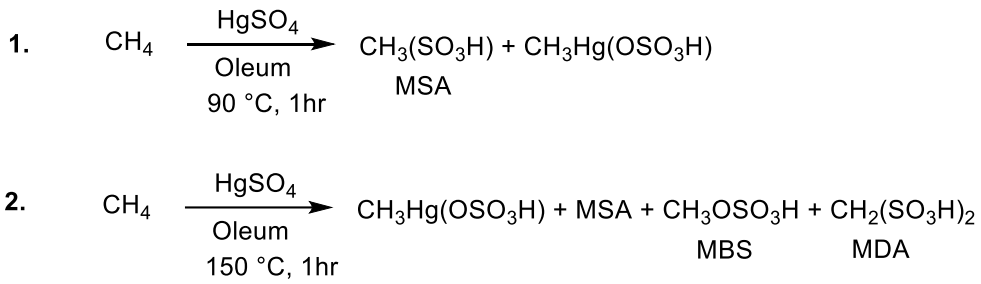


Figure S1: Overlay of ^{1}H NMR spectra of crude reaction mixtures of methane functionalization in 98% H_2SO_4 with $HgSO_4$ taken after diluting with D_2O. ***Top***: ^{1}H NMR spectra of reaction run at 150 °C for 3.5 hr. ***Middle***: ^{1}H NMR spectra of reaction run at 110 °C for 5 hr. ***Bottom*:** ^{1}H NMR spectra of reaction run at 90 °C for 3 hrs.



Scheme S2: Temperature dependent product selectivity of methane functionalization with $HgSO_4$ in oleum. *Note: reactions are not balanced.*

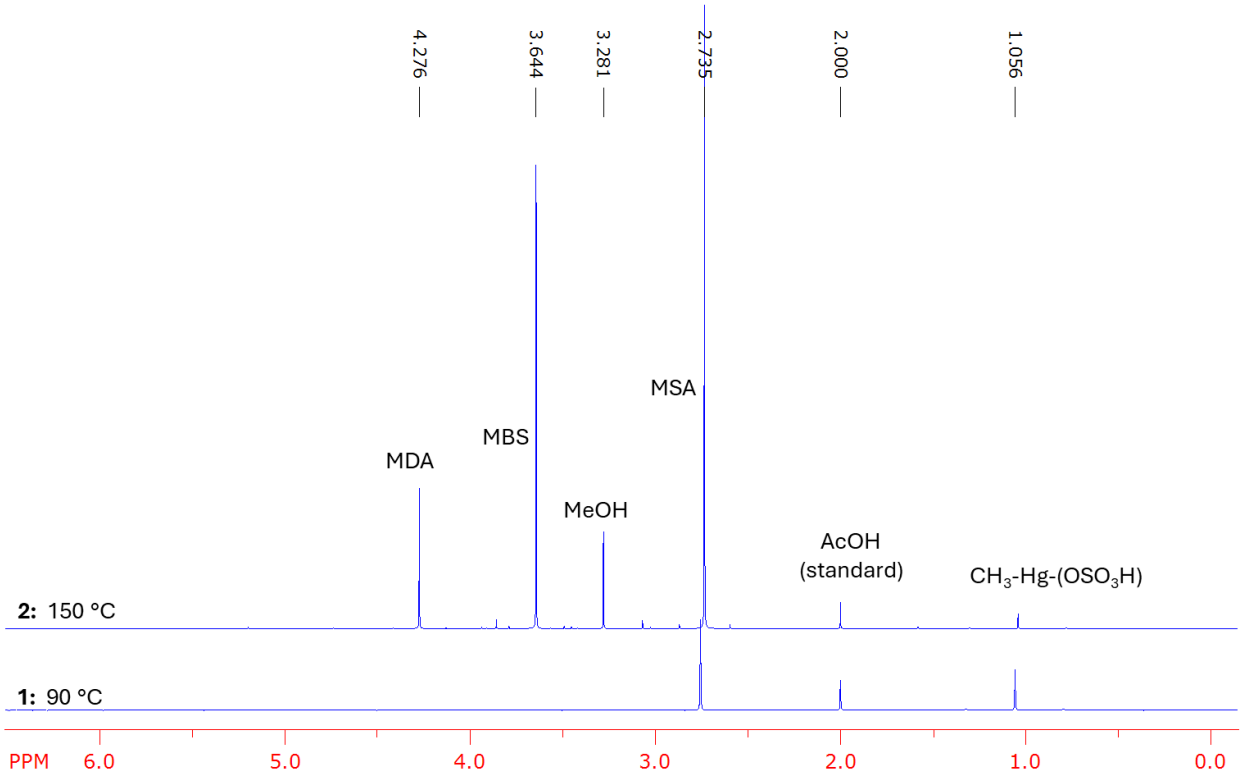
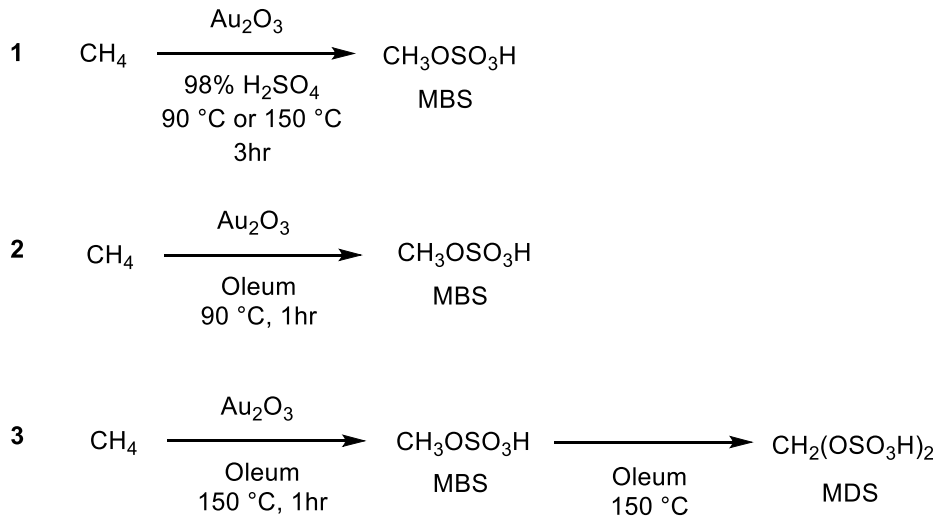


Figure S2: Overlay of ^{1}H NMR spectra of crude reaction mixtures of methane functionalization in oleum with $HgSO_4$ taken after diluting with D_2O. ***Top***: ^{1}H NMR spectra of reaction run at 150 °C for 1 hr. ***Bottom*:** ^{1}H NMR spectra of reaction run at 90 °C for 1 hr.



Scheme S3: Temperature and solvent dependent product selectivity of methane functionalization with Au_2O_3 in 98% H_2SO_4 and in oleum. *Note: reactions are not balanced.*

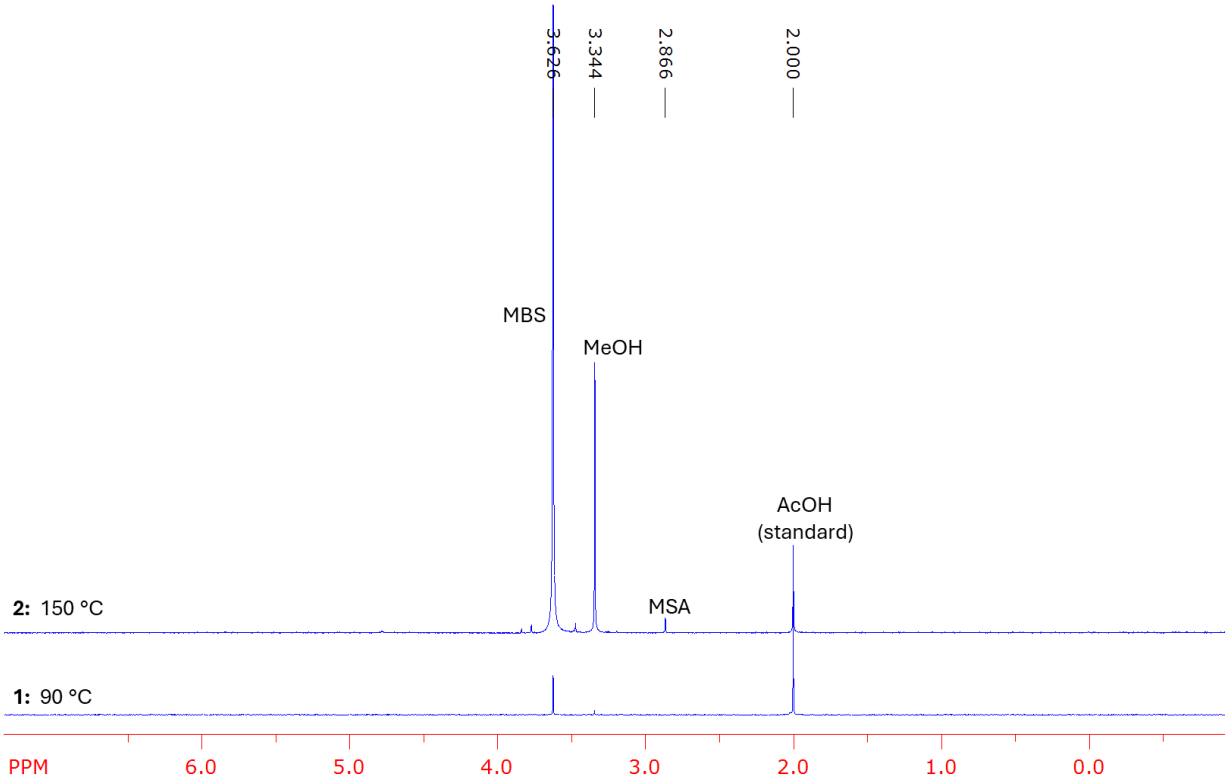


Figure S3: Overlay of ^{1}H NMR spectra of crude reaction mixtures of methane functionalization in 98% H_2SO_4 with Au_2O_3 taken after diluting with D_2O. ***Top****:* ^{1}H NMR spectra of reaction run at 150 °C for 3.5 hr. ***Bottom*****:** ^{1}H NMR spectra of reaction run at 90 °C for 3 hr.

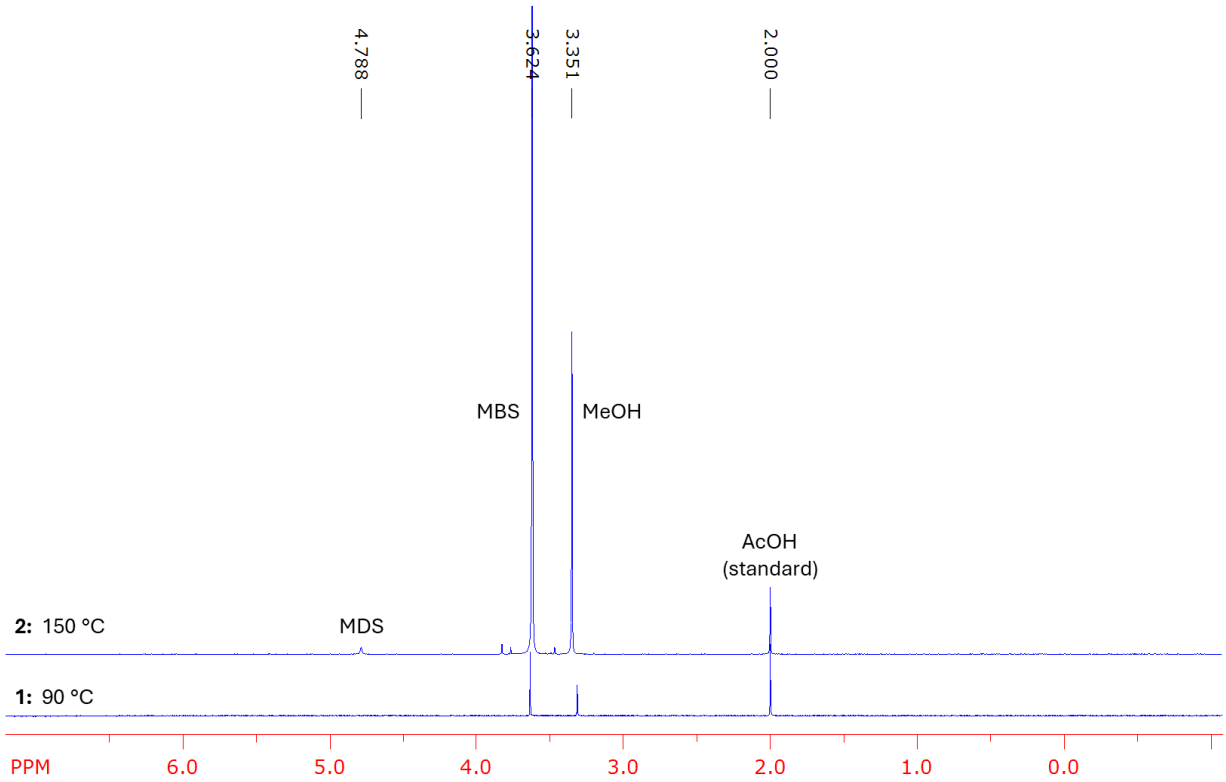


Figure S4: Overlay of ^{1}H NMR spectra of crude reaction mixtures of methane functionalization in oleum with Au_2O_3 taken after diluting with D_2O. ***Top****:* ^{1}H NMR spectra of reaction run at 150 °C for 1 hr. ***Bottom*****:** ^{1}H NMR spectra of reaction run at 90 °C for 1.5 hrs.

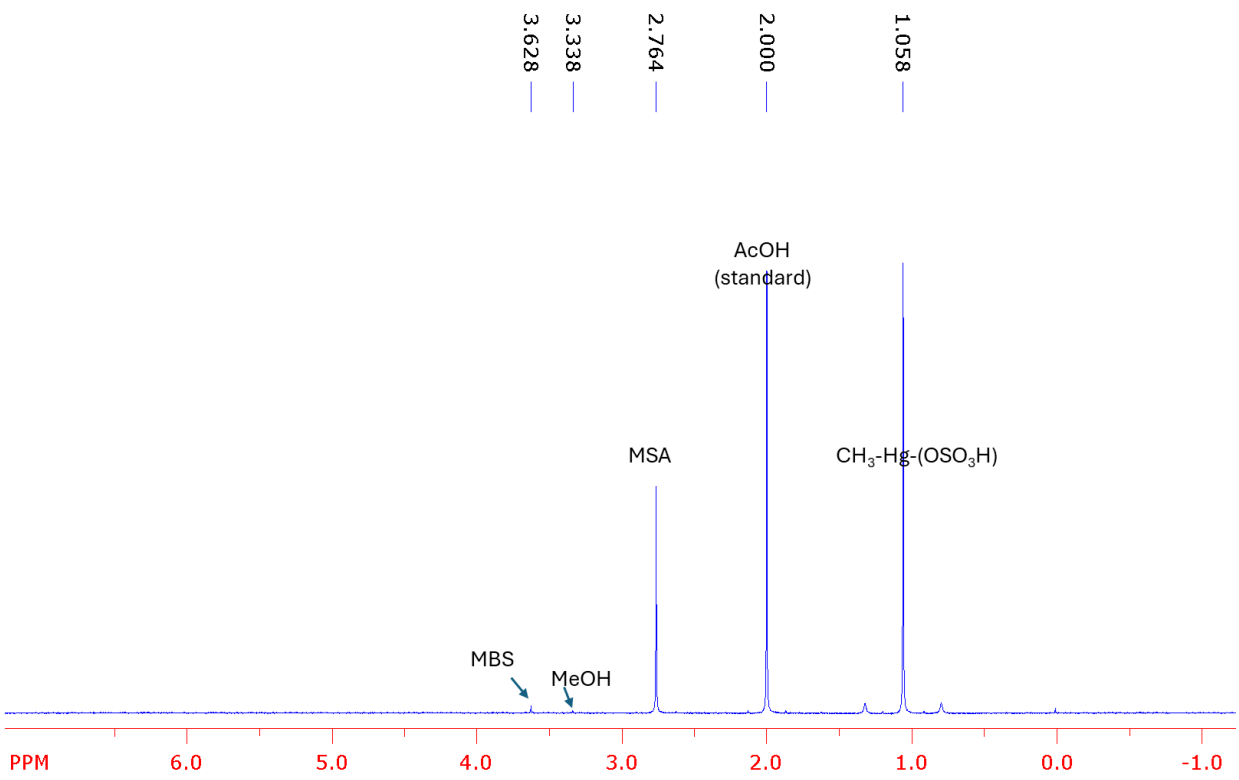


Figure S5 : ^{1}H NMR spectra of crude reaction mixture of methane functionalization with $Hg(SO_4)$ carried out at 90 °C for 3 hrs in a 1:1 mixture of oleum and 98% H_2SO_4. ^{1}H NMR spectra were taken after diluting the reaction mixture with D_2O.

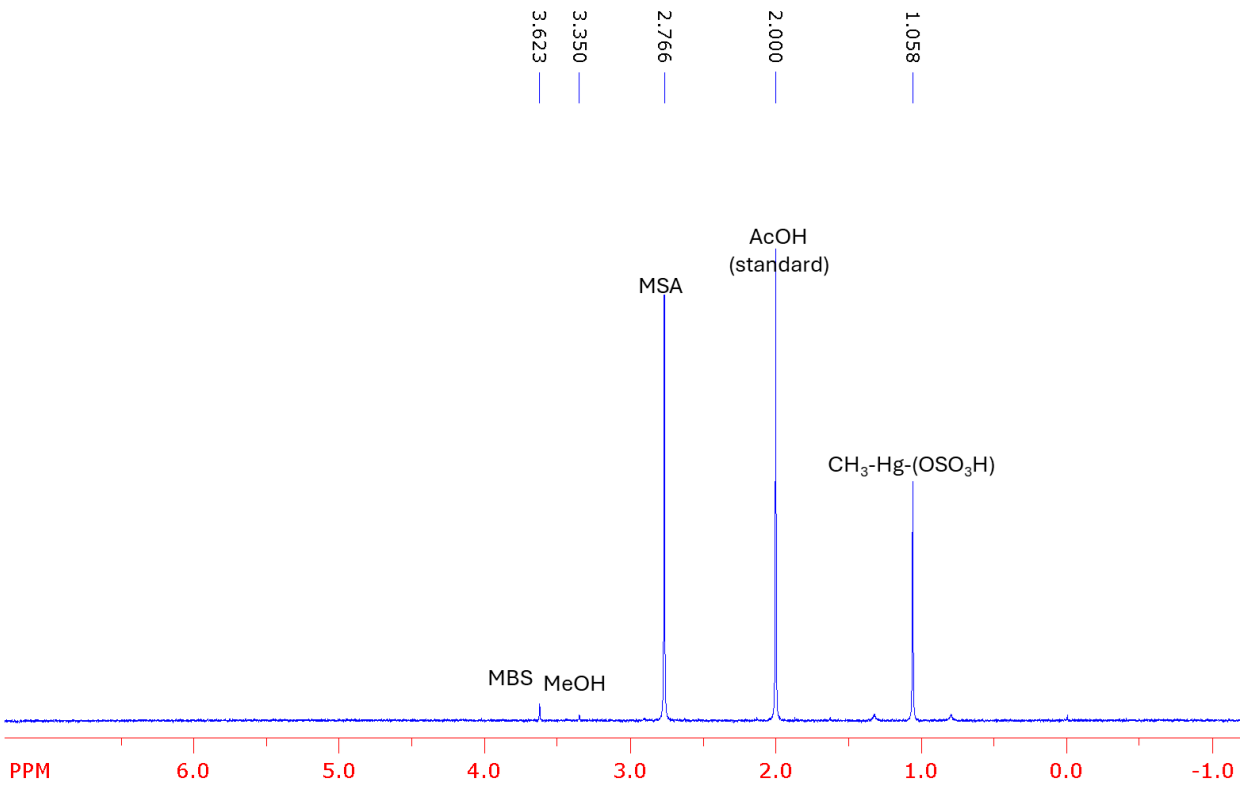


Figure S6: ^{1}H NMR spectra of crude reaction mixture of methane functionalization with $Hg(SO_4)$ carried out at 110 °C for 1hr in a 1:1 mixture of oleum and 98% H_2SO_4. ^{1}H NMR spectra were taken after diluting the reaction mixture with D_2O.

3. Methane functionalization reactions in the presence of oxygen.

In accordance with the general procedure outlined in Section 2, solutions of $Hg(SO_4)$ and Au(III) were prepared using 98% H_2SO_4 and oleum in 2 mL glass inserts equipped with stir bars. Following sample preparation, the glass insert was placed into a stainless-steel pressure reactor, which was promptly sealed and connected to a high-pressure gas manifold equipped with independent argon and methane gas lines. With the reactor inlet valve open, the contents were degassed by pressurizing to 500 psig with argon, followed by slow venting. This argon purge cycle was repeated three times under continuous stirring at 500 rpm. The same procedure was then applied using oxygen at 80 psig. After the final oxygen purge, the reactor was maintained at 1 atm O_2 pressure. Subsequently, the manifold was disconnected from the oxygen line and connected to the methane line. The reactor was pressurized directly with methane to achieve a total pressure of 500 psig (methane + oxygen), after which the inlet valve was closed. The reactor was then detached from the manifold and placed into a preheated aluminum heating block. Stirring was increased to 1000 rpm, and the reaction was allowed to proceed for a predetermined duration. ***Note:*** *No change in the color or state of catalyst was observed when the solutions of catalysts were stirred in the reactor in the presence of 60psig of oxygen only atmosphere before carrying out the methane functionalization reactions*.

Upon completion, the reactor was removed from the heating block and rapidly cooled in a dry ice/acetone bath. It was then gradually brought to room temperature before being depressurized. The reactor was opened, and the reaction mixture was cooled to 0 °C. Approximately 0.5 mL of D_2O was added dropwise under vigorous stirring, followed by the addition of an internal standard—acetic acid prepared in D_2O. An aliquot (400–500 µL) of the reaction mixture was transferred to a Wilmard NMR tube fitted with J. Young

Teflon vacuum/pressure valves, and ^{1}H NMR spectra were recorded. No significant influence of oxygen on product selectivity was observed; the product distribution closely resembled that obtained under oxygen-free conditions. In certain cases, a modest increase in product yield was noted, potentially attributable to oxygen-induced side reactions, such as reoxidation of the reduced metal complex or direct interaction with methane. See Table S1 for product distribution and yields. **Safety Note:** Due to the risk of explosion, reactions were not conducted with higher oxygen concentrations.

Table S1: Product selectivity in the functionalization of methane with $HgSO_4$ and Au_2O_3 catalysts. MSA = methanesulfonic acid. MBS = methyl bisulfate. MDA = methanedisulfonic acid. MDS = methylenedisulfuric acid. ***Reactions in the presence of 1 atm of oxygen. Note: M = Hg or Au, tr= traces. % yields are based on added mmol of metal oxidant.*

#	Oxidant (mmol)	Temp (°C)	Time	Reaction medium	% yield of Products				
					Intermediate CH_3-M-OSO_3H	MSA	MBS	MDA	MDS
1	$HgSO_4$ (0.18)	90 °C	3 hr	98% H_2SO_4	tr (<2)	-	-	-	-
2	$HgSO_4$ (0.18)	90 °C	6 hr	98% H_2SO_4	tr (~2)	-	-	-	-
3	$HgSO_4$ (0.12)	90 °C	1 hr	Oleum	31	65	-	-	-
4	$HgSO_4$ (0.12) *	90 °C	1 hr	Oleum	41	57	-	-	-
5	$HgSO_4$ (0.08)	90 °C	3 hr	Oleum+98% H_2SO_4 (1:1)	48	21	tr	-	-
6	$HgSO_4$ (0.13)	110 °C	5 hr	98% H_2SO_4	40	-	3	-	-
7	$HgSO_4$ (0.11)	110 °C	1 hr	Oleum+98% H_2SO_4 (1:1)	17	27	tr	-	-
8	$HgSO_4$ (0.15)	150 °C	3.5 hr	98% H_2SO_4	19	-	93	-	-
9	$HgSO_4$ (0.12) *	150 °C	3.5 hr	98% H_2SO_4	27	tr, (<2)	138	-	-
10	$HgSO_4$ (0.135)	150 °C	1 hr	Oleum	7	359	256	102	tr
11	Au(III) (0.1)	90 °C	3 hr	98% H_2SO_4	-	-	tr (~2)	-	-
12	Au(III) (0.07)	RT	2.5days	Oleum	-	-	5	-	-
13	Au(III) (0.023)	90 °C	90 min	Oleum	-	-	41	-	-
14	Au(III) (0.078) *	90 °C	90 min	Oleum	-	-	75	-	-
15	Au(III) (0.22)	150 °C	3.5 hr	98% H_2SO_4	-	tr	87	-	-
16	Au(III) (0.1) *	150 °C	3.5 hr	98% H_2SO_4	-	-	~100	-	-
17	Au(III) (0.25)	150 °C	1 hr	Oleum	-	-	158	-	3

4. Product stability studies.

4.1. Stability of MSA in 98%H_2SO_4 in the absence of Hg(II) and Au(III).

4.2. A ~380 mM solution of MSA in 98% H_2SO_4 was prepared in a 5 mL Schlenk bomb flask fitted with PTFE high vacuum valve sealing under an atmosphere of argon. Flask was then sealed and placed in an oil bath preheated to 150 °C. After 3 hrs of heating at 150 °C, reaction mixture was cooled to 0 °C and diluted with D_2O and then added acetic acid standard and analyzed by quantitative ^{1}H NMR. ^{1}H NMR data analysis indicated more than 95% of MSA recovery and no decomposition or conversion of MSA to MBS was observed.

4.3. Stability of MSA in oleum in the absence of Hg(II) and Au(III).

A ~ 323 mM solution of MSA in oleum was prepared in 5mL Schlenk bomb flask fitted with PTFE high vacuum valve sealing. Flask was then sealed and placed in an oil bath preheated to 120 °C. After 30 minutes of heating, the reaction mixture was cooled to 0 °C and diluted with D_2O and then added acetic acid standard and analyzed by quantitative ^1H NMR. ^1HNMR data analysis indicated conversion of MSA to MBS (~ 10%) in oleum. Also observed MDA in minor quantities (~3%). More than 95% of total products were observed based on initial MSA concentration. Similarly, stability study was also carried out at 150 °C for 1hr. at 150 °C, ~97% of MSA got converted to MBS (~73%) and MDA (~23%). Only traces of MDS were observed. See Figure S7.

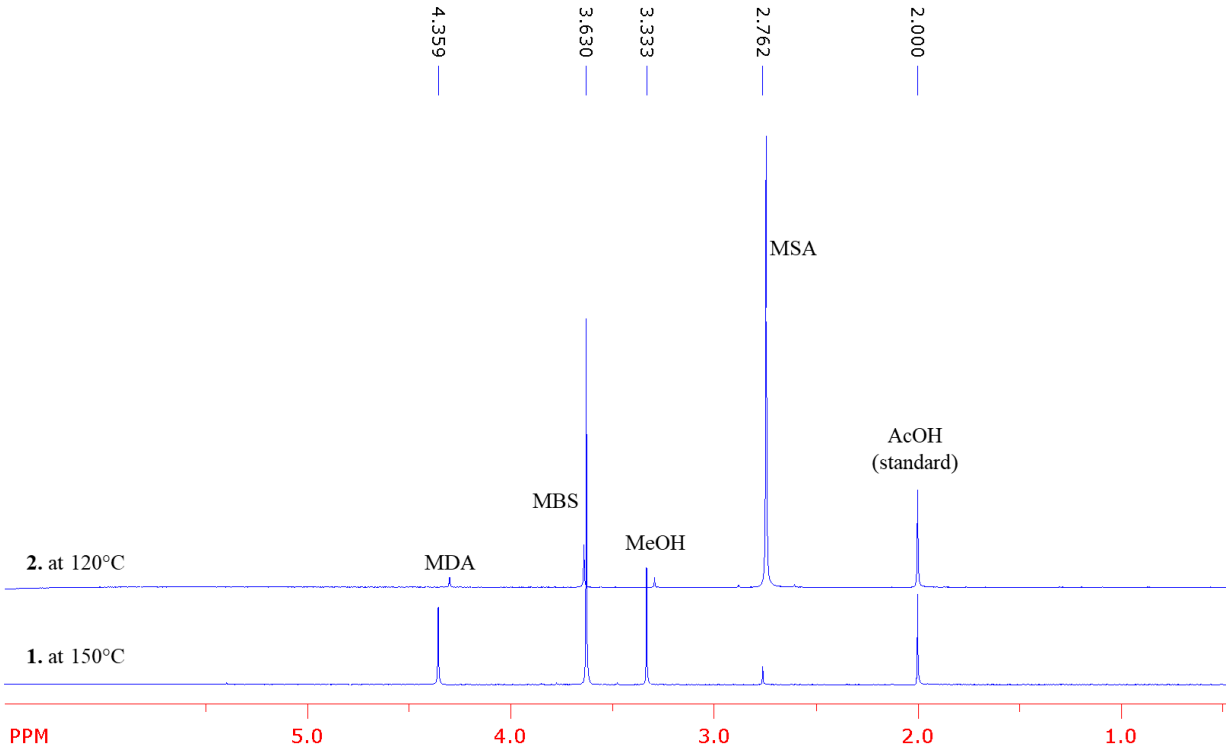


Figure S7: Overlay of ^1H NMR spectra of crude reaction mixtures of thermal stability of MSA in oleum taken after diluting with D_2O. ***Top****:* ^1H NMR spectra of reaction run at 150 °C for 1 hr. ***Bottom*****:** ^1H NMR spectra of reaction run at 120 °C for 30 min.

4.4. Stability of MBS in oleum in the absence of Hg(II) and Au(III).

A ~ 900mM solution of MBS in oleum was prepared in 5 mL Schlenk bomb flask fitted with PTFE high vacuum valve sealing. Flask was then sealed and placed in an oil bath preheated to 150 °C. After 60 minutes of heating, the reaction mixture was cooled to 0 °C and diluted with D_2O and then added acetic acid standard and analyzed by quantitative ^1H NMR. ^1H NMR data analysis indicated no conversion of MBS to other products with a recovery of more than 97% of starting material.

4.5. Product stability studies in the presence of Hg(II) and Au(III).

MBS was found to be stable under reaction conditions in 98% H_2SO_4 in the presence of both Hg(II) and Au(III) as presented in the references (See the following reference: *Science* **1993**, *259*, 340-343 and *Angew.*

Chem. Int. Ed. **2004**, *43*, 4626-4629). MBS was found to be stable in the presence of both Hg(II) and Au(III) in oleum at lower temperatures of 90 °C with more than 95% recovery after 90 mins. But at higher temperatures of over 120 °C interference from SO_3 complicated the accurate product stability studies and not much effort was placed to further study these reactions in the presence of Hg(II) and Au(III). Also refer to section 3.5 for MSA product stability in oleum at 90 °C

4.6. MSA stability in the presence of Au(III) in oleum.

A test solution containing ~ 135 mM of MSA and 60 mM of Au(III) solution *(by heating appropriate amount of Au_2O_3 in oleum at 90 °C for 45 mins)* was prepared in 2 mL of oleum in a 5 mL Schlenk bomb flask fitted with PTFE high vacuum valve. The sealed flask was then heated at 90 °C for 90 mins in an oil bath. After 90mins reaction mixture was cooled to 0 °C and diluted with D_2O and then added acetic acid standard and analyzed an aliquot by ^{1}H NMR. ^{1}HNMR data analysis of products post-reaction indicated over 95% recovery of MSA with only traces of MBS and methanol (total of ~ 2% based on initial [MSA]) as indicated by the ^{1}H NMR spectrum shown in **Figure S8**. Control experiments without Au(III) also indicated similar product selectivity under same conditions indicating MSA is completely stable in the presence of Au(III) in oleum under experimental conditions that are used for alkyl transfer and methane functionalization reactions.

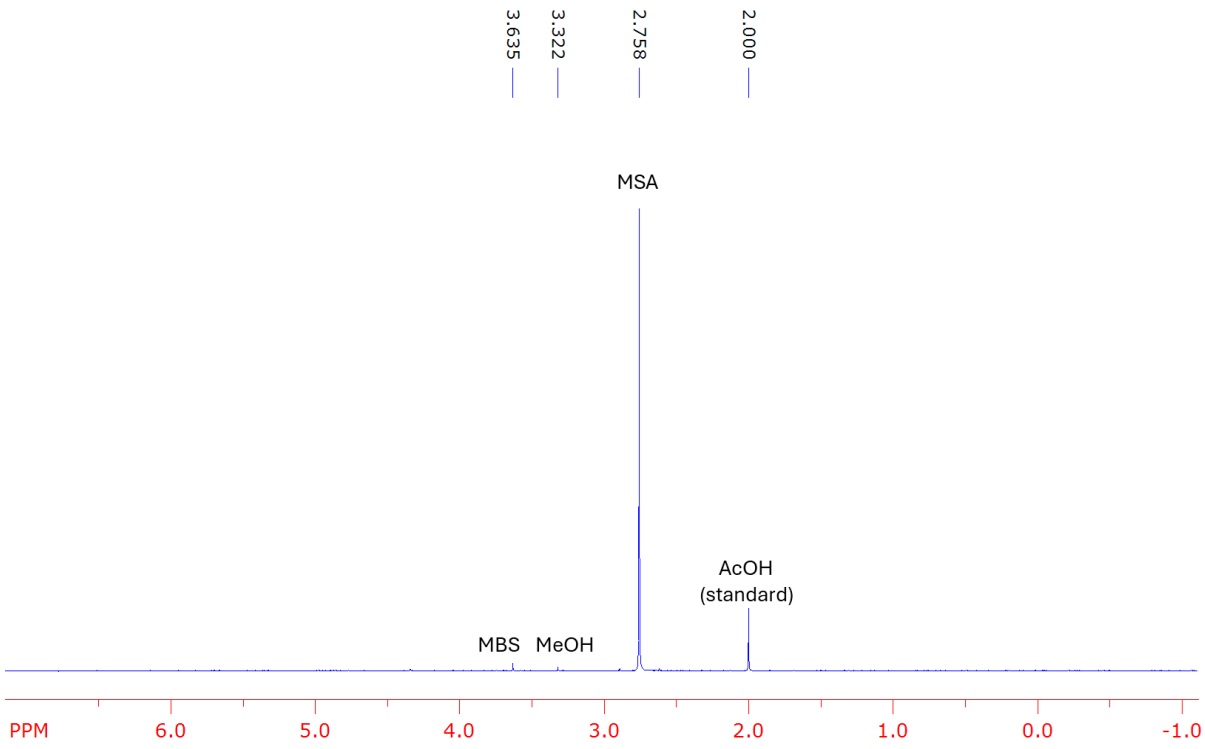
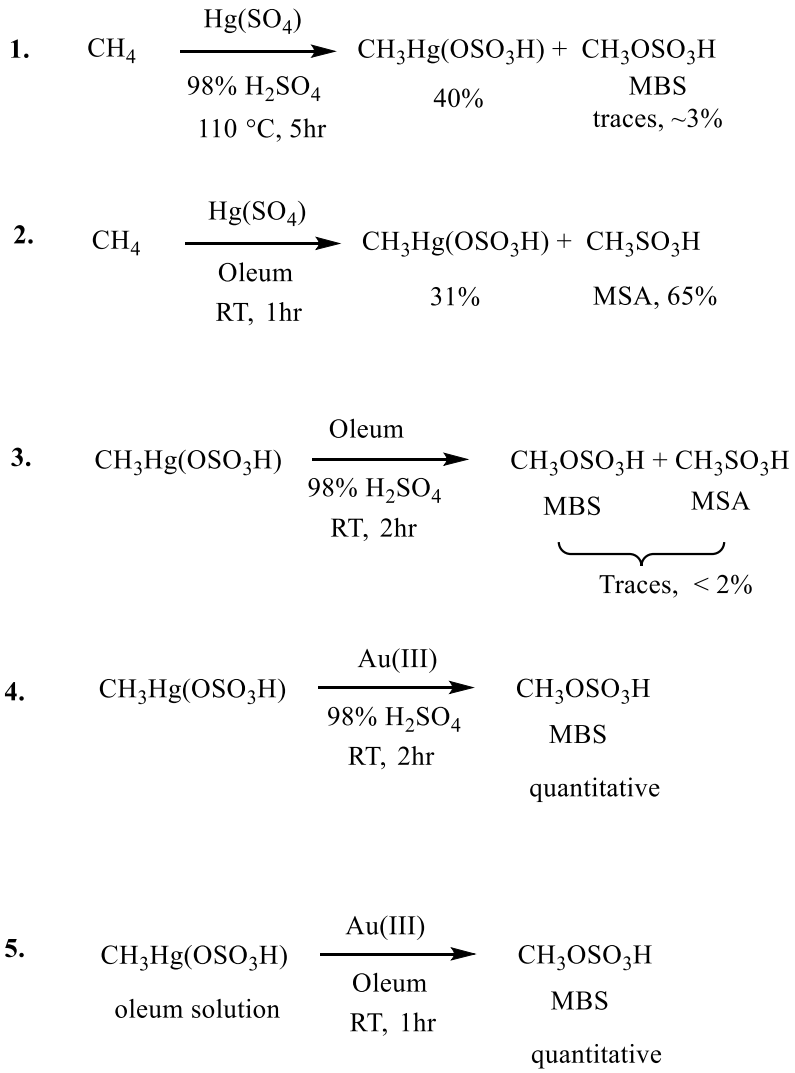


Figure S8: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of MSA and Au(III) carried out in oleum at 90 °C for 90 min.

5. Alkyl transfer reactions between Me-Hg-OSO_3H and SO_3, and Au(III).

5.1. Preparation of Me-Hg- OSO_3H in 98% H_2SO_4 and Oleum:

Following the general procedure described in section 2, $HgSO_4$ (38 mg, 0.13 mmol, 128mM), solutions were prepared in 98% H_2SO_4 and reacted with methane at 110 °C for 5 hrs. ^1H NMR analysis of reaction mixture indicated formation of Me-Hg-OSO_3H in ~21 mM concentration with only minor functionalized product MBS (<3% based on [HgSO4]). See Scheme S4 and Figure S9. Similarly, Me-Hg-OSO_3H was prepared in Oleum by reacting $HgSO_4$ (38 mg, 0.13 mmol, 128 mM), with 500 psig of methane at 90 °C for 60 mins. Reaction in oleum also generated MSA in 52 mM along with Me-Hg-OSO_3H in 25 mM concentrations. See Scheme S4 and Figure S10.



Scheme S4: Alkyl transfer and subsequent functionalization in the presence of added SO_3 (from oleum) and Au(III) in 98% H_2SO_4 and in oleum medium. *Note: reactions are not balanced.* % yields are based on added catalyst (reaction 1 and 2) or based on taken Me-$HgOSO_3H$ (reactions 3 to 5).

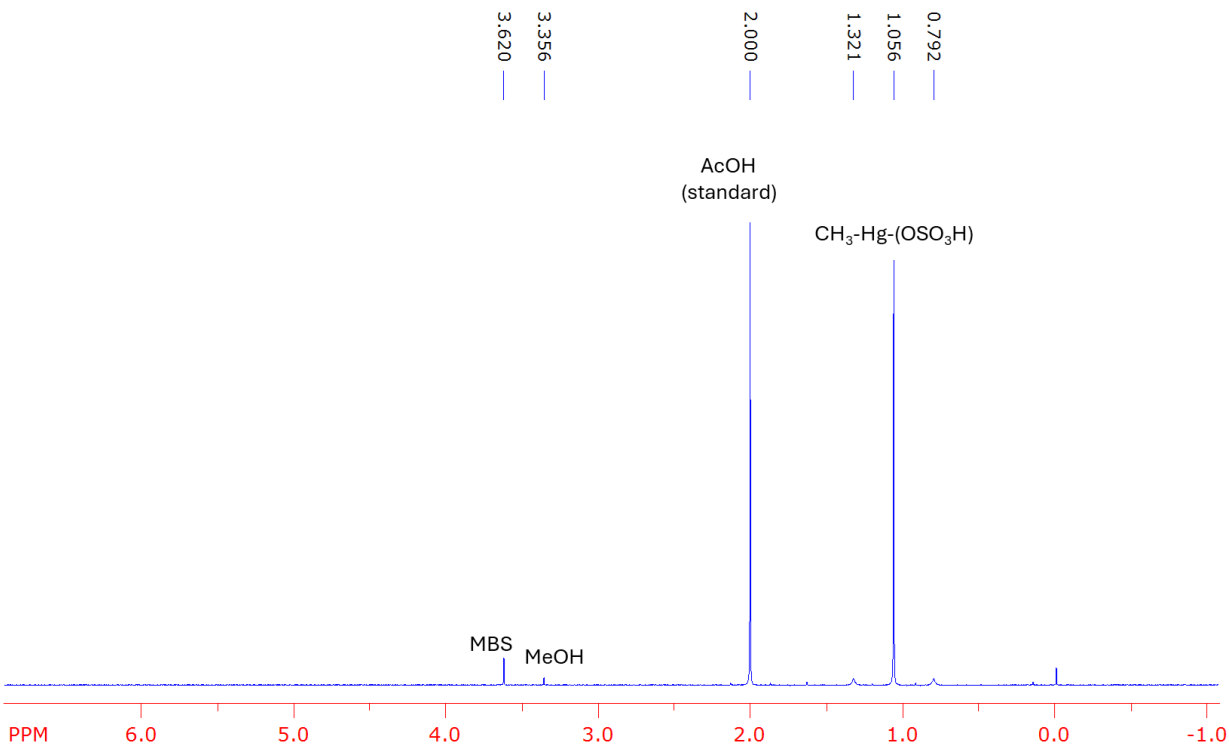


Figure S9: ^{1}H NMR spectrum *(taken in a solvent mixture of H_2SO_4 and D_2O)* of reaction mixture of methane and $HgSO_4$ in 98% H_2SO_4 run at 110 °C for 5 hrs.

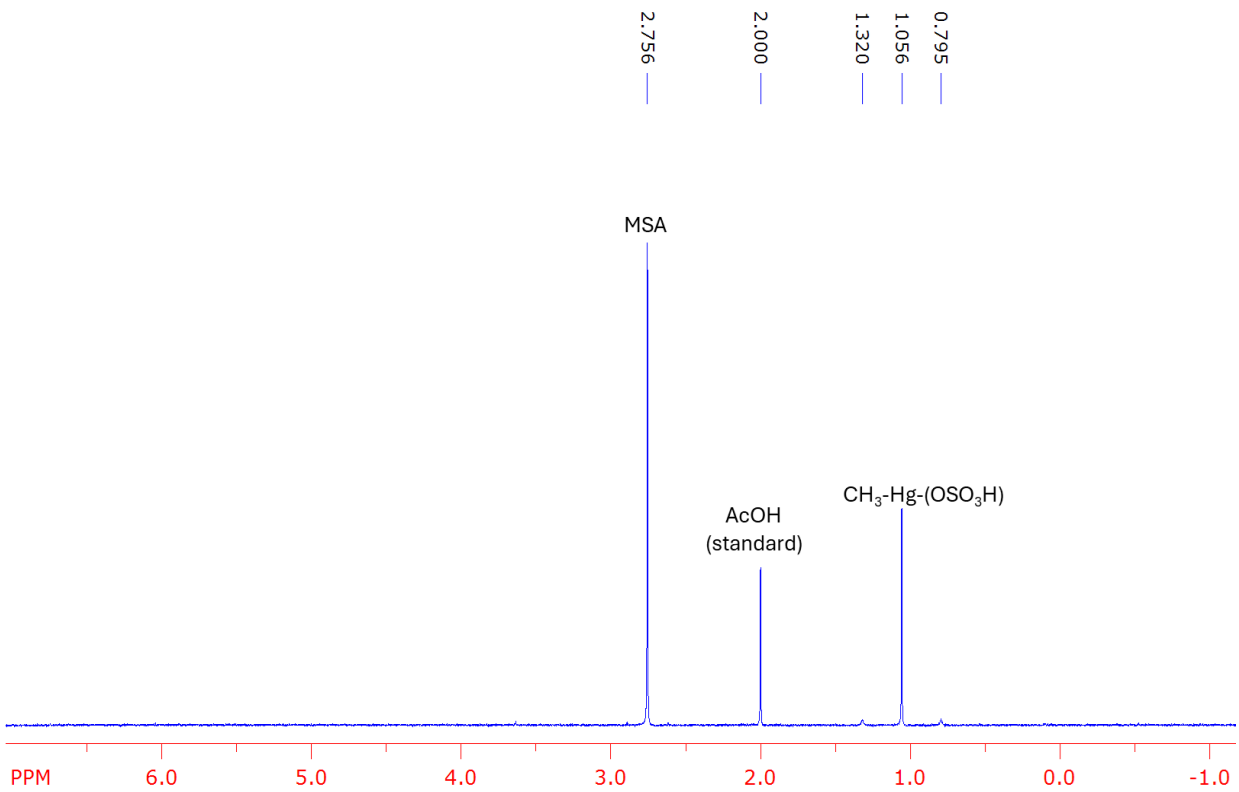


Figure S10: ^{1}H NMR spectrum *(taken in a solvent mixture of H_2SO_4 and D_2O)* of reaction mixture of methane and $HgSO_4$ in oleum run at 90 °C for 1 hr.

5.2. Reaction of Me-Hg-OSO_3H (generated in 98% H_2SO_4) with SO_3 in oleum.

A 0.31 mL (0.0064 mmol) of Me-Hg-OSO_3H solution initially generated in 98% H_2SO_4 *(above section 3.1)* was added to 1 mL of oleum in a 2 mL Schlenk flask cooled to 0 °C while stirring vigorously. After the complete addition of Me-Hg-OSO_3H solution was slowly allowed to warm to room temperature and stirred at RT for 2 hrs before diluting with D_2O and analyzing the reaction mixture by ^{1}H NMR. Which indicated only traces of MSA, MBS and methanol products and near quantitative recovery of Me-Hg-OSO_3H indicating sluggish reactivity of Me-Hg-OSO_3H with SO_3 at room temperature. Figure S11.

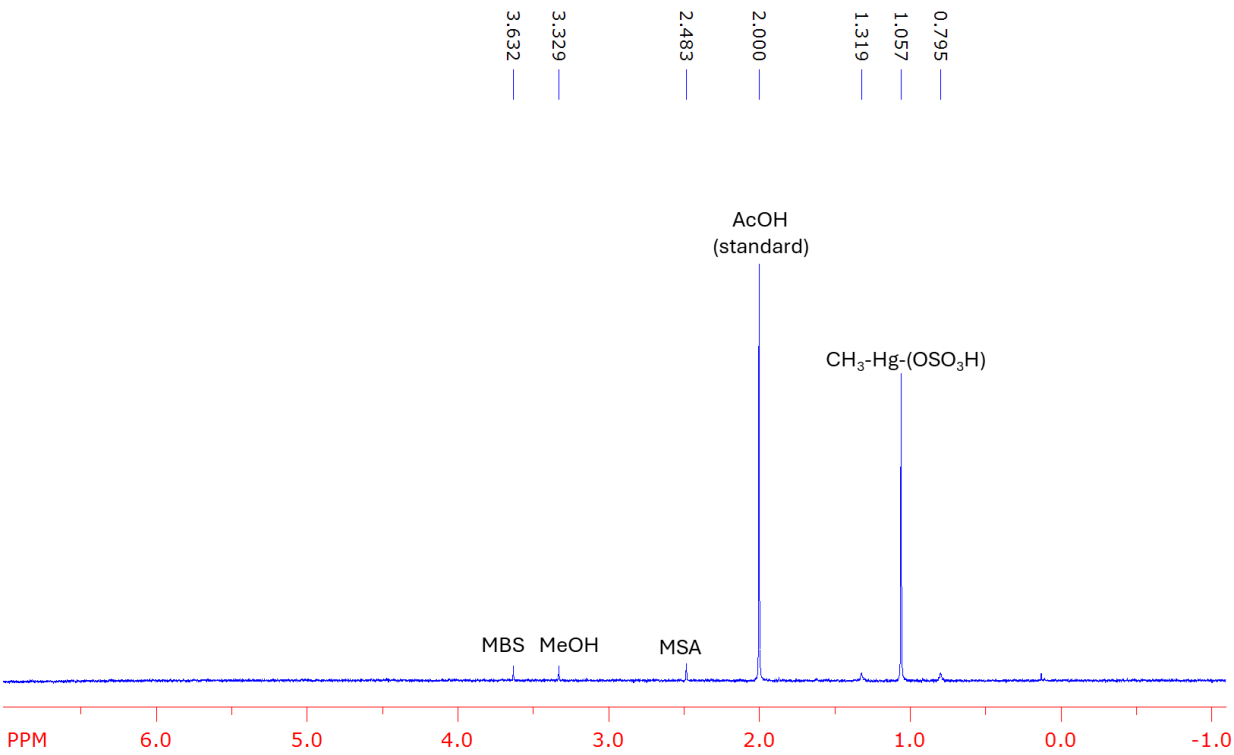


Figure S11: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me-Hg-OSO_3H (Section 5.1, Figure S9) with oleum run at room temperature for 2 hrs.

5.3. Reaction of Me-Hg-OSO_3H generated in 98% H_2SO_4 with Au(III) in 98% H_2SO_4.

Following the procedure described in Section 3.2, a 0.0087 mmol (0.42mL, section 3.1) of Me-Hg-OSO_3H solution generated in 98% H_2SO_4 was added to 0.016 mmol (0.1mL of 163mM)) of Au(III) solution (*prepared by dissolving Au_2O_3 in 98% H_2SO_4 at 90 °C until a homogeneous bright yellow solution was obtained*) in a 1 mL Schlenk flask cooled to 0 °C while stirring vigorously. After the complete addition of Me-Hg-OSO_3H solution was slowly allowed to warm to room temperature and stirred at RT for 90 minutes before dilution with D_2O and analyzing the reaction mixture by ^{1}H NMR. Quantitative conversion of Me-Hg-OSO_3H to MBS and methanol. Figure S12.

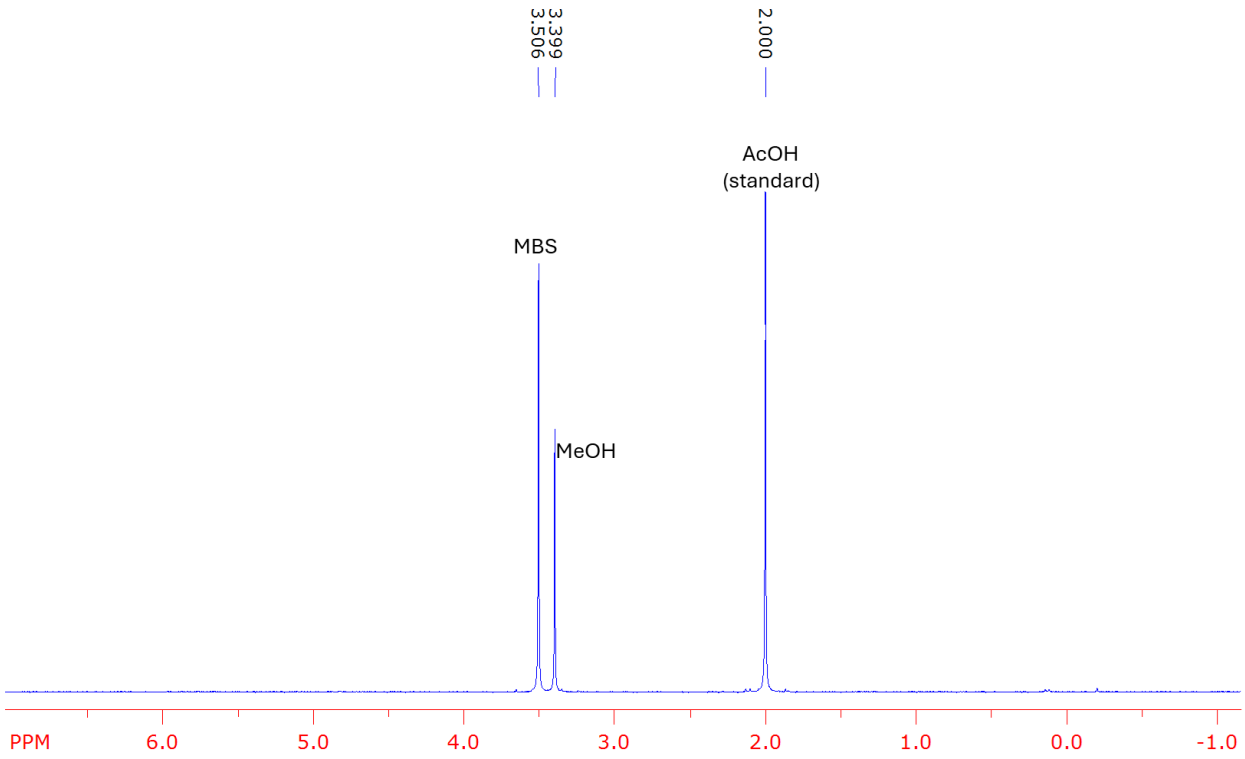


Figure S12: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me-Hg-OSO_3H (Section 5.1, Figure S9) with Au(III) in 98% H_2SO_4 run at room temperature for 1.5 hrs.

5.4. Competition reaction between oleum and Au(III) with Me-Hg-OSO_3H : Reaction of Me-Hg-OSO_3H generated in 98% H_2SO_4 with oleum followed by Au(III) generated in 98% H_2SO_4.

Following the same procedure as in section 3.2 above, a 0.0087 mmol (0.42mL, section 3.1) of Me-Hg-OSO_3H solution generated in 98% H_2SO_4 was added toa 0.5mL of oleum in a 2 mL Schlenk flask at 0 *°C.* After stirring the reaction mixture for 30 minutes at this temperature, a 0.016 mmol of Au(III) solution *(0.1mL of 163mM prepared by dissolving Au_2O_3 in 98% H_2SO_4 at 110 °C or until solution is homogeneous bright yellow in color*) was added. Reaction mixture was then cooled to 0 °C while stirring vigorously. After the complete addition of Me-Hg-OSO_3H solution was slowly allowed to warm to room temperature and stirred at RT for 90 minutes before dilution with D_2O and analyzing the reaction mixture by ^{1}H NMR.

Following the procedure described in Section 3.2, a 0.0087 mmol aliquot (0.42 mL; see Section 3.1) of Me-Hg-OSO_3H solution, generated in 98% H_2SO_4, was added to 0.5 mL of oleum in a 2 mL Schlenk flask at 0 °C. The reaction mixture was stirred at this temperature for 30 minutes. Subsequently, 0.016 mmol of Au(III) solution *(0.1 mL of a 163 mM stock prepared by dissolving Au_2O_3 in 98% H_2SO_4 at 110 °C until a homogeneous bright yellow solution was obtained)* was introduced at 0 °C under vigorous stirring. After complete addition, the reaction gradually warmed to room temperature and stirred for an additional 90 minutes. The mixture was then diluted with D_2O and analyzed by ^{1}H NMR.

Near quantitative conversion of Me-Hg-OSO_3H to MBS (and methanol) was observed with only traces of MSA indicating comparatively much faster reaction rates of Au(III) with Me-Hg-OSO_3H than SO_3 with Me-Hg-OSO_3H to make MBS and MSA products respectively. Figure S13.

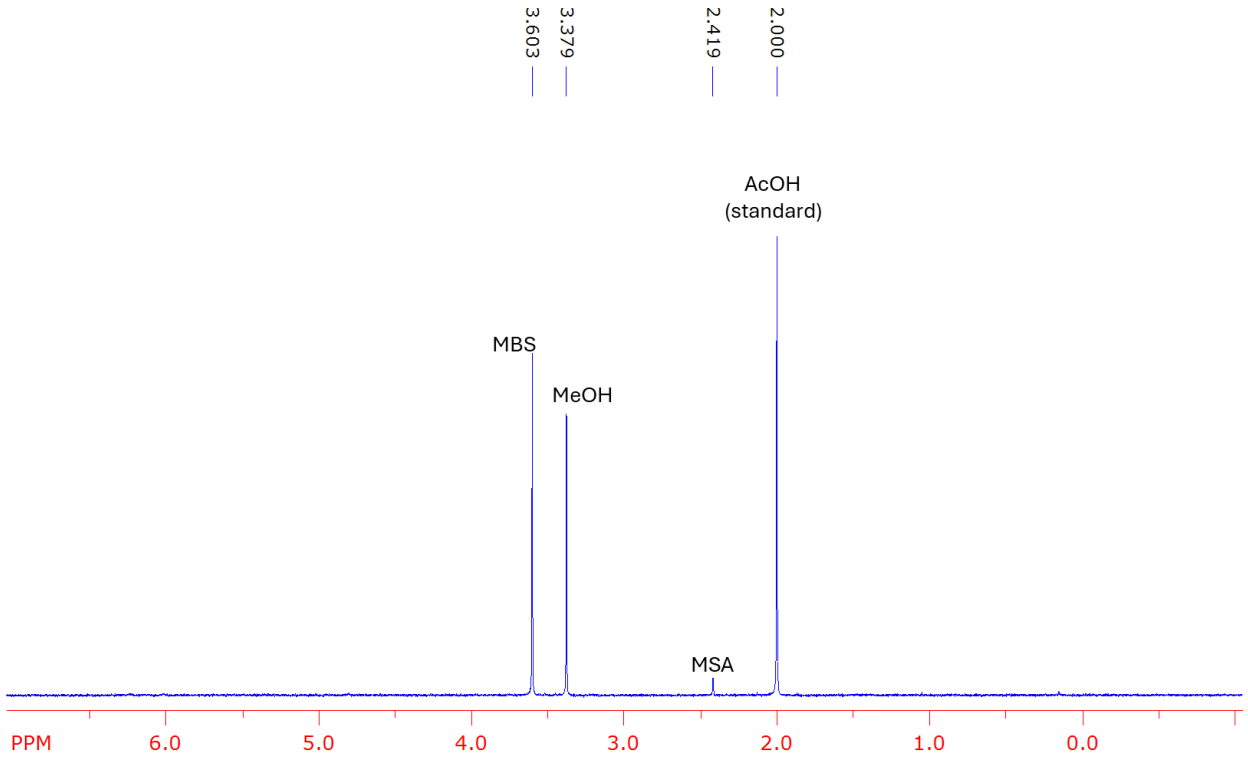


Figure S13: ^1H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of competition reaction between oleum and Au(III) with Me-Hg-OSO_3H (Section 5.1, Figure S9) in a mixture of oleum + 98% H_2SO_4 run at room temperature for 90 minutes.

5.5. Reaction of Me-Hg-OSO_3H generated in oleum with Au(III) generated in oleum.

A 0.3 mL reaction of Me-Hg-OSO_3H (0.011 mmol) generated in oleum (also containing MSA) from section 3.1 was added to 1 mL of oleum containing 0.022 mmol of Au(III) (*prepared by dissolving Au_2O_3 in oleum at 90°C*) in a 2 mL Schlenk flask at 0°C while vigorously stirring the solution. After the complete addition of Me-Hg-OSO_3H, the solution gradually warmed to room temperature and stirred at RT for 30 minutes before diluting with D_2O for subsequent ^1H NMR analysis of the reaction mixture. The analysis indicated quantitative conversion of Me-Hg-OSO_3H to MSA and methanol. Additionally, no change in the concentration of MSA was observed post reaction with Au(III), indicating significantly faster reaction rates of Au(III) with Me-Hg-OSO_3H compared to SO_3 with Me-Hg-OSO_3H. Figure S14.

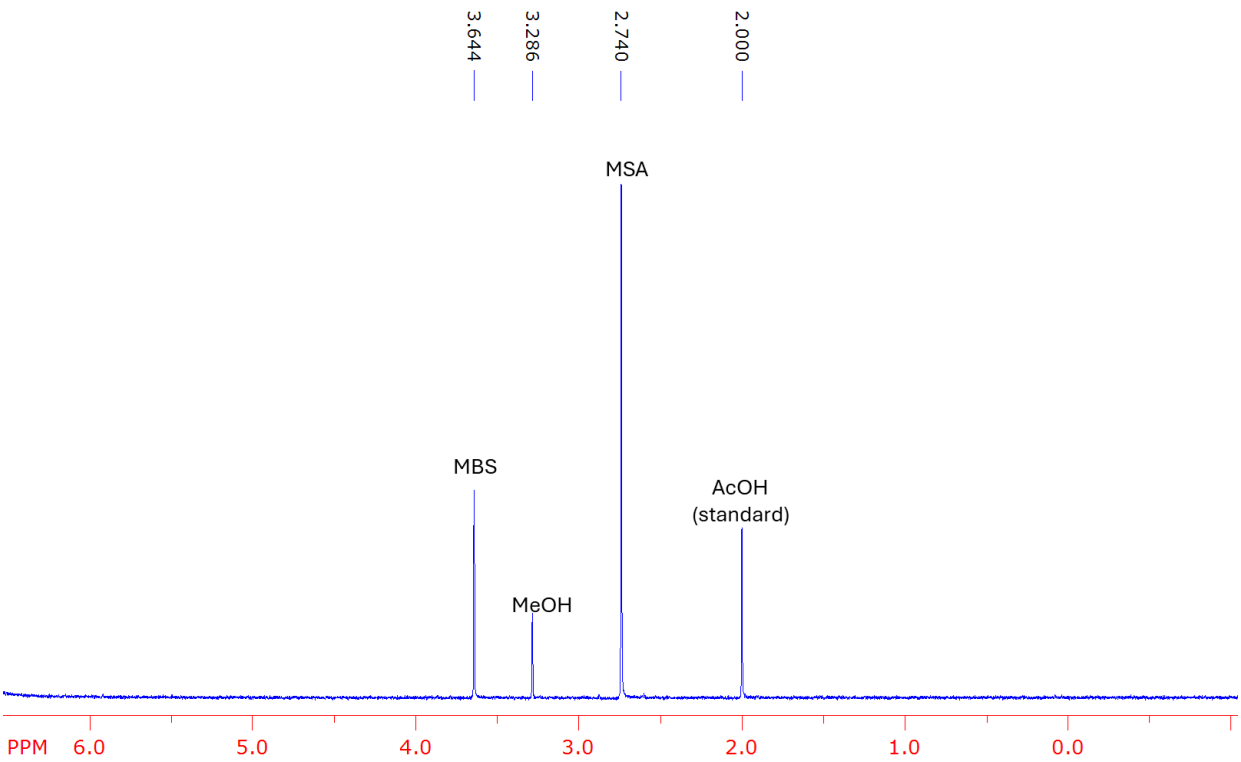


Figure S14: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me-Hg-OSO_3H generated in oleum (Section 5.1, Figure S10) with Au(III) in oleum run at room temperature for 30 minutes.

6. Alkyl transfer reactions between Me_4Sn and Au(III) in oleum and in 98% H_2SO_4.

To a 55 mM solution of Au(III) solution prepared in 98% H_2SO_4 (1mL) (*prepared by dissolving Au_2O_3 in 98% H_2SO_4 at 110 °C for 60 min or until solution is homogeneous bright yellow in color*) in a 2 mL Schlenk bomb flask at 0°C, directly added 4 eq of Me_4Sn under a flow of argon while vigorously stirring the solution. After complete addition reaction mixture was stirred at room temperature for 2hrs before diluting with D_2O for ^{1}H NMR analysis. The quantitative ^{1}H NMR analysis indicated quantitative formation of MBS with respect to Au(III). Only traces of MSA was observed (see Figure S15). Control studies without Au(III) showed that Me_4Sn does not undergo functionalization to MBS in 98% H_2SO_4 at room temperature even after 22 hrs (see Figure S16).

Similarly, to Au(III) solution prepared in oleum (55 mM in 1 mL oleum) 4eq of neat Me_4Sn is directly added at 0 ºC under argon flow while stirring vigorously. After complete addition reaction mixture stirred at room temperature for 2hrs before diluting with D_2O for subsequent ^{1}H NMR analysis. ^{1}H NMR analysis indicated quantitative formation of MBS with respect to Au(III). Here MSA was also observed due to

functionalization of methyltin species in oleum (see Figure S17). Control studies without Au(III) showed that Me_4Sn undergoes functionalization to make MSA and does not make MBS in oleum at room temperature (see Figure S18).

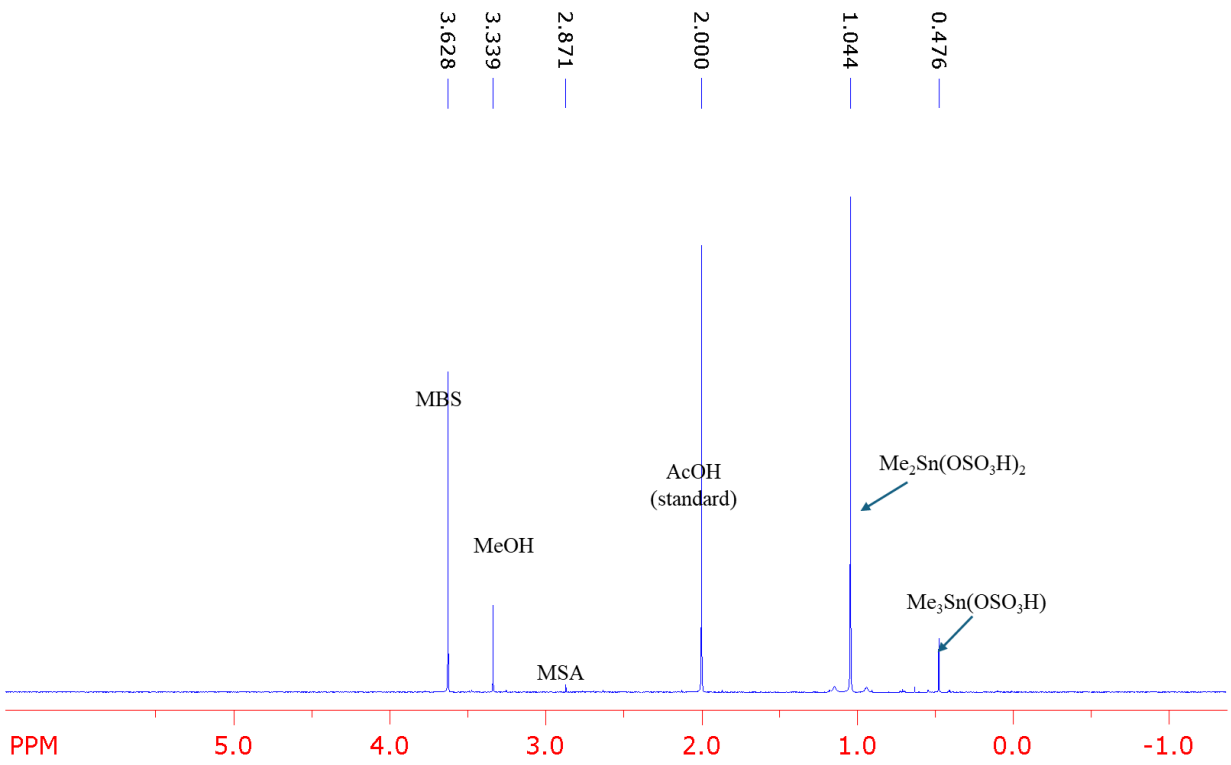


Figure S15: ^1H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me_4Sn with Au(III) in 98% H_2SO_4 run at room temperature for 2 hrs.

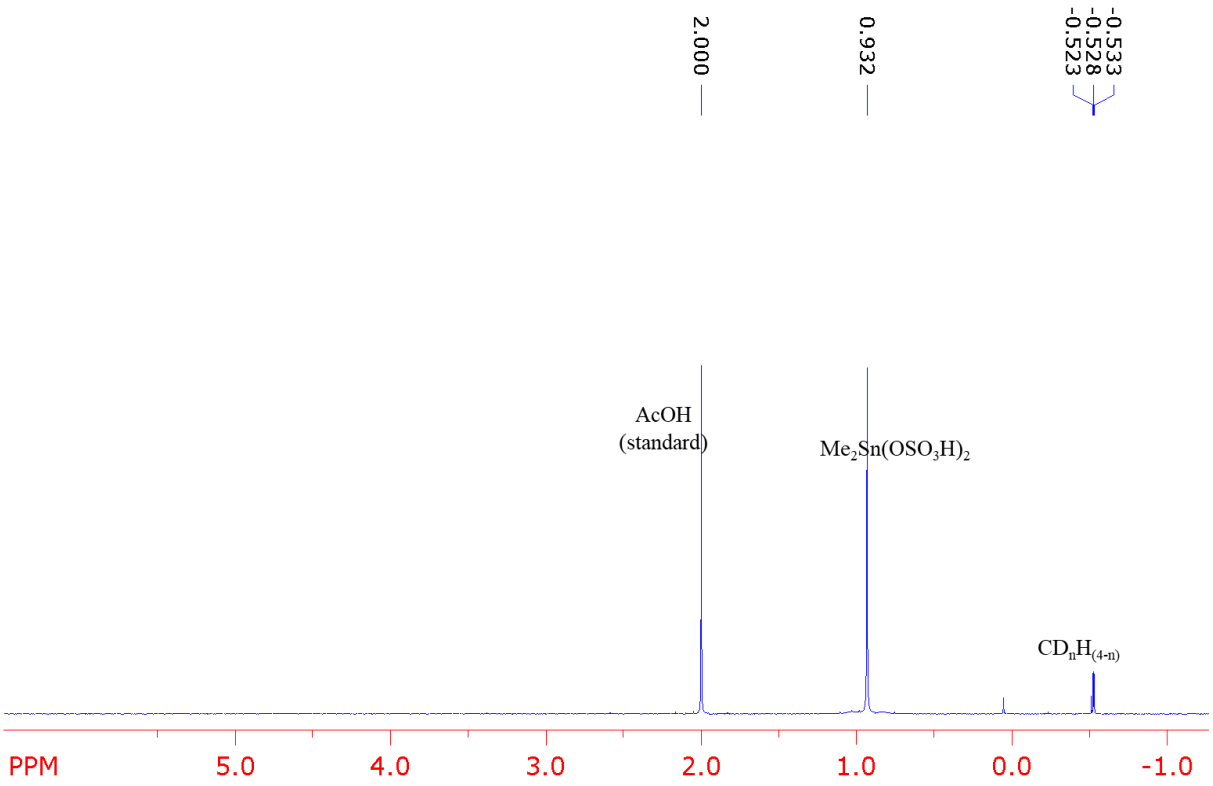


Figure S16: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me_4Sn in 98% H_2SO_4 run at room temperature for 22 hrs.

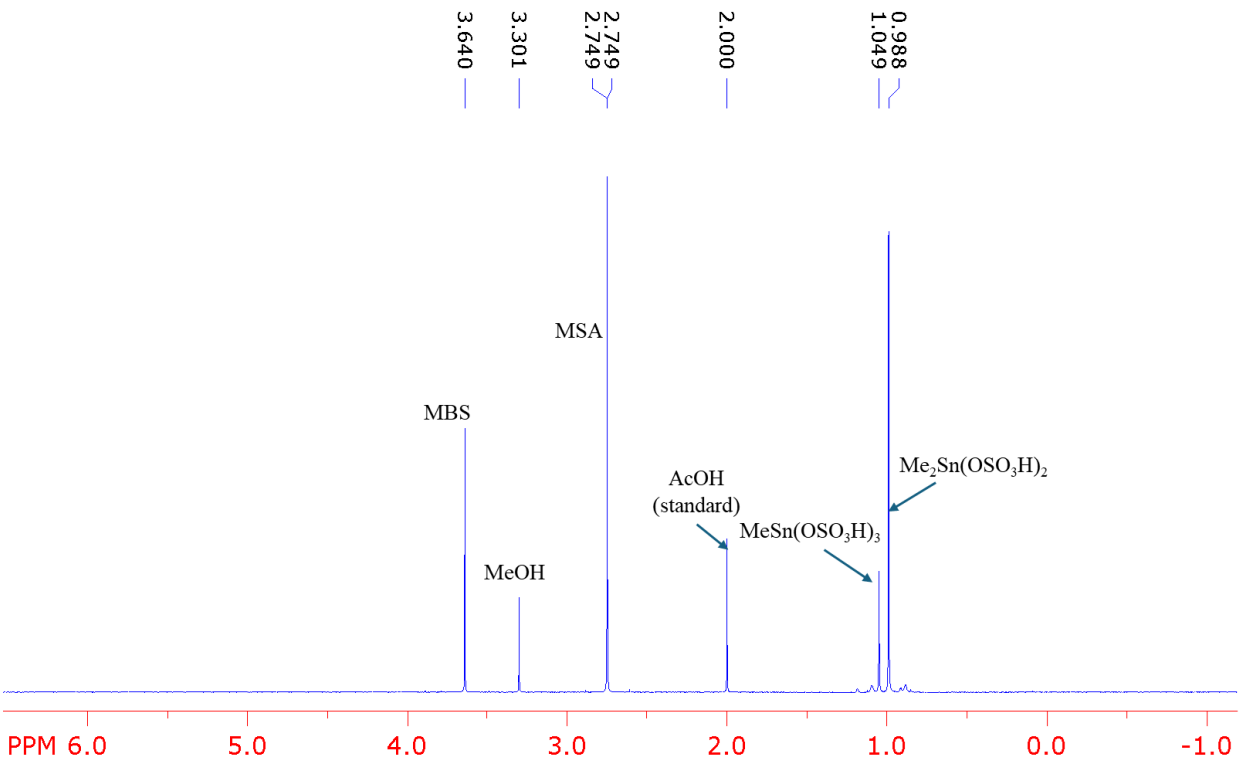


Figure S17: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me_4Sn with Au(III) in oleum run at room temperature for 2 hrs.

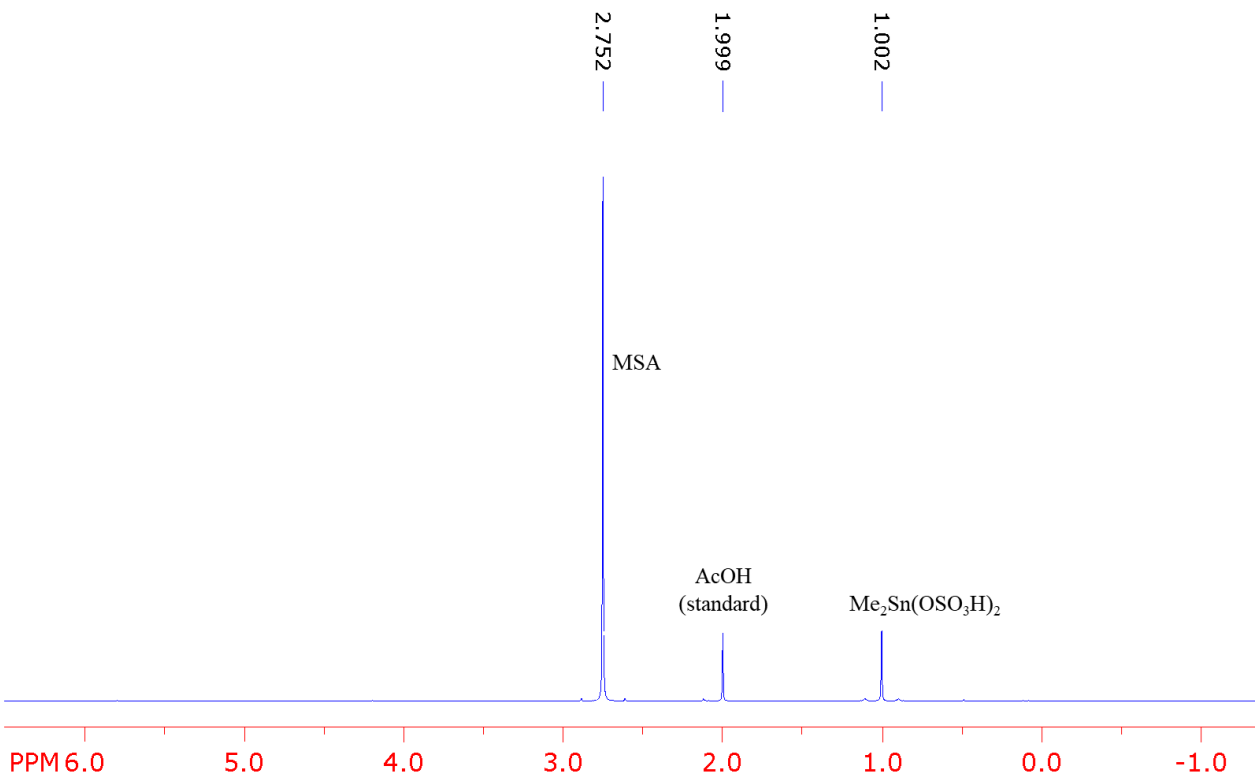


Figure S18: ^{1}H NMR spectrum (taken in a solvent mixture of H_2SO_4 and D_2O) of reaction mixture of Me_4Sn in oleum run at room temperature for 2 hrs.

7. Computational Energies. See the main manuscript for details.

M06 Absolute Energies in Hartree units.

Neutral Hg

NAME	*SCF* (def2-SVP)	*H* (def2-SVP)	*G* (def2-SVP)	*SCF* (def2-TZVPD)	*H* (def2-TZVPD)	*G* (def2-TZVPD)
$SO_3(H_2SO_4)$	-1323.108545	-1323.044908	-1323.091499	-1324.141705	-1324.078068	-1324.124659
$(HSO_4)Hg^{II}$-CH_3	-1592.323525	-1592.202231	-1592.263658	-1593.500139	-1593.378845	-1593.440272
TS1	-1592.262627	-1592.141927	-1592.205842	-1593.444476	-1593.323777	-1593.387691
Hg^0	-153.5581833	-153.555823	-153.57569	-153.5631981	-153.5608381	-153.5807041
MBS	-1438.728117	-1438.606215	-1438.657869	-1439.89852	-1439.776618	-1439.828272
TS2	-2915.428675	-2915.243157	-2915.326762	-2917.633481	-2917.447963	-2917.531567
TS2_frontside	-2915.417167	-2915.230479	-2915.313809	-2917.621969	-2917.435282	-2917.518612
$[(HSO_4)Hg^{II}]^+$	-1552.29467	-1552.211913	-1552.267295	-1553.426045	-1553.343294	-1553.398688
MSA	-1363.182302	-1363.080174	-1363.130498	-1364.264554	-1364.162426	-1364.21275
$Hg(HSO_4)$ radical	-1552.480127	-1552.397785	-1552.454302	-1553.61124	-1553.528898	-1553.585415

CH_3 radical	-39.76654248	-39.733626	-39.756747	-39.81534402	-39.78242702	-39.80554802
$(H_2SO_4)_{17}$	-11895.86894	-11895.06552	-11895.29478	-11905.34585	-11904.54244	-11903.96828
$(H2O)(SO_3)(H_2SO_4)_{16}$	-11895.83628	-11895.03243	-11895.26011	-11905.31208	-11904.50823	-11903.93207

Neutral Au

NAME	*SCF* (def2-SVP)	*H* (def2-SVP)	*G* (def2-SVP)	*SCF* (def2-TZVPD)	*H* (def2-TZVPD)	*G* (def2-TZVPD)
$(SO_3)(H_2SO_4)$	-1323.108545	-1323.044908	-1323.091499	-1324.141705	-1324.078068	-1324.124659
$(H_2SO_4)(HSO_4)_2Au^{III}$-$CH_3$	-2273.634447	-2273.477217	-2273.549532	-2275.370598	-2275.213368	-2275.285683
TS3	-2273.584997	-2273.42981	-2273.502454	-2275.327668	-2275.172481	-2275.245125
TS4	-3596.699076	-3596.47768	-3596.567697	-3599.457646	-3599.236249	-3599.326267
$Au(HSO_4)_2$ radical	-2233.766729	-2233.649798	-2233.719492	-2235.457733	-2235.340802	-2235.410495
Au^{I}-CH_3	-175.5911184	-175.552167	-175.581631	-175.6444874	-175.6055364	-175.6350004
$Au^{III}(HSO_4)_3$	-2233.11902	-2233.013254	-2233.079395	-2234.814591	-2234.708825	-2234.774966
$Au^{I}(HSO_4)$	-834.8898234	-834.853982	-834.895631	-835.4609474	-835.4251064	-835.4667554
$(HSO_4)_2Au^{III}$-CH_3	-1573.856461	-1573.746782	-1573.809053	-1575.0392	-1574.929522	-1574.991792

Anionic Au

NAME	*SCF* (def2-SVP)	*H* (def2-SVP)	*G* (def2-SVP)	*SCF* (def2-TZVPD)	*H* (def2-TZVPD)	*G* (def2-TZVPD)
$[(HSO_4)_3Au^{III}$-$CH_3]^-$	-2273.214074	-2273.068991	-2273.142453	-2274.956163	-2274.811085	-2274.884546
SO_3	-623.3598511	-623.343022	-623.373953	-623.8325947	-623.8157657	-623.8466967
TS3	-2273.188211	-2273.044288	-2273.116834	-2274.932837	-2274.788913	-2274.861459
TS4	-2896.513882	-2896.352599	-2896.432269	-2898.721767	-2898.560484	-2898.640154
$Au(HSO_4)_3$ radical	-2233.355883	-2233.250031	-2233.319412	-2235.050538	-2234.944686	-2235.014068

M06/def2-TZVPD//M06/def2-SVP Relative Energies in kcal/mol

Neutral Hg

NAME	ΔSCF (def2-SVP)	ΔH (def2-SVP)	ΔG (def2-SVP)	ΔSCF (def2-TZVPD)	ΔH (def2-TZVPD)	ΔG (def2-TZVPD)
TS1	38.2	37.8	36.3	34.9	34.6	33
TS2	2.1	2.5	17.8	5.2	5.6	20.9
TS2_frontside	9.4	10.5	25.9	12.5	13.6	29.1

$Hg(HSO_4) – CH_3$ Homolysis	48.2	44.4	33	46.2	42.4	30.9
$H_2SO_4 \rightarrow H_2O + SO_3$	20.5	20.8	21.8	21.2	21.5	22.7

Neutral Au

NAME	ΔSCF (def2-SVP)	ΔH (def2-SVP)	ΔG (def2-SVP)	ΔSCF (def2-TZVPD)	ΔH (def2-TZVPD)	ΔG (def2-TZVPD)
TS3_neutral	31	29.7	29.5	26.9	25.7	25.5
TS4_neutral	27.6	27.9	46	34.3	34.6	52.8
$Au(HSO_4)_2 – CH_3$ Homolysis	63.5	58.9	46	61.2	56.6	43.7
ligand exchange	-22.7	-22.2	-27.4	-25.8	-25.3	-30.5

Anionic Au

NAME	ΔSCF (def2-SVP)	ΔH (def2-SVP)	ΔG (def2-SVP)	ΔSCF (def2-TZVPD)	ΔH (def2-TZVPD)	ΔG (def2-TZVPD)
TS3_anionic	16.2	15.5	16.1	14.6	13.9	14.5
TS4_anionic	37.7	37.3	52.8	42	41.6	57.2
$Au(HSO_4)_3 – CH_3$ Homolysis	57.5	53.5	41.6	56.7	52.7	40.7

DFT Functional/Basis set comparison

Neutral Hg

NAME	M06/def2-tzvpd	M06/aug-cc-pVTZ-PP/aug-cc-pVTZ	B3LYP-D3/def2-tzvpd	TPSSH/def2-tzvpd	wB97XD/def2-tzvpd
TS1	34.9	35.7	33.1	34.7	41.3
TS2	5.2	3.7	1.2	11.3	5
TS2_frontside	12.5	10.9	6.9	15.4	9.9
$Hg(HSO_4) – CH_3$ Homolysis	46.2	46.9	43.2	45	46.7

Neutral Au

NAME	M06/def2-tzvpd	M06/aug-cc-pVTZ-	B3LYP-D3/def2-tzvpd	TPSSH/def2-tzvpd	wB97XD/def2-tzvpd	M06/x2c-TZVPall

		PP/aug-cc-pVTZ				
TS3_neutral	26.9	27.3	29.1	28.3	28.6	24.7
TS4_neutral	34.3	31.4	29.3	38.2	33.6	29.4
$Au(HSO_4)_2$ – CH_3 homolysis	61.2	61.9	60.8	57.9	59.7	

Anionic Au

NAME	M06/def2-tzvpd	M06/aug-cc-pVTZ-PP/aug-cc-pVTZ	B3LYP-D3/def2-tzvpd	TPSSH/def2-tzvpd	wB97XD/def2-tzvpd	M06/x2c-TZVPall
TS3_anionic	14.6	22.8	15.7	15.4	17.5	21.0
TS4_anionic	42	31.1	40.9	40.1	43.4	39.3
$Au(HSO_4)_3$ – CH_3 homolysis	56.7	61.6	57.9	55.8	55.2	

Cartesian Coordinates of the M06/def2-SVP Optimized Structures

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O -4.041711 2.024054 2.286172
O -3.466955 -0.341053 1.891003
S -0.783983 -1.963801 3.881090
O 0.277692 -1.200198 4.723548
H 1.151954 -1.188963 4.228967
O -0.607150 -1.209167 2.518913
H -1.024773 -1.685797 1.748315
O -0.486260 -3.379750 3.754083

O -2.093768 -1.648379 4.449741
S 2.817203 2.425241 -1.936064
O 1.528250 2.922580 -2.660137
H 0.855588 2.229444 -2.900658
O 2.361564 1.487928 -0.780925
H 2.294983 1.985934 0.088478
O 3.632122 1.626370 -2.826415
O 3.383413 3.668215 -1.383729
S 2.775859 -1.271115 1.756290
O 3.554812 -2.548354 1.314448
H 3.437140 -2.712086 0.336697
O 3.862491 -0.150699 1.901733
H 4.188258 0.184419 1.020826
O 1.827310 -0.875063 0.716272
O 2.305851 -1.531928 3.101841
S -3.285521 4.240343 -0.397582
O -3.243383 5.792583 -0.430084
H -2.277728 6.078267 -0.396776
O -2.545602 3.954683 0.960872
H -2.978111 3.215036 1.456227
O -4.672525 3.817846 -0.299020
O -2.497564 3.709592 -1.503843
S -0.741768 0.866510 0.021284
O -2.551840 1.341883 -0.067799
H -2.791712 1.309176 -1.044257
O -0.291079 1.589745 -1.130647
O -0.484938 1.386828 1.354695
O -0.905961 -0.575812 -0.114088
S 3.549496 -4.218499 -1.979120
O 3.818405 -5.514977 -1.157662
H 3.058022 -5.683100 -0.532316
O 2.546164 -4.736114 -3.060849
H 1.960621 -3.996844 -3.398847
O 2.857958 -3.238880 -1.136141
O 4.800280 -3.823489 -2.591358
S -4.348385 -2.078473 -2.656034
O -3.830121 -3.534802 -2.769336
H -3.752858 -3.958839 -1.860528
O -3.415052 -1.568133 -1.460059
H -3.915190 -0.845008 -1.001442
O -4.040348 -1.400978 -3.893388
O -5.721069 -2.026070 -2.164722
S -3.174315 -3.689195 0.920405
O -4.410360 -2.833845 1.381996
H -4.097222 -1.965266 1.744689
O -3.041089 -4.701585 2.108066
H -2.125754 -5.098229 2.052304
O -3.574450 -4.396415 -0.282324
O -1.992184 -2.845930 0.882682
S 0.780295 -5.003079 1.348759
O 1.420462 -4.995614 2.776695
H 0.862293 -4.419774 3.360943
O 0.772295 -3.456184 1.079362
H 0.438406 -3.237290 0.157570
O 1.698638 -5.684208 0.459609

O -0.584107 -5.509958 1.392736
S 0.367640 -2.126896 -2.442840
O -0.952853 -1.408612 -2.906034
H -1.477433 -1.142760 -2.112197
O 1.265363 -0.943731 -1.947205
H 1.519639 -1.000442 -0.985009
O 0.036111 -3.050739 -1.366514
O 0.964328 -2.671180 -3.647450
S 2.140250 2.693437 2.824776
O 3.326982 2.628386 3.825086
H 4.194698 2.527331 3.331403
O 1.449390 1.312815 3.125187
H 0.633765 1.221142 2.555898
O 1.245608 3.779722 3.177915
O 2.684645 2.703195 1.465863
S 0.517453 5.324136 0.046726
O 1.137896 5.850308 1.398239
H 1.140906 5.124692 2.077518
O 1.597342 5.766824 -1.007958
H 2.261900 5.045182 -1.146615
O 0.417477 3.883328 0.097843
O -0.650647 6.136931 -0.250743
S 6.047030 -0.727602 -1.296906
O 6.679444 -2.010498 -1.928246
H 5.980512 -2.651567 -2.229585
O 5.893742 0.216113 -2.544131
H 5.011832 0.678000 -2.568801
O 4.728924 -1.031219 -0.757757
O 7.082204 -0.185985 -0.430456
S 5.722070 2.504424 0.916969
O 7.226069 2.276017 0.566362
H 7.313521 1.365992 0.148831
O 5.459217 3.947711 0.366611
H 4.767312 3.899810 -0.347345
O 4.917958 1.563401 0.137499
O 5.572908 2.525080 2.360549
S -6.295453 0.639391 -0.190839
O -6.714473 2.126239 -0.327197
H -5.927204 2.749202 -0.334225
O -7.245523 -0.023426 -1.230821
H -6.787263 -0.807639 -1.653249
O -4.904496 0.483282 -0.637304
O -6.603089 0.147872 1.140782
S -1.986343 1.429396 -3.782207
O -2.517130 0.616650 -5.004413
H -3.094489 -0.124368 -4.680614
O -2.661233 2.825672 -4.042617
H -2.629193 3.345096 -3.194483
O -2.601529 0.846686 -2.580983
O -0.550179 1.540733 -3.872710
H -3.087470 0.681042 0.435306

$Au(HSO_4)_2$_rad | Energy: -2235.45773323
O 1.957423 -1.329459 -0.414969
S 2.940413 -0.454156 0.378621

O 3.884665 -1.536878 1.069832
O 3.808118 0.321213 -0.472003
O 2.220555 0.243729 1.460080
Au -0.061453 -0.937907 -0.484057
O -2.096449 -0.782036 -0.732968
S -3.060768 -0.341951 0.376499
O -2.597768 0.919017 0.985292
O -4.415010 -0.430573 -0.104534
O -2.919611 -1.449570 1.524530
H -2.212786 -1.201231 2.148155
H 3.381554 -2.076398 1.706910
O -1.306514 2.841348 -0.148684
S 0.203771 2.490305 -0.169164
O 0.463630 2.153783 1.336944
O 0.446227 1.246852 -0.959940
O 0.931721 3.638560 -0.630649
H 1.202786 1.469482 1.433819
H -1.867299 2.107709 0.272862

CH_3_rad | Energy: -39.8153440213
C -0.000000 -0.000000 0.000171
H 0.000000 1.090679 -0.000343
H -0.944556 -0.545340 -0.000343
H 0.944556 -0.545340 -0.000343

$(H_2SO_4)(HSO_4)_2Au\text{-}CH_3$ | Energy: -2275.37062524
O -1.425867 -2.109917 -0.149025
S 0.009180 -2.694178 -0.140848
O 0.603399 -2.294121 1.284221
O -0.078720 -4.129847 -0.179024
C -2.095042 -0.119478 1.813881
H -1.687862 0.818510 2.209099
H -3.190404 -0.154835 1.753020
H -1.625976 -1.033473 2.196386
O 0.818191 -1.993390 -1.154832
Au -1.569368 -0.087241 -0.180554
O -1.654306 1.938613 -0.138989
S -0.298148 2.688337 -0.139957
O 0.585971 2.081539 -1.150592
O -0.556373 4.103192 -0.189775
O 0.340685 2.375384 1.287758
H 0.934520 1.581617 1.249602
H 1.086759 -1.428242 1.243993
O 3.240578 -1.104453 -0.744018
S 3.179106 0.169033 0.162556
O 3.088490 1.378137 -0.827008
O 1.905400 0.117220 0.920769
O 4.423272 0.264912 0.869169
H 2.138852 1.647364 -1.022676
H 2.326484 -1.451212 -0.986205

$Au\text{-}CH_3$ | Energy: -175.644487418
Au 0.000000 -0.000000 0.220771
C 0.000000 -0.000000 -1.818563
H -1.041079 0.000000 -2.176507

H 0.520540 0.901601 -2.176507
H 0.520540 -0.901601 -2.176507

$Au(HSO_4)_3$ | Energy: -2234.81459146
O 2.201394 -1.237171 0.093482
S 3.171830 -0.047684 0.175657
O 3.454844 0.126707 1.709044
O 4.386946 -0.135831 -0.573897
O 2.202961 1.087992 -0.193980
O -0.858758 1.251043 -0.871960
S -1.739746 2.008718 0.194901
O -3.170283 1.860478 -0.447744
O -1.686970 1.262673 1.457567
O -1.427558 3.412641 0.210940
Au 0.511316 -0.112613 -0.350178
O -0.782679 -1.638109 -0.511239
S -2.213518 -1.767733 0.119924
O -3.122252 -0.794068 -0.481576
O -2.551311 -3.165437 0.054129
O -2.015079 -1.393558 1.643956
H -1.988621 -0.402772 1.745263
H -3.364225 0.887426 -0.530504
H 4.411831 0.220088 1.891812

$Au(HSO_4)$ | Energy: -835.460947428
Au 1.191769 0.002499 -0.001740
O -0.712822 -0.300658 -0.873174
S -1.943218 -0.129037 0.020112
O -1.992592 1.469739 0.311989
H -2.241501 1.934588 -0.504993
O -1.763233 -0.703724 1.343171
O -3.133452 -0.473787 -0.741904

$Hg(HSO_4)$_rad | Energy: -1553.61124038
O 2.613249 -0.861641 1.163805
S 3.588480 -0.788089 0.074527
O 4.744652 -1.644143 0.102893
O 2.835210 -1.040144 -1.283783
Hg -2.586275 -0.401799 -0.000148
O 4.094895 0.696459 -0.043167
H 3.294978 1.324669 -0.011394
O 0.380930 0.717676 1.350710
S 0.597581 1.429544 -0.083741
O 0.633401 0.319186 -1.079076
O -0.529234 2.337125 -0.219318
O 1.922065 2.103733 0.005355
H 1.945594 -0.546759 -1.275517
H 1.123073 0.076719 1.466855

Hg | Energy: -153.563198116
Hg 0.000000 0.000000 0.000000

$[(HSO_4)_3Au\text{-}CH_3]^-$ | Energy: -2274.95616302
C -0.155151 -2.765606 -0.735839
H -0.138766 -2.684598 -1.831335

H 0.718342 -3.293984 -0.334231
H -1.110947 -3.155809 -0.363169
S -0.012233 2.464902 -0.079995
O -1.437852 2.724593 -0.337512
O 0.741616 3.582252 0.461095
O 0.564131 2.104216 -1.538253
O 0.207041 1.208205 0.731532
H 1.445153 1.665195 -1.425004
Au -0.020695 -0.851990 -0.063448
O 1.909720 -1.218068 0.495999
S 3.015355 -0.168858 0.237784
O 2.739111 0.583417 -0.991559
O 4.274753 -1.113777 -0.052986
O 3.371802 0.560855 1.431005
H 4.144989 -1.600738 -0.886456
O -1.907937 -0.583499 -0.736601
S -3.075673 -0.327677 0.275320
O -2.563035 -0.346476 1.639681
O -4.200856 -1.177961 -0.055120
O -3.524012 1.141791 -0.111199
H -2.727998 1.752517 -0.150740

$(HSO_4)Hg\text{-}CH_3$ | Energy: -1593.50013913
O 0.705776 1.389153 -0.227632
S -0.656888 0.817151 -0.074923
O -1.706005 1.844187 -0.205069
O -0.891974 -0.372029 -0.921441
Hg 2.471692 -0.031052 -0.009672
C 3.980563 -1.494000 0.039714
H 3.983980 -1.964820 1.031798
H 3.758432 -2.237878 -0.737503
H 4.947882 -1.012339 -0.157480
O -0.665596 0.312696 1.444972
H -1.549000 -0.103400 1.601480
O -5.444855 -1.026007 0.154021
S -4.109741 -0.500166 0.083288
O -3.216660 -0.620392 1.235062
O -3.403097 -1.155036 -1.164576
O -4.222683 1.024665 -0.303815
H -3.311963 1.448695 -0.272501
H -2.421292 -0.931771 -1.156296

$(HSO_4)Hg^+$ | Energy: -1553.42604487
O -1.405860 1.514501 0.022909
S 0.075514 1.785779 0.068316
O 0.362001 3.207517 0.112492
O 0.733453 0.966261 1.113179
Hg -2.070470 -0.626991 0.004314
O 0.550258 1.190579 -1.344543
H 1.518527 0.985425 -1.318554
O 4.595917 -1.354250 -0.020537
S 3.341330 -0.651822 -0.056015
O 3.128764 0.430923 -1.006554
O 2.135918 -1.656951 -0.365715
O 3.031878 -0.154890 1.395181

H 2.160984 0.364217 1.381232
H 2.229925 -2.483226 0.144075

MBS | Energy: -1439.89852033
S 2.146607 -0.104584 0.112446
O 1.691349 -1.171459 -0.947323
O 1.200283 -0.072594 1.220425
O 3.546533 -0.312213 0.356007
S -1.951175 -0.388219 -0.090510
O -2.324847 1.152682 -0.014100
O -3.191232 -1.091179 -0.242131
O -0.876420 -0.543172 -1.070652
H 0.708465 -1.086248 -1.100374
O -1.376278 -0.702414 1.342157
H -0.391644 -0.540901 1.377222
O 1.894389 1.284743 -0.626361
H 2.570802 1.449881 -1.310264
C -1.254356 2.106032 0.052615
H -0.660470 2.088025 -0.872354
H -1.734518 3.082453 0.177850
H -0.603628 1.900296 0.917073

MSA | Energy: -1364.26455434
S -1.829433 0.121305 -0.006191
O -1.105709 -0.346268 -1.234526
O -1.074750 -0.239198 1.236902
O -2.233875 1.529208 -0.065355
C -3.308324 -0.855654 0.056260
H -3.027283 -1.915691 0.100944
H -3.872365 -0.566024 0.952553
H -3.893804 -0.647829 -0.848889
S 2.011971 0.068662 -0.014490
O 3.441718 -0.139208 -0.027472
O 1.467363 1.407358 -0.174733
O 1.392507 -0.873076 -1.115417
H 0.389997 -0.679274 -1.207714
O 1.471768 -0.547853 1.334564
H 0.460607 -0.424431 1.364740

SO_3_solvated | Energy: -1324.14170517
S -1.797764 0.001999 0.038483
O -2.444337 -0.699062 -1.034995
O -1.274397 -0.750001 1.164835
O -1.859754 1.435329 0.133192
S 1.510195 -0.018149 -0.185800
O 0.289614 -0.024320 -1.005867
O 2.779774 -0.092516 -0.845220
O 1.435231 -1.162904 0.883844
H 0.510581 -1.241851 1.225494
O 1.417952 1.223008 0.806200
H 1.337873 2.063986 0.315667

SO_3 | Energy: -623.832594691
S 0.000048 0.000006 -0.000035
O -0.604019 -1.307597 0.000023

O -0.830488 1.176842 0.000023
O 1.434412 0.130743 0.000023

TS1 | Energy: -1593.44447581
Hg -3.732418 -0.345810 0.015722
C -1.364349 0.850536 -0.321775
H -1.327680 0.914427 0.766530
H -1.086097 -0.083299 -0.809008
H -1.930598 1.596694 -0.876133
S 1.505006 1.125548 -0.058708
O 0.271379 1.738670 -0.660697
O 1.502068 -0.338627 -0.125191
O 1.403088 1.408234 1.520510
O 2.705020 1.802696 -0.563036
H 1.459249 2.365122 1.693326
S 4.871058 -0.768943 0.094451
O 3.746360 -1.757412 -0.427276
O 4.433310 -0.176544 1.344237
O 4.903440 0.357770 -1.020259
O 6.118305 -1.482790 -0.003243
H 4.130159 0.976201 -0.889826
H 2.853737 -1.329197 -0.304235

TS2_frontside | Energy: -2917.62196936
O 0.503311 0.786035 -0.889593
S 1.957750 0.371983 -0.820035
O 2.750212 1.473548 -0.262791
O 2.137874 -0.947336 -0.215474
Hg -1.188899 -0.803933 -0.756672
C -2.945629 -2.262787 -0.738972
H -2.326998 -2.544211 -1.628559
H -3.913679 -1.972518 -1.166960
S -3.640313 -1.336751 1.240522
O -2.557572 -1.618580 2.166167
O -3.884184 0.072829 0.902055
O -4.811440 -2.189951 1.254504
H -2.967781 -3.203731 -0.172966
O 2.403166 0.147820 -2.338246
H 2.386364 0.990806 -2.826696
O -2.351922 4.155922 0.830923
S -1.834334 2.923575 0.287338
O -1.880482 1.779341 1.391873
O -2.375412 2.395765 -0.952354
O -0.272509 3.115417 0.176152
H 0.127064 2.302427 -0.237785
H -2.654369 1.170683 1.226809
O 6.573105 -0.804703 1.492576
S 5.355713 -0.505113 0.784596
O 4.857428 0.903913 1.316733
O 5.299535 -0.502834 -0.664799
O 4.256473 -1.506815 1.336871
H 3.432209 -1.416569 0.786366
H 4.101172 1.222352 0.751922

TS2 | Energy: -2917.63348078

O -0.037809 1.011378 0.772098
S 0.632545 1.788079 -0.271526
O 0.033443 3.117357 -0.505694
O 2.112762 1.854054 -0.085191
Hg -2.456200 -1.751600 -0.076293
C -0.293985 -2.072092 0.154316
H -0.130859 -2.486420 -0.848201
H -0.159616 -0.996882 0.360318
H -0.255741 -2.775055 0.994421
S 2.025938 -1.813050 0.134472
O 2.159600 -1.116387 1.396994
O 2.395533 -3.209539 0.047074
O 2.050447 -1.033808 -1.103429
S 5.021808 0.462704 0.115058
O 4.447393 1.252813 -1.135462
H 3.478218 1.455514 -1.006102
O 4.681893 -0.945008 0.006635
O 6.407978 0.828127 0.260342
O 4.233990 1.119620 1.327780
H 3.270163 1.220468 1.103159
O 0.424258 1.042141 -1.678645
H 0.975412 0.224712 -1.661669
S -3.334214 2.349025 0.123531
O -2.317142 3.481016 0.495465
H -1.387387 3.306673 0.116453
O -4.647664 2.951085 0.085120
O -2.829882 1.563575 -0.981091
O -3.275642 1.367532 1.393326
H -3.780763 1.751758 2.132032

TS3_anion | Energy: -2274.93283690
C -0.275633 1.132274 -0.480576
H -0.947194 0.756863 -1.254990
H -0.505266 0.944940 0.570324
H 0.430411 1.931665 -0.719694
S -3.246852 1.818350 -0.104925
O -1.964444 2.567279 -0.259185
O -4.423531 2.660857 -0.234392
O -3.293886 1.288363 1.417461
O -3.244973 0.586607 -0.946605
H -2.686816 0.513243 1.524046
H -3.225225 -0.952382 -0.494964
Au 1.034225 -0.673772 -0.562828
O -0.679977 -1.805125 -0.592556
S -1.676024 -1.973018 0.569906
O -3.078234 -1.890933 -0.154320
O -1.576913 -0.823705 1.493330
O -1.594403 -3.292478 1.156650
H 3.074465 -0.205286 2.098814
O 2.338494 1.949286 1.162426
S 3.351220 1.162879 0.470887
O 3.801775 -0.020359 1.479573
O 4.585021 1.785444 0.045673
O 2.750589 0.409005 -0.736879

TS3 | Energy: -2275.32766813
C 0.253414 1.104318 -0.538018
H 1.057023 0.739750 -1.184148
H -0.418465 1.870514 -0.941971
H 0.433172 1.106006 0.540845
S 3.356884 1.795763 -0.089569
O 2.126404 2.612262 -0.223537
O 3.269033 0.559996 -0.932918
O 3.401986 1.251049 1.431598
O 4.594415 2.545050 -0.235654
H 2.722938 0.543918 1.553584
S -3.569691 1.028384 0.376141
O -2.736941 0.447421 -0.700039
O -4.742492 1.751506 -0.009512
O -2.558335 1.907860 1.202034
O -3.881614 -0.197608 1.309585
H -3.002469 2.602720 1.729855
Au -0.967476 -0.670683 -0.563208
O 0.750539 -1.736851 -0.628026
S 1.699194 -1.926030 0.595141
O 1.557850 -0.776207 1.505915
O 3.116067 -1.860352 -0.082034
O 1.558019 -3.247555 1.161262
H 3.275004 -0.921996 -0.443711
H -4.578682 -0.005277 1.970312

TS4_anion | Energy: -2898.72176706
O 0.802717 1.779601 -0.824128
S 0.971427 2.805420 0.354222
O -0.460895 2.802366 1.074910
O 1.952240 2.337816 1.315286
C -0.490341 -1.970918 0.653451
H -1.443479 -2.517886 0.552767
H -0.181591 -2.133621 -0.425609
H 0.309037 -2.453216 1.230837
S -1.346568 -0.898491 2.250930
O -0.522175 0.314118 2.391252
O -2.710742 -0.680083 1.768439
O -1.164262 -1.920197 3.260072
O 1.106236 4.106518 -0.259593
Au 0.150178 -0.085462 -0.293077
O 1.988336 -0.603525 0.360873
S 2.913511 -1.373743 -0.655378
O 2.248831 -2.593011 -1.086670
O 3.471162 -0.475264 -1.639023
O 4.115397 -1.734423 0.329915
H 3.861993 -2.464978 0.923481
H -0.532272 2.037848 1.695775
S -2.786002 -0.232245 -1.533527
O -1.662434 0.609314 -0.827153
O -3.986885 -0.038589 -0.512612
O -3.196377 0.426115 -2.751203
O -2.394741 -1.634212 -1.575082
H -3.664841 -0.278546 0.392913

TS4 | Energy: -3599.45764611
O 0.899314 0.391621 -1.326186
S 0.681233 1.953817 -1.300680
O -0.698453 2.150225 -2.035205
O 0.535654 2.402651 0.084569
C -1.820544 -2.410117 0.291826
H -2.588832 -3.159631 -0.009009
H -0.978521 -3.134259 0.163225
H -1.984007 -2.064529 1.322185
S -3.175077 -1.344224 -0.993901
O -2.082617 -0.483273 -1.644511
O -3.779552 -2.287880 -1.889351
O -3.954053 -0.673357 0.021633
S -2.488544 2.227750 1.343779
O -3.604838 1.297298 1.944373
H -3.762793 0.531821 1.342186
O -2.518732 2.099171 -0.113891
O -2.629142 3.526294 1.943700
O -1.203071 1.486085 1.898688
H -0.402542 1.782427 1.382498
O 1.718797 2.520269 -2.122409
Au -0.436072 -0.986341 -0.550501
O 1.108964 -1.668214 0.523093
S 1.282341 -1.162427 2.012866
O 1.614766 0.266260 1.982268
O 0.186070 -1.583583 2.847994
O 2.552017 -1.994499 2.402877
H 3.310272 -1.692344 1.827073
H -1.439994 2.195864 -1.366021
S 4.274667 0.187333 -0.286170
O 3.398149 1.352374 0.318884
H 2.739637 1.006743 0.988907
O 3.553955 -0.119131 -1.657026
O 5.578866 0.693402 -0.607758
O 4.163912 -0.979409 0.585328
H 2.565803 -0.050881 -1.58327