

## Supporting Information

### **KF-Promoted Copper-Catalyzed Highly Efficient and Selective Oxidation of Methane and other Light Alkanes with Dramatic Additive Effect**

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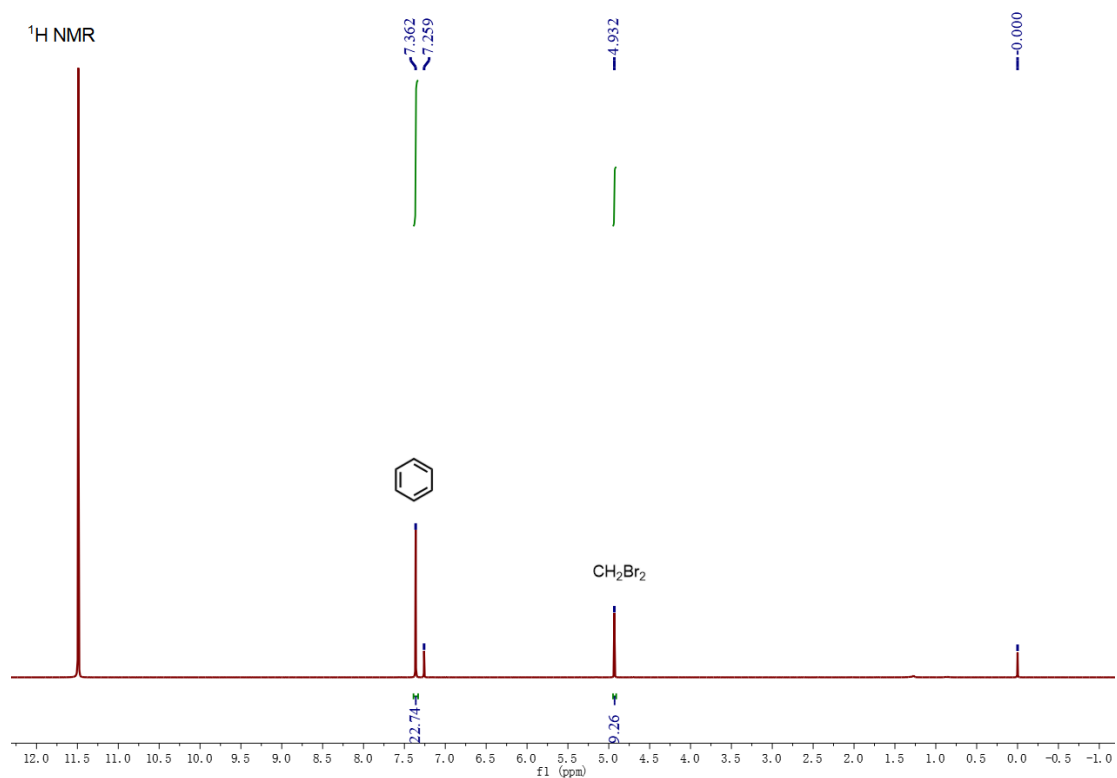
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## 1. General information

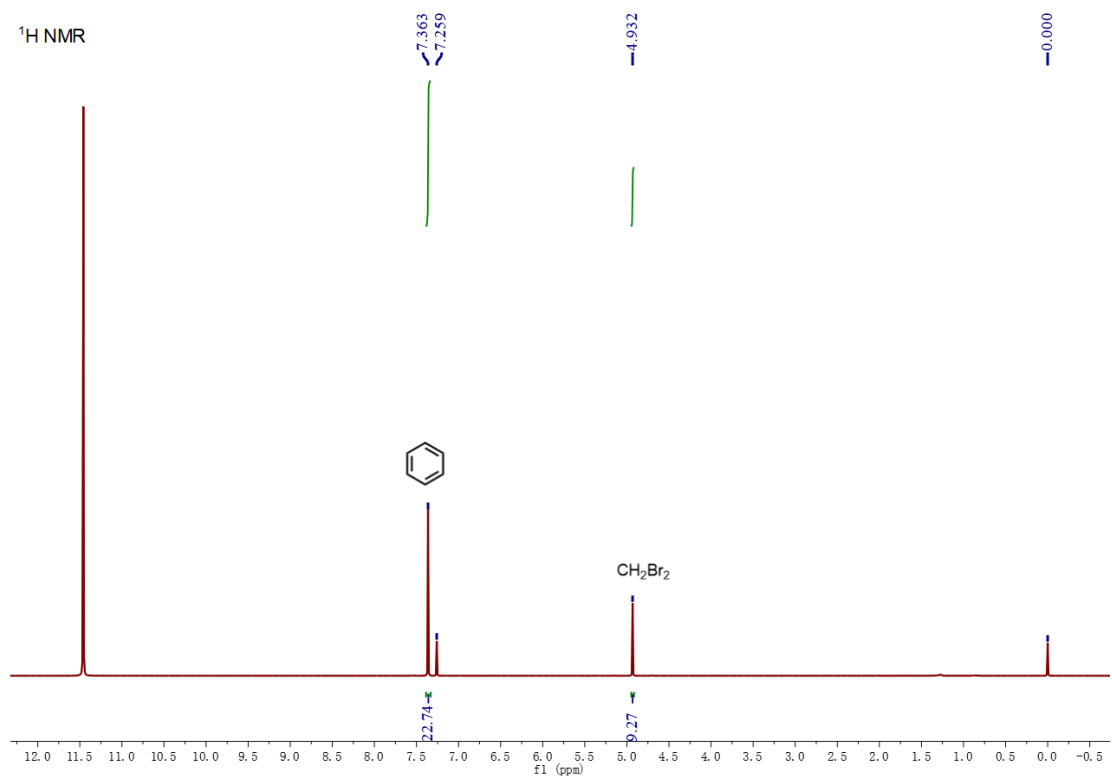
All reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar, Sigma-Aldrich, Energy Chemical and Macklin. The purity of methane is  $\geq 99.99\%$ ; TFA (Macklin) is 99.9%; TFAA (Energy Chemical) is 99%;  $K_2S_2O_8$  (Macklin) is 99.5%. Purification of CuCl: CuCl was dissolved in conc. HCl, precipitated out with water, filtered, washed with ethanol and ether, and then dried to obtain purified white powder CuCl. The body of the autoclave is made of titanium, the pressure gauge and the valve are made of stainless steel (316L). Flash column chromatography was performed using silica gel (300-400 mesh).  $^1H$  NMR spectra were acquired on a Bruker Ascend<sup>TM</sup> 400 (at 400 MHz) and are reported relative to  $SiMe_4$  ( $\delta$  0.00) or the residual solvents from the deuterium solvents.  $^{13}C$  NMR spectra were acquired on a Bruker Ascend<sup>TM</sup> 400 (at 100 MHz) and are reported relative to  $CDCl_3$  ( $\delta$  77.16). NMR acquisitions were performed at 295 K unless otherwise noted. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; bs, broad singlet; app., approximate peak. The gas compositions were analyzed by Agilent 7890B gas chromatography equipped with GS-ALUMINA, 8Ft 1/8 2mm Molsieve 5A 60/80 UM, 2Ft 1/8 2mm Unibeads 1S 60/80 UM and 4Ft 1/8 2mm Unibeads 1S 60/80 UM. FID and TCD detectors were used to detect different gases ( $CH_4$ ,  $CO_2$ , CO,  $CH_2F_2$ ,  $CF_3H$ ,  $CF_4$ ,  $C_2F_6$  *etc.*).

### 2.1 The Stability of Internal Standard $CH_2Br_2$ in Reaction Mixture

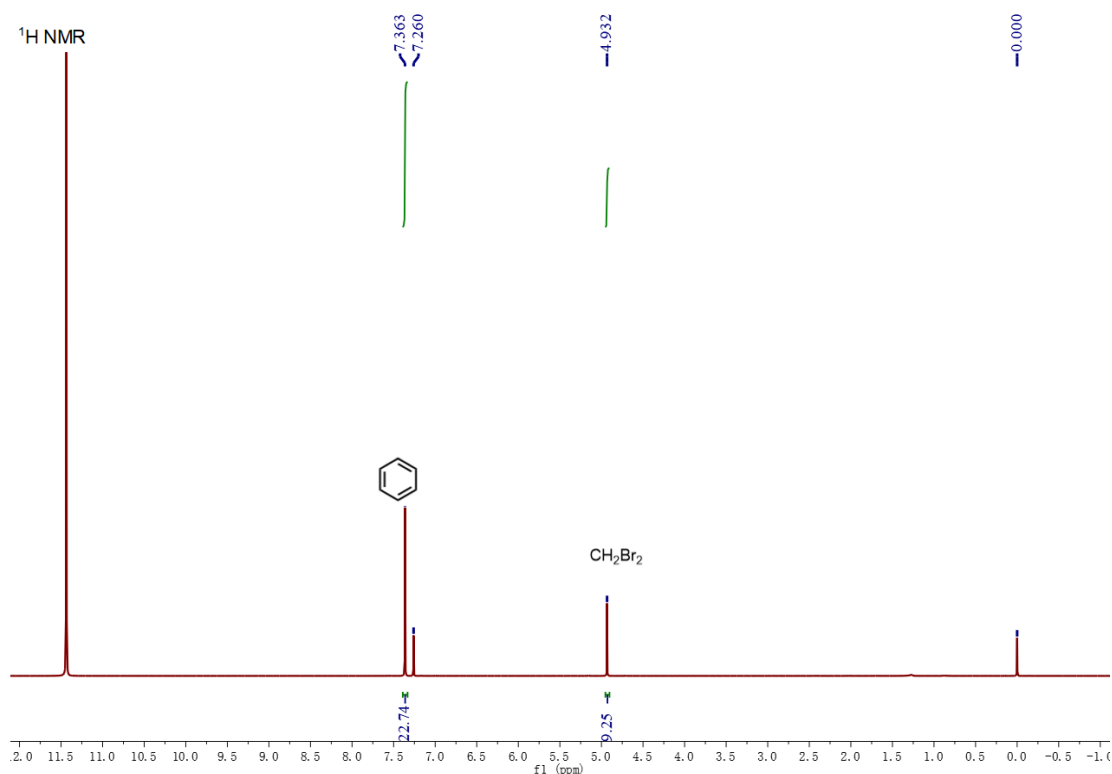
Benzene was used as the reference to test the stability of  $CH_2Br_2$  in the similar reaction mixture without methane. Three  $^1H$  NMR spectra were recorded from the following samples: (a) benzene (3.79 mmol)/  $CH_2Br_2$  (4.76 mmol) mixture in TFA/TFAA; (b) the mixture after adding 10 mmol of  $K_2S_2O_8$ , 3 mmol of KF and 0.005 mmol of CuCl and stirring at room temperature for 5 min; (c) the above mixture after stirring at room temperature for 24 h. No obvious change in the ratio of benzene/ $CH_2Br_2$  indicates the stability of  $CH_2Br_2$  in the reaction mixture at room temperature. The  $^1H$  NMR spectra are as follow:



**Figure S1.** <sup>1</sup>H NMR spectrum of sample **a** (before adding K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KF and CuCl).

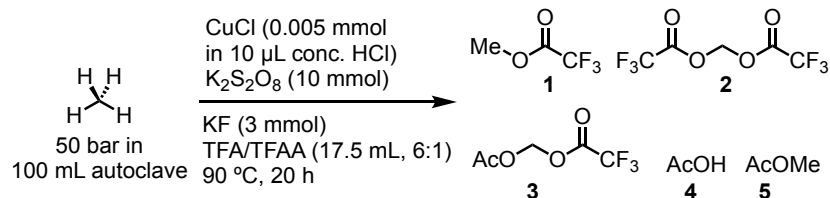


**Figure S2.** <sup>1</sup>H NMR spectrum of sample **b** (after adding K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KF and CuCl, and stirring at rt for 5 min).

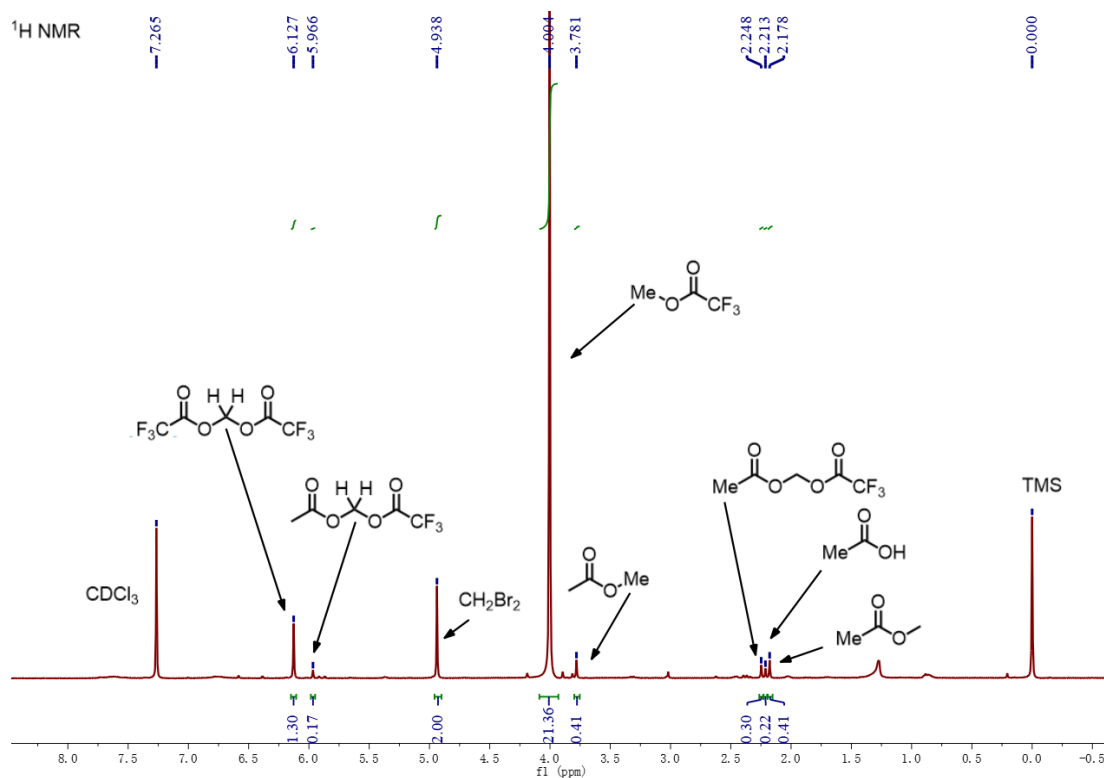


**Figure S3.**  $^1\text{H}$  NMR spectrum of sample **c** (after adding  $\text{K}_2\text{S}_2\text{O}_8$ , KF and CuCl, and stirring at rt for 24 h).

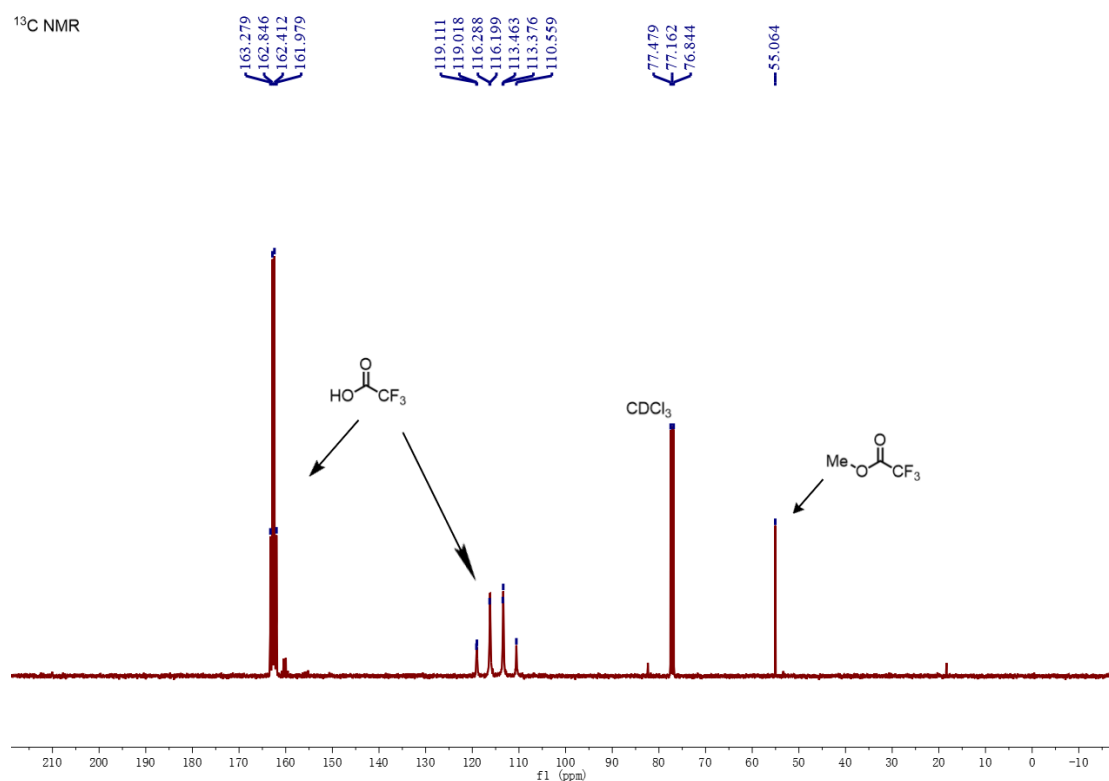
## 2.2 Typical Procedure for Methane Oxidation (Table 3, entry 5)



A 100 ml autoclave with PTFE lining was added  $\text{K}_2\text{S}_2\text{O}_8$  (10 mmol, 2.703 g), KF (3 mmol, 174 mg). Subsequently TFA (15 mL), TFAA (2.5 mL) and CuCl (0.5 M in conc. HCl, 10  $\mu\text{L}$ , freshly prepared by dissolving 9.9 mg of CuCl in 200  $\mu\text{L}$  conc. HCl with 30 s sonication) were added. The autoclave was sealed and filled with 50 bar  $\text{CH}_4$  gas. After stirring for 20 h at  $90^\circ\text{C}$ , the autoclave was cooled with cryostat at  $-15^\circ\text{C}$ , then the autoclave was opened and the internal standard ( $\text{CH}_2\text{Br}_2$ , 70  $\mu\text{L}$ ) was added. The mixture was stirred for 2 minutes, then several drops of reaction solution was mixed with  $\text{CDCl}_3$  (1 mL) in an eppendorf tube and shaken for several seconds. The supernatant isolated by centrifugation was tested  $^1\text{H}$  NMR to determine the yields based on the integral of proton of these products as comparing with the integral of  $\text{CH}_2\text{Br}_2$  (Figure S4), **1**: 7.12 mmol; **2**: 0.65 mmol; **3**: 0.09 mmol; **4**: 0.07 mmol, **5**: 0.14 mmol. 1 mL of the reaction mixture were treated with similar procedure and  $^{13}\text{C}$  NMR was tested to confirm the formation of MeOTFA (Figure S5).

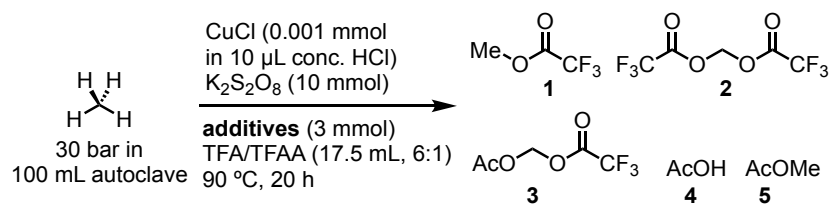


**Figure S4.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation under optimized reaction conditions.



**Figure S5.** <sup>13</sup>C NMR spectrum of the reaction mixture of methane oxidation under optimized reaction conditions.

### 2.3 Standard Deviation



Additive: KF

No.	1	2	3	4	5	Sel. of 1	average	Standard Deviation
1	4.62	0.44	0.19	0.15	0.14	83.39%		
2	4.64	0.46	0.22	0.17	0.18	81.83%	83.82%	2.23%
3	4.57	0.26	0.11	0.22	0.14	86.23%		

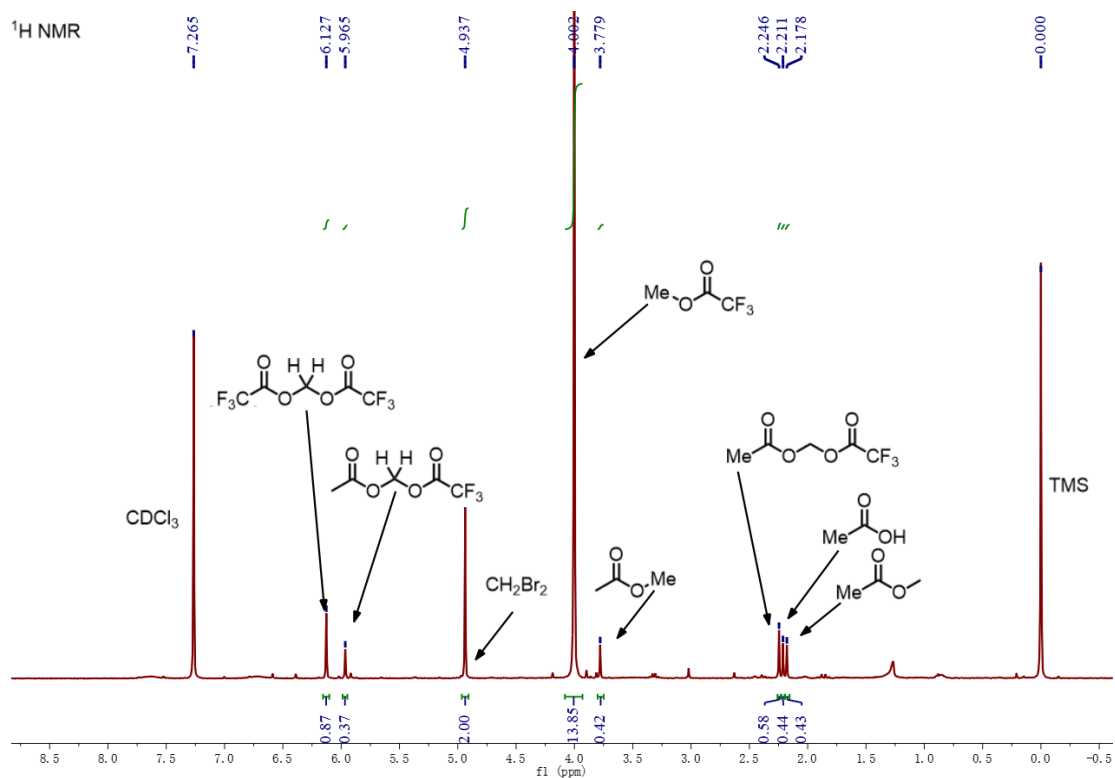
Additive: Na<sub>2</sub>FPO<sub>3</sub>

No.	1	2	3	4	5	Sel. of 1/%	average	Standard Deviation
1	2.02	0.21	0.17	1.03	0.26	54.74%		
2	1.93	0.29	0.11	1.32	0.35	48.25%	51%	3.36%
3	2.01	0.44	0.2	1.08	0.29	50%		

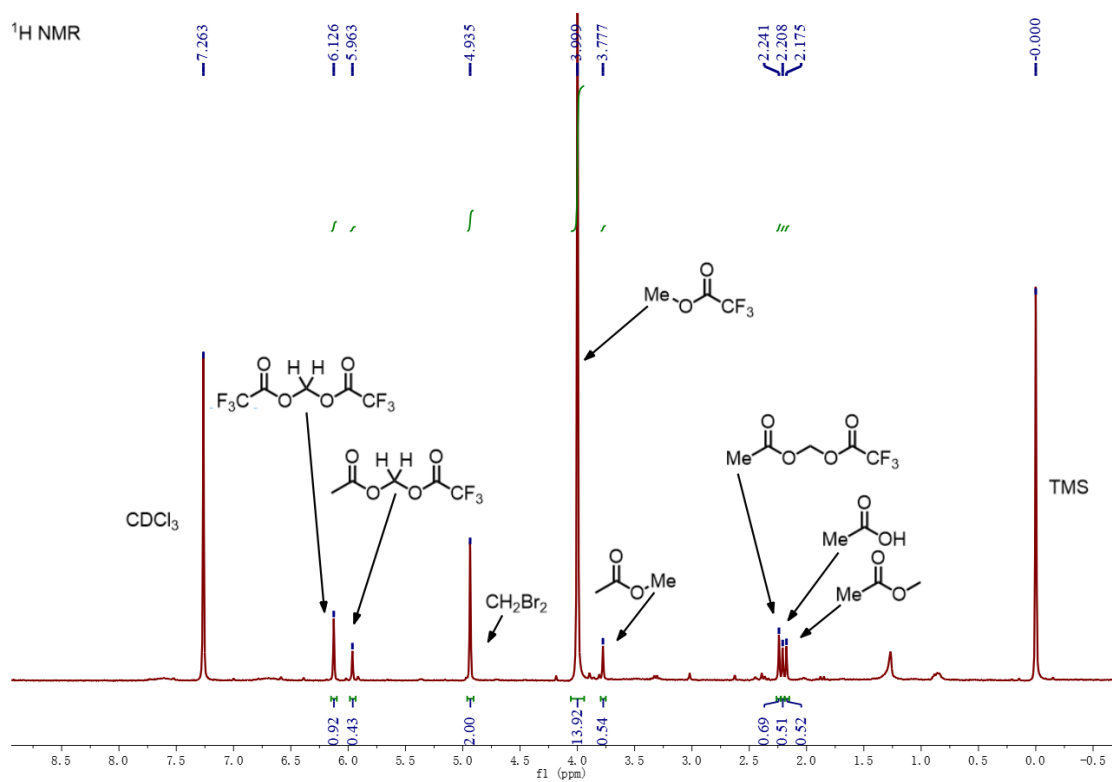
Additive: CsF

No.	1	2	3	4	5	Sel. of 1/%	average	Standard Deviation
1	3.84	0.21	0.21	0.48	0.32	75.89%		
2	3.94	0.18	0.22	0.42	0.25	78.64%	75.2%	3.84%
3	3.83	0.2	0.44	0.68	0.24	71.06%		

The crude NMR spectra of above experiments were attached as follow (Figure S6 ~ Figure S14).



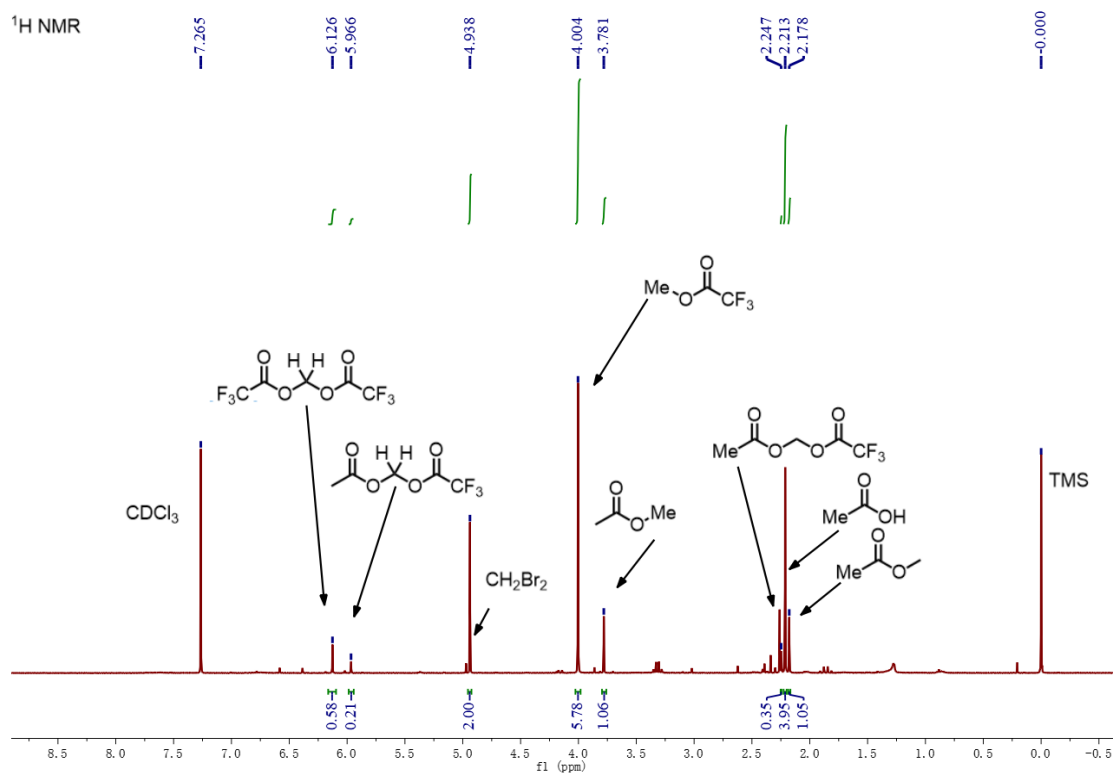
**Figure S6.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: KF, No.1).



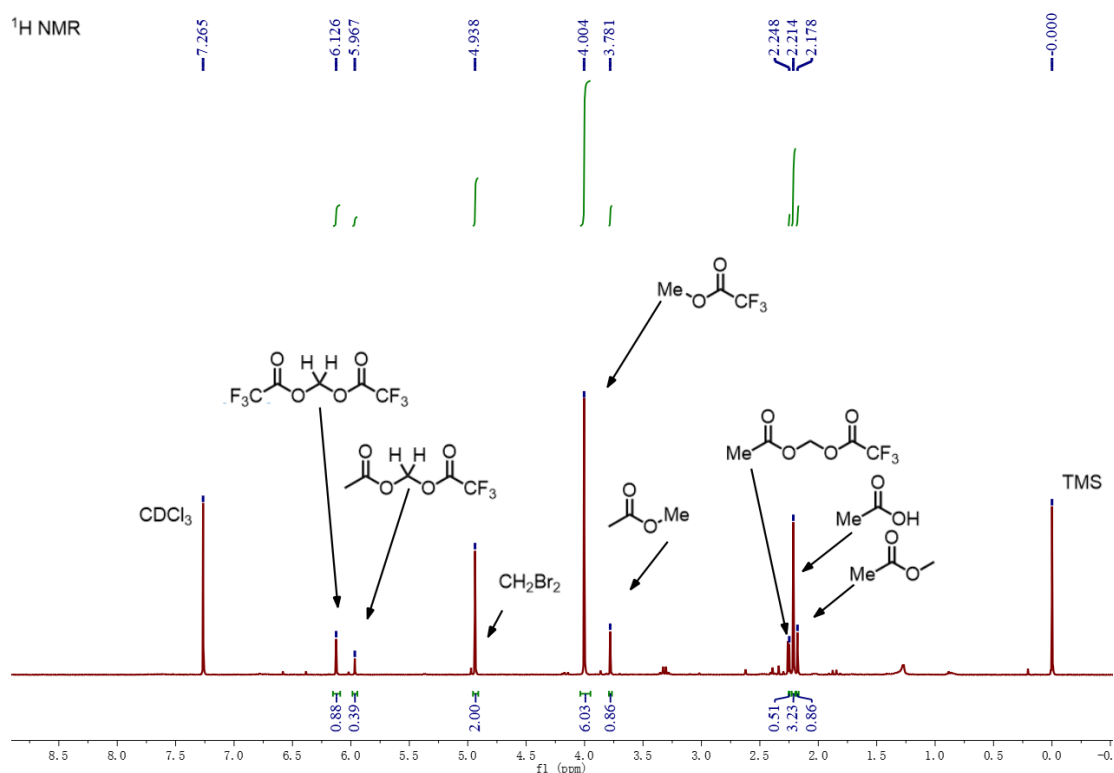
**Figure S7.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: KF, No.2).



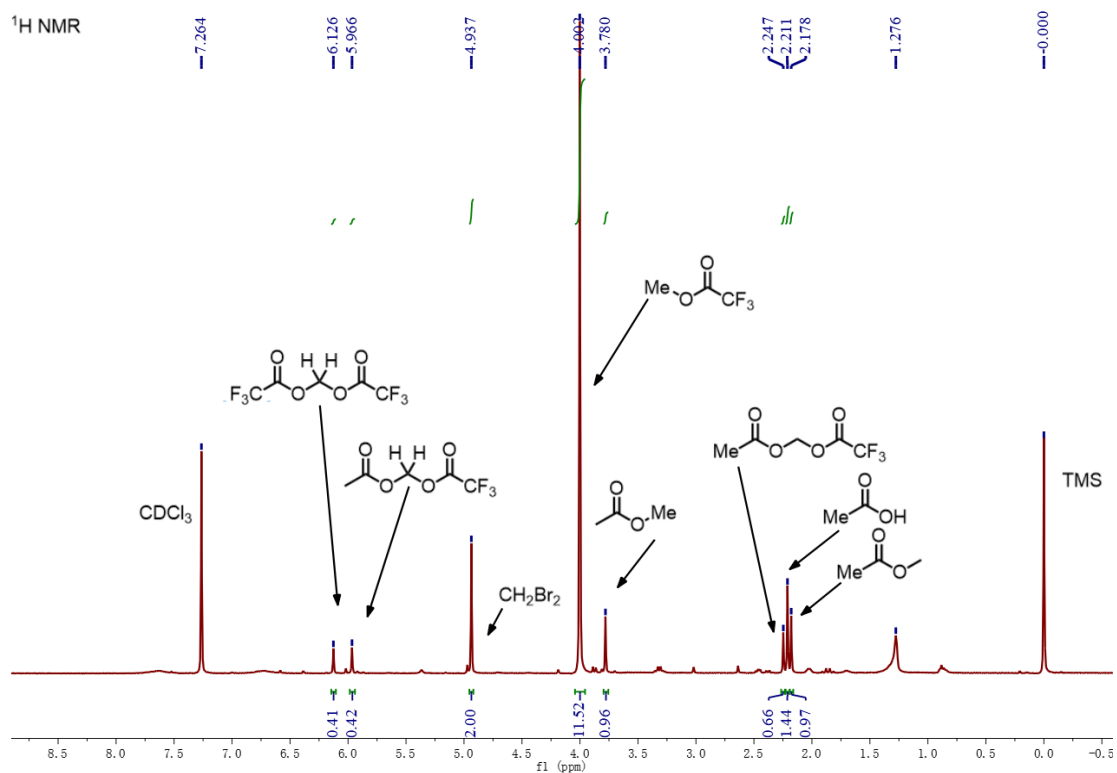




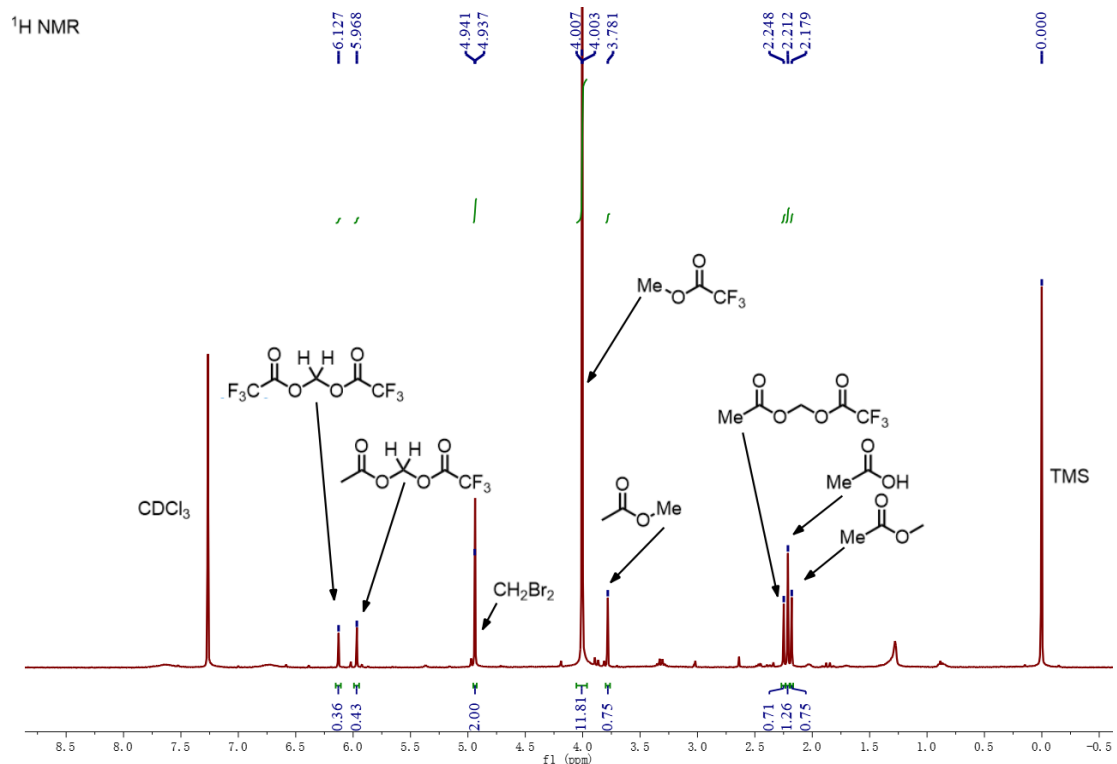
**Figure S10.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: Na<sub>2</sub>FPO<sub>3</sub>, No.2).



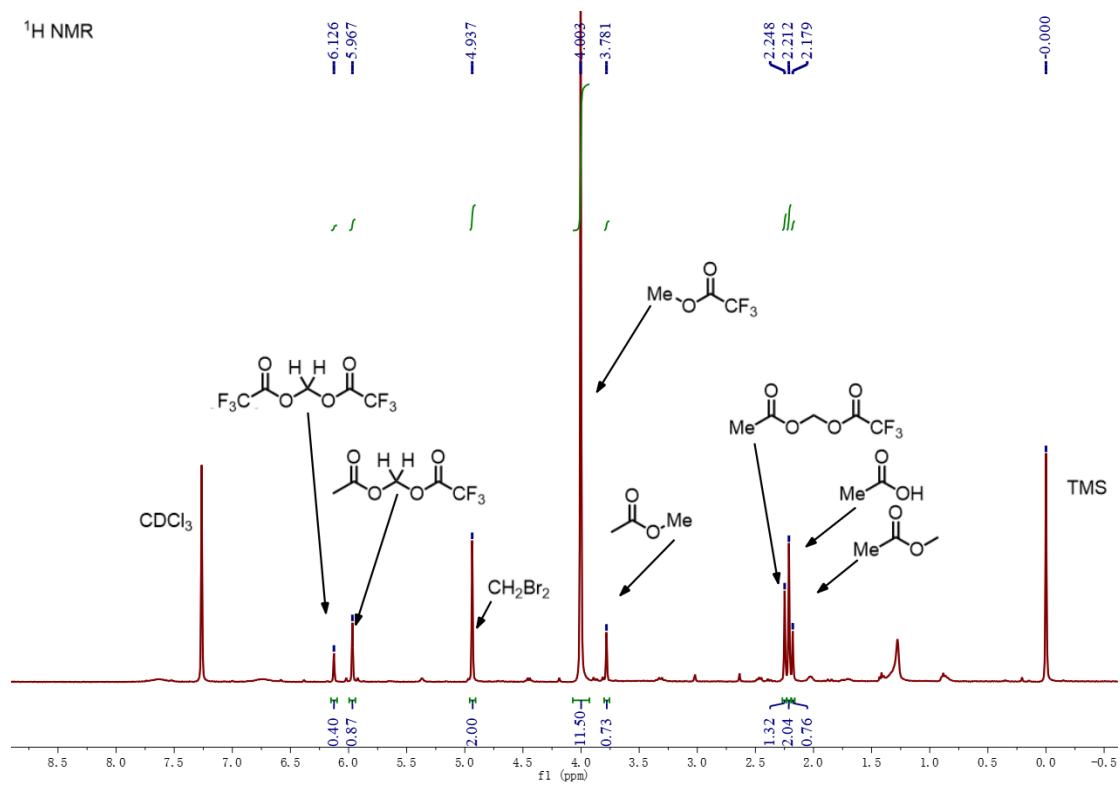
**Figure S11.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: Na<sub>2</sub>FPO<sub>3</sub>, No.3).



**Figure S12.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: CsF, No.1).



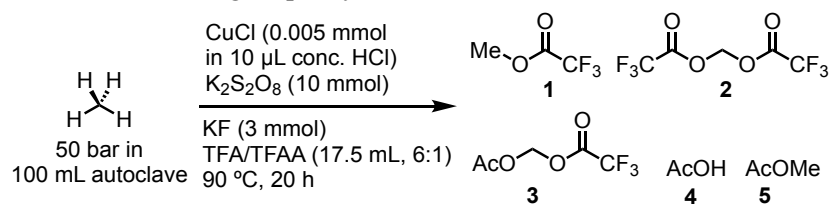
**Figure S13.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: CsF, No.2).



**Figure S14.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation (additive: CsF, No.3).

## 2.4 The Influence of Reagent Purity on Oxidation Efficiency

**Table S1.** The influence of reagent purity



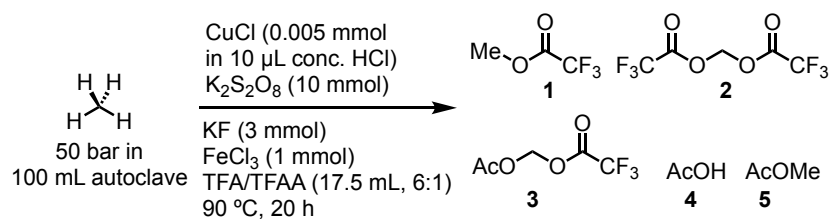
entry	CuCl	Yields (mmol) <sup>a</sup>				
		1	2	3	4	5
1	Energy 99%	7.12	0.65	0.09	0.07	0.14
2	Alfa 99.999%	6.87	0.53	0.09	0.09	0.14

entry	KF	Yields (mmol) <sup>a</sup>				
		1	2	3	4	5
1	Energy 99%	7.12	0.65	0.09	0.07	0.14
2	Alfa 99.99%	7.00	0.49	0.07	0.07	0.13
		7.03	0.36	0.13	0.15	0.19

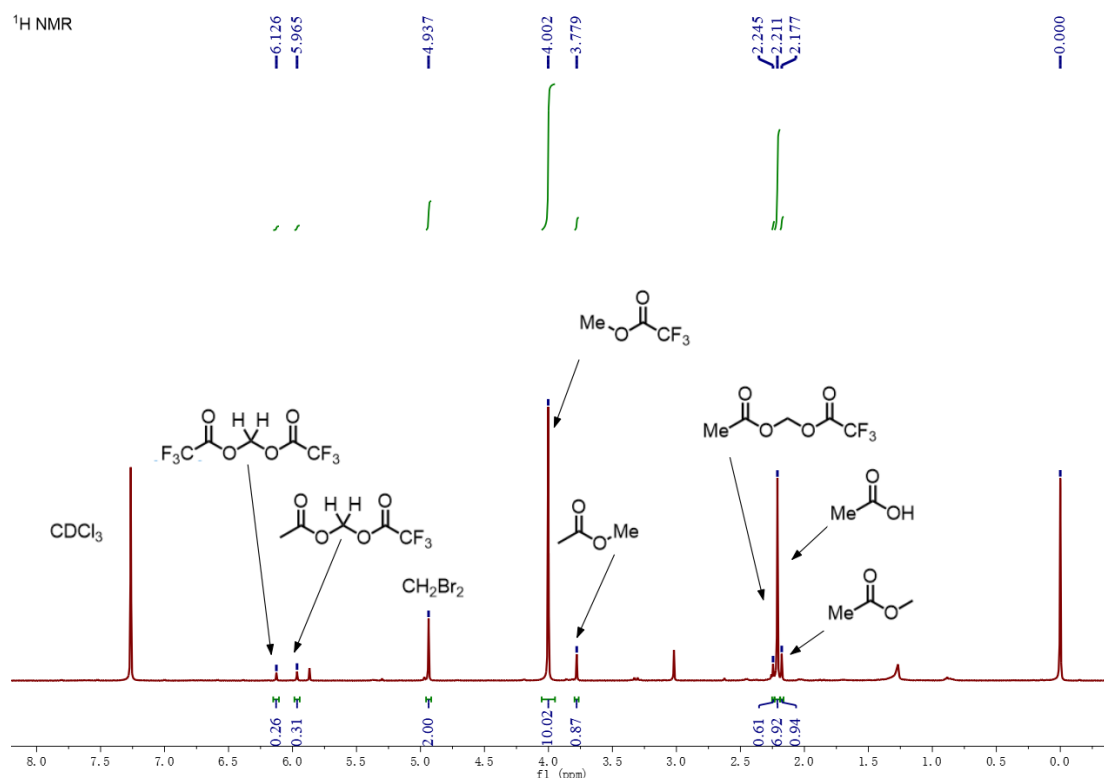
entry	$K_2S_2O_8$	Yields (mmol) <sup>a</sup>				
		1	2	3	4	5
1	Macklin 99.5%	7.12	0.65	0.09	0.07	0.14
2	Aldrich 99.99%	6.89	0.34	0.14	0.22	0.18
3 <sup>[b, c]</sup>	Aldrich 99.99%	0.34	0.09	1.24	0.55	0.58

<sup>a</sup>Determined by <sup>1</sup>H NMR spectroscopy (CDCl<sub>3</sub>) using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>b</sup>without CuCl and KF. <sup>c</sup>There is an unidentified peak in crude <sup>1</sup>H NMR with chemical shift at 3.04 ppm.

## 2.5 The Oxidation of Methane under Optimized Conditions with extra FeCl<sub>3</sub>

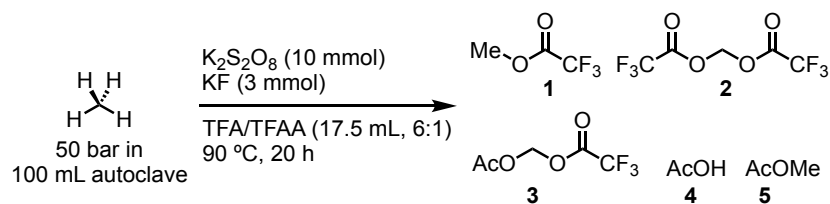


Following the typical procedure for methane oxidation in **2.2** with extra FeCl<sub>3</sub> (1 mmol, 162 mg). <sup>1</sup>H NMR yields (70  $\mu$ L of CH<sub>2</sub>Br<sub>2</sub> as the internal standard): **1**: 3.34 mmol; **2**: 0.13 mmol; **3**: 0.16 mmol; **4**: 2.31 mmol, **5**: 0.29 mmol. ), the crude <sup>1</sup>H NMR spectra is as follow:

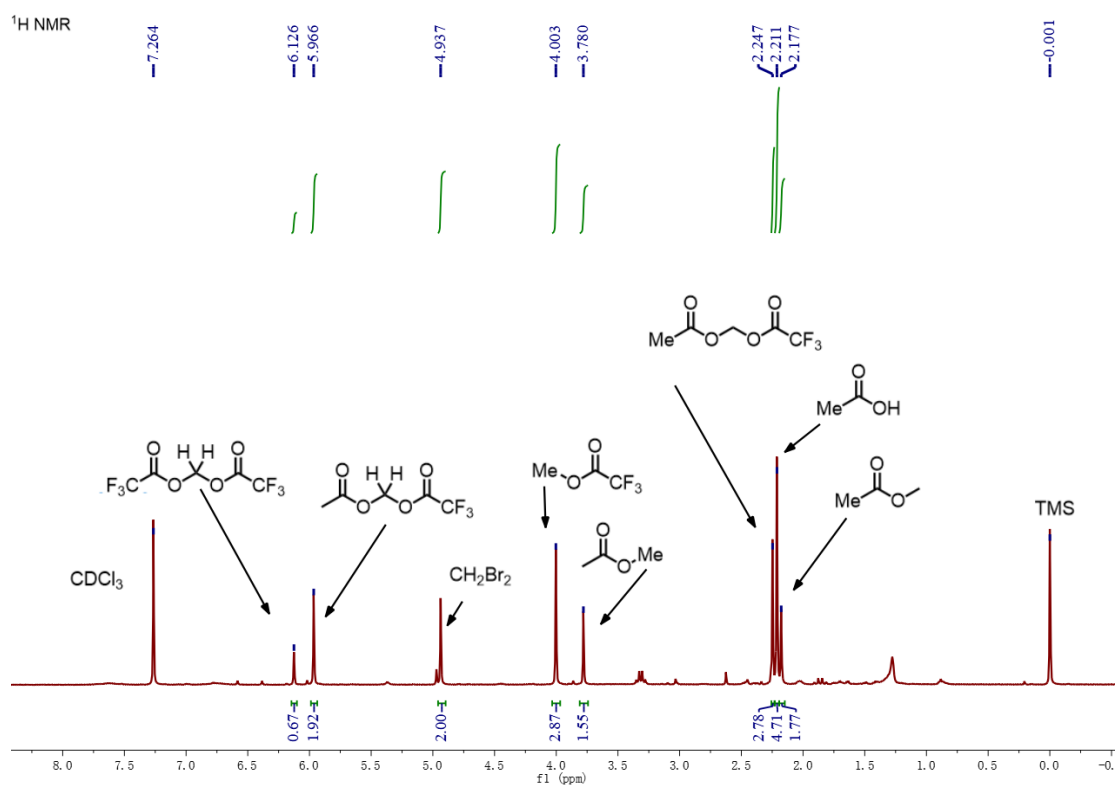


**Figure S15.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation under optimized reaction conditions with extra FeCl<sub>3</sub> (1 mmol). (Reaction conditions: 10 mmol of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 3 mmol of KF, 15 mL of TFA, 2.5 mL of TFAA, 1 mmol FeCl<sub>3</sub>, 0.005 mmol CuCl in 10  $\mu$ L conc. HCl, 50 bar CH<sub>4</sub> in 100 mL titanium autoclave, 90 °C, 20 h.)

## 2.6 The Oxidation of Methane without CuCl

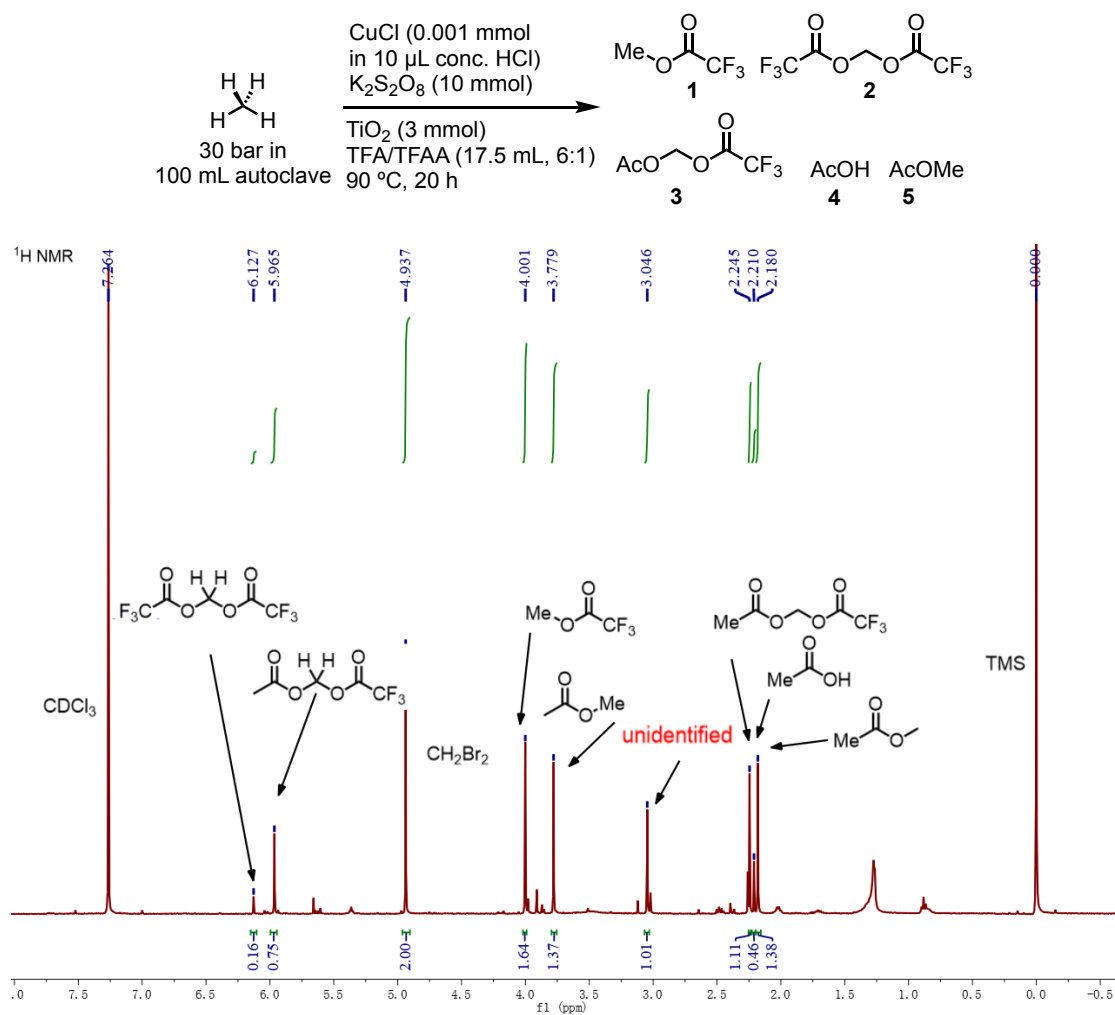


Following the typical procedure in **2.2** without adding CuCl ( $^1\text{H}$  NMR yields: **1**: 0.96 mmol; **2**: 0.34 mmol; **3**: 0.96 mmol; **4**: 1.57 mmol, **5**: 0.52 mmol), the crude  $^1\text{H}$  NMR is as follow:



**Figure S16.**  $^1\text{H}$  NMR spectrum of the reaction mixture of methane oxidation without CuCl. (Reaction conditions: 10 mmol of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 3 mmol of KF, 15 mL of TFA, 2.5 mL of TFAA, 50 bar CH<sub>4</sub> in 100 mL titanium autoclave, 90 °C, 20 h.)

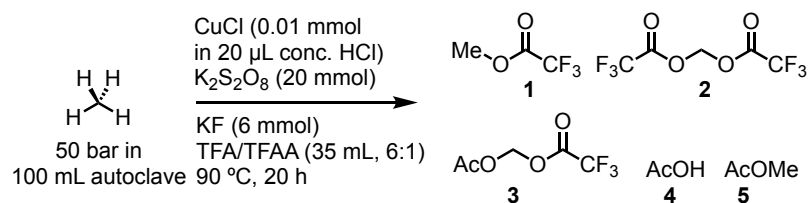
## 2.7 Oxidation of Methane in the Presence of TiO<sub>2</sub> instead of KF



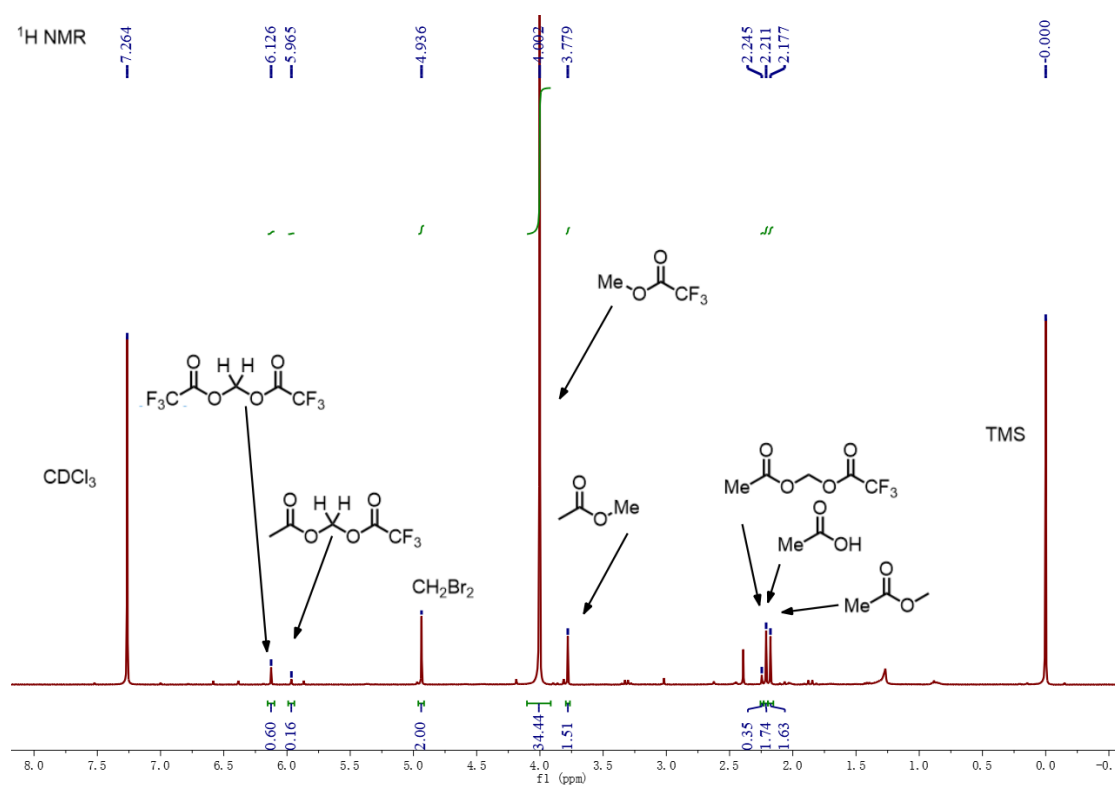
**Figure S17.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation in the Presence of TiO<sub>2</sub> instead of KF. (Reaction conditions: 10 mmol of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 3 mmol of TiO<sub>2</sub>, 0.001 mmol CuCl in 10 μL conc. HCl, 15 mL of TFA, 2.5 mL of TFAA, 30 bar CH<sub>4</sub> in 100 mL titanium autoclave, 90 °C, 20 h). The peak at 3.04 ppm hasn't been identified after several attempts.



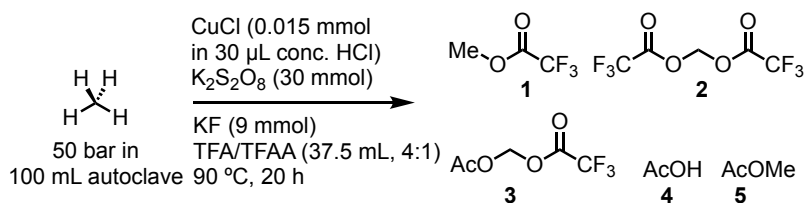
## 2.8 Scale-up reactions



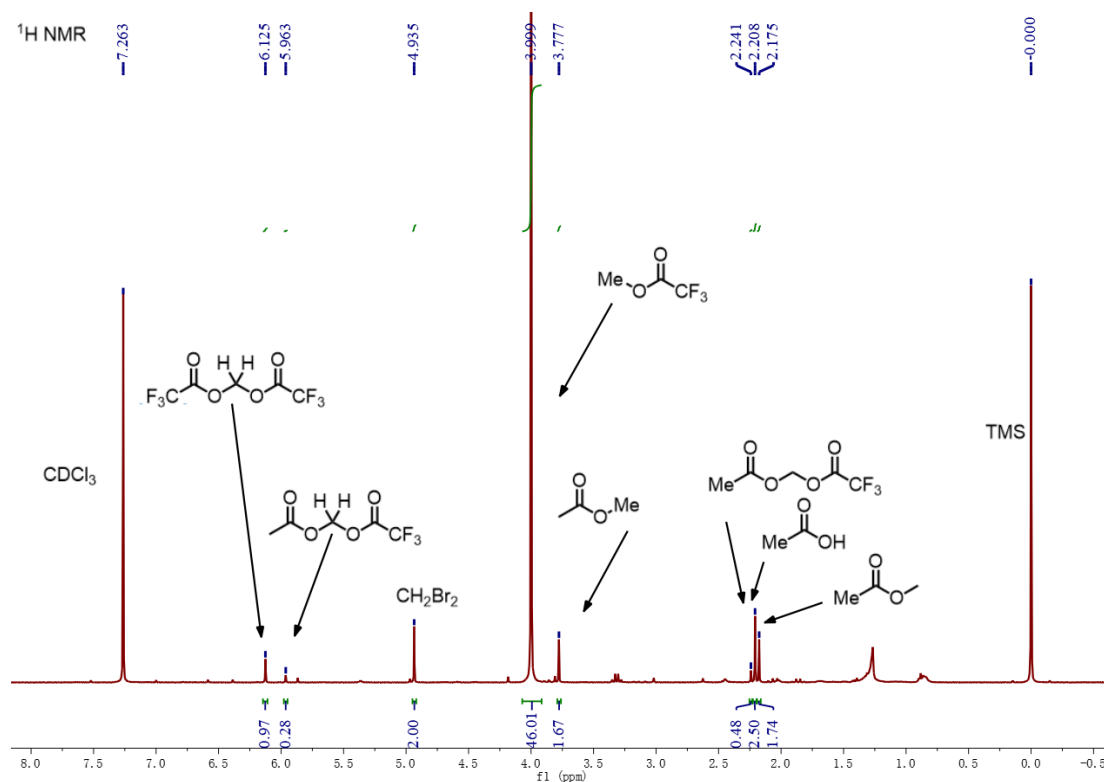
Following the typical procedure in **2.2** with 20 mmol of  $K_2S_2O_8$ , 6 mmol of KF, 0.01 mmol of CuCl in 20  $\mu$ L conc. HCl, 30 mL of TFA, 5 mL of TFAA, 50 bar  $CH_4$  in 100 mL titanium autoclave at 90  $^{\circ}$ C for 20 h.  $^1H$  NMR yields (70  $\mu$ L of  $CH_2Br_2$  as the internal standard): **1**: 11.48 mmol; **2**: 0.3 mmol; **3**: 0.08 mmol; **4**: 0.58 mmol, **5**: 0.5 mmol. ), the crude  $^1H$  NMR spectrum is as follow:



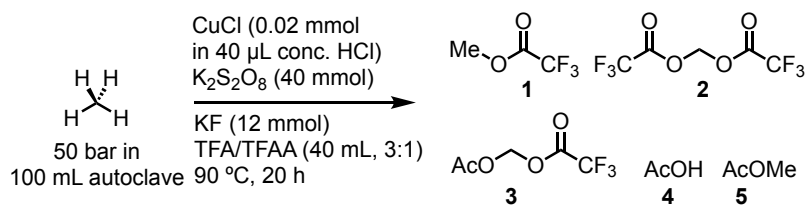
**Figure S18.**  $^1H$  NMR spectrum of the reaction mixture of methane oxidation (20 mmol of  $K_2S_2O_8$ ).



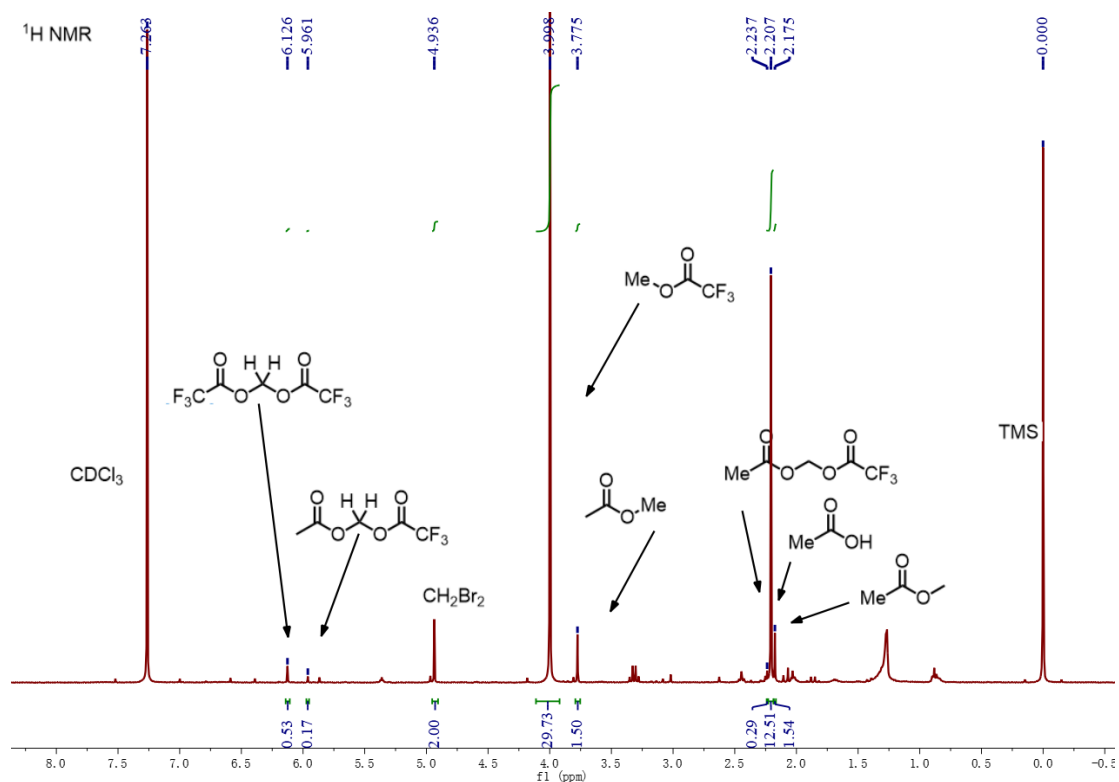
Following the typical procedure in **2.2** with 30 mmol of  $\text{K}_2\text{S}_2\text{O}_8$ , 9 mmol of KF, 0.015 mmol of CuCl in 30  $\mu\text{L}$  conc. HCl, 30 mL of TFA, 7.5 mL of TFAA, 50 bar  $\text{CH}_4$  in 100 mL titanium autoclave at 90  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR yields (70  $\mu\text{L}$  of  $\text{CH}_2\text{Br}_2$  as the internal standard): **1**: 15.34 mmol; **2**: 0.49 mmol; **3**: 0.14 mmol; **4**: 0.83 mmol, **5**: 0.56 mmol. ), the crude  $^1\text{H}$  NMR spectrum is as follow:



**Figure S19.**  $^1\text{H}$  NMR spectrum of the reaction mixture of methane oxidation. (30 mmol of  $\text{K}_2\text{S}_2\text{O}_8$ ).



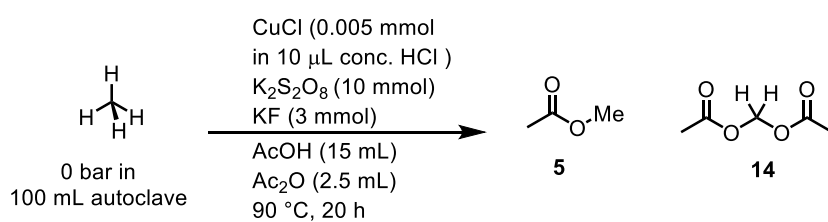
Following the typical procedure in **2.2** with 40 mmol of  $K_2S_2O_8$ , 12 mmol of KF, 0.02 mmol of CuCl in 40  $\mu$ L conc. HCl, 30 mL of TFA, 10 mL of TFAA, 50 bar  $CH_4$  in 100 mL titanium autoclave at 90  $^{\circ}$ C for 20 h.  $^1H$  NMR yields (70  $\mu$ L of  $CH_2Br_2$  as the internal standard): **1**: 9.91 mmol; **2**: 0.27 mmol; **3**: 0.09 mmol; **4**: 4.17mmol, **5**: 0.5 mmol. ), the crude  $^1H$  NMR spectrum is as follow:



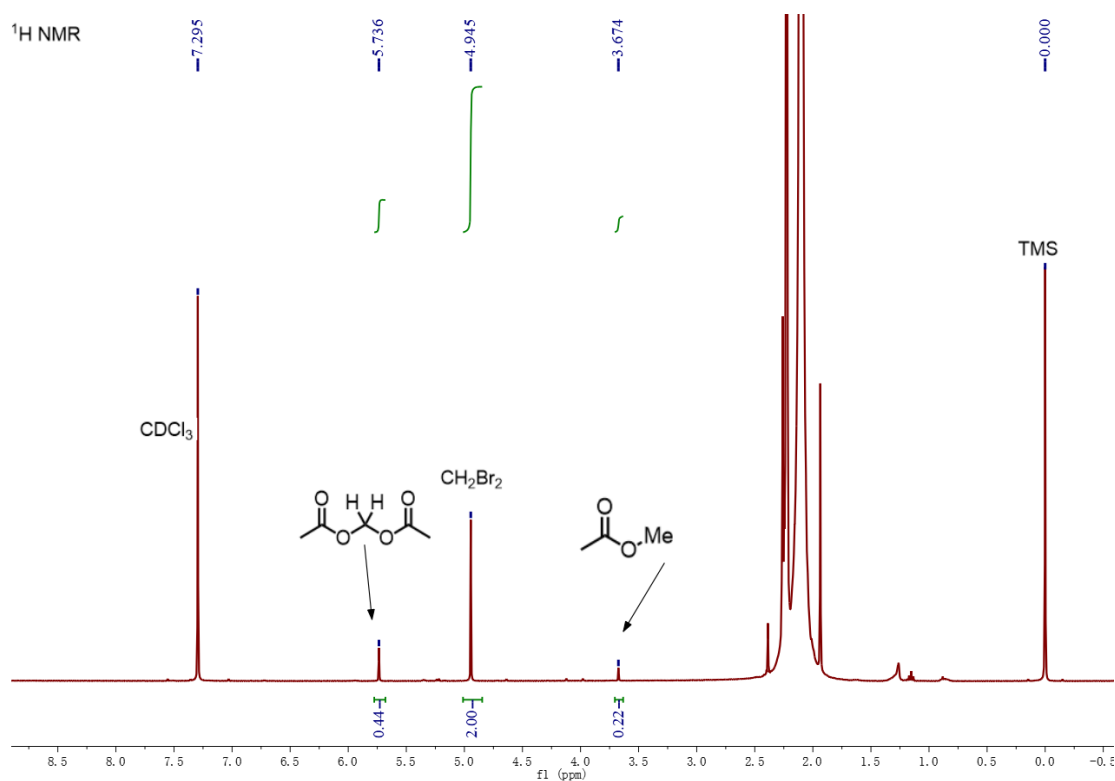
**Figure S20.**  $^1H$  NMR spectrum of the reaction mixture of methane oxidation. (40 mmol of  $K_2S_2O_8$ ).

## 2.9 Oxidation of Methane with AcOH and Ac<sub>2</sub>O as Solvents

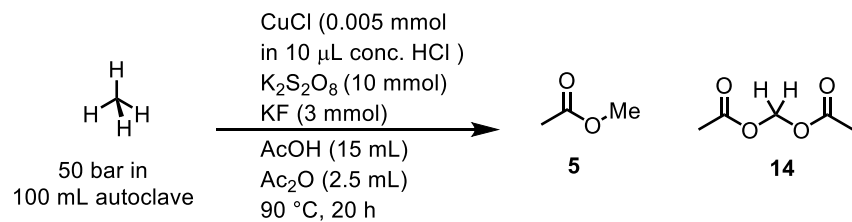
### Control experiment without methane



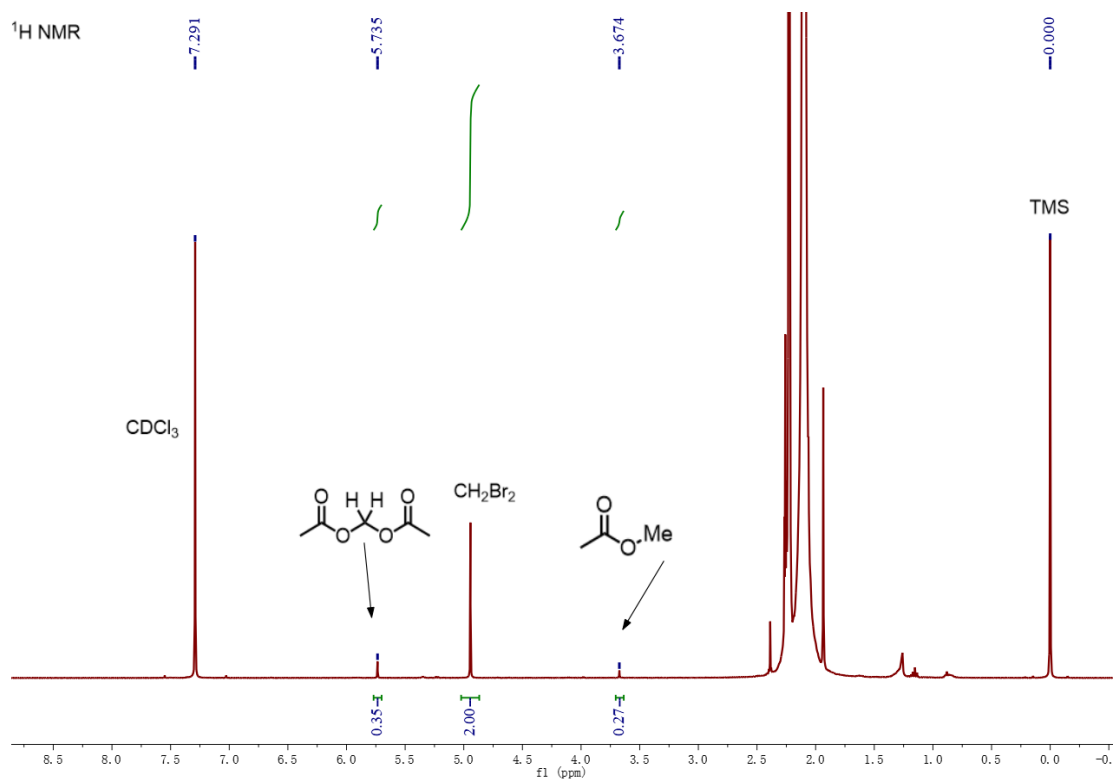
Following the typical procedure in **2.2** in the presence of AcOH, Ac<sub>2</sub>O instead of TFA, TFAA, and without methane (<sup>1</sup>H NMR yields: **5**: 0.07 mmol, **14**: 0.22 mmol), the crude <sup>1</sup>H NMR spectrum is as follow:



**Figure S21.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation in the presence of AcOH, Ac<sub>2</sub>O instead of TFA, TFAA, and without methane.



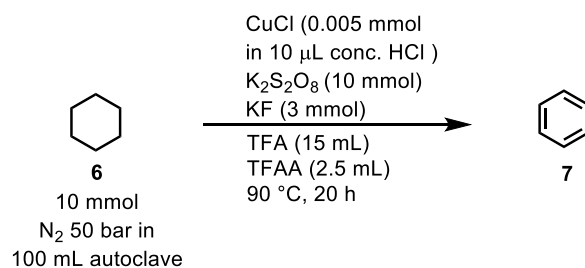
Following the typical procedure in **2.2** in the presence of AcOH, Ac<sub>2</sub>O instead of TFA, TFAA (<sup>1</sup>H NMR yields: **5**: 0.09 mmol, **14**: 0.18 mmol), the crude <sup>1</sup>H NMR spectrum is as follow:



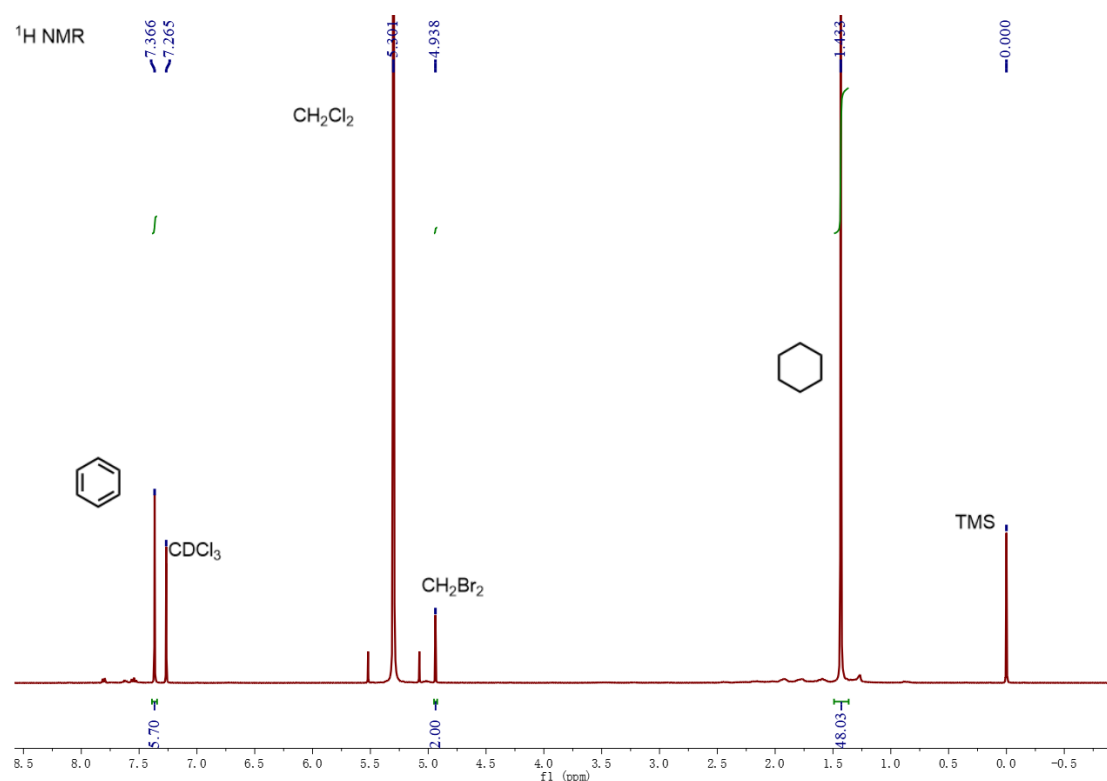
**Figure S22.** <sup>1</sup>H NMR spectrum of the reaction mixture of methane oxidation in the presence of AcOH, Ac<sub>2</sub>O instead of TFA, TFAA.

## 2.10 Oxidation of Cyclohexane, 6-a and Adamantane

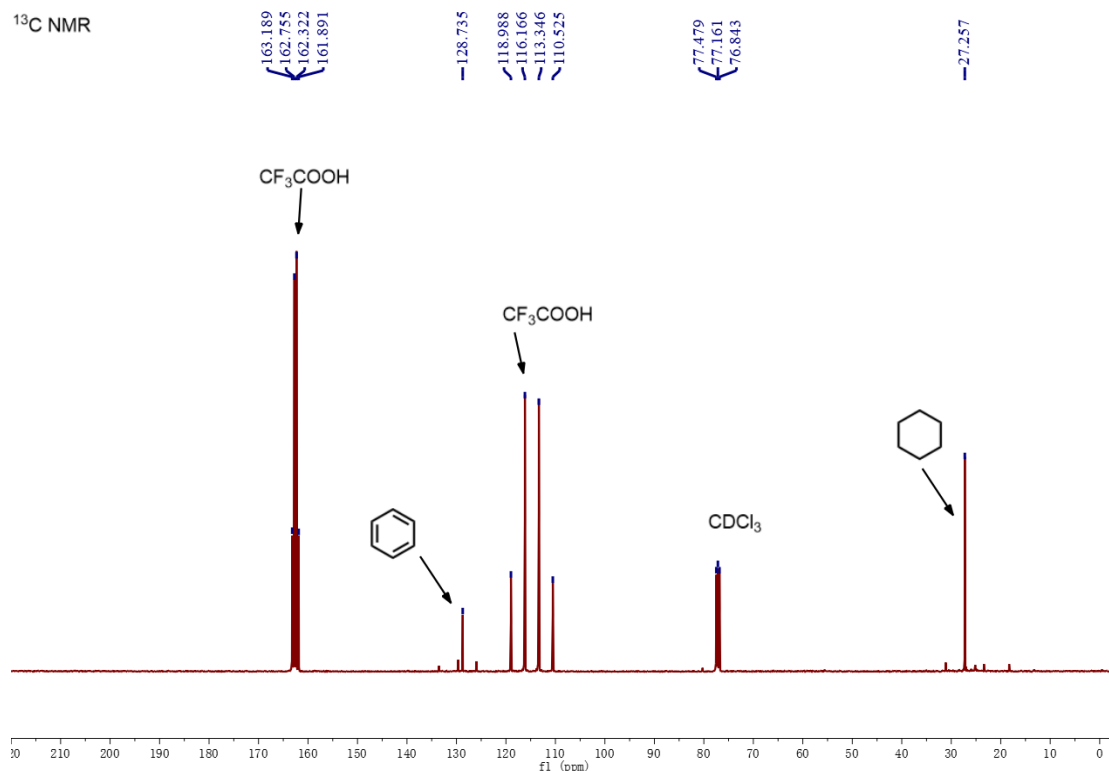
### 2.10.1 Oxidation of Cyclohexane



A 100 ml autoclave with PTFE lining was added cyclohexane (10 mmol, 1080 µL), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mmol, 2.703 g), KF (3 mmol, 174 mg), TFA (15 mL), TFAA (2.5 mL), CuCl (0.5 M in conc. HCl, 10 µL, freshly prepared by dissolving 9.9 mg of CuCl in 200 µL conc. HCl with 30 s sonication). The autoclave was sealed and filled with 50 bar N<sub>2</sub>. After stirring for 20 h at 90 °C, the autoclave was cooled with cryostat at -15 °C. The autoclave was opened and 5 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction mixture to form a homogeneous solution because cyclohexane and benzene do not dissolve well in TFA. The internal standard (CH<sub>2</sub>Br<sub>2</sub>, 70 µL) was added and the mixture was stirred for 2 minutes, then several drops of reaction solution was mixed with CDCl<sub>3</sub> (1 mL) in an eppendorf tube and shaken for several seconds. The supernatant isolated by centrifugation was tested <sup>1</sup>H NMR to determine the yields (0.95 mmol, 9.5 % NMR yield with 4.00 mmol cyclohexane recovered) based on the integral of proton of these products as comparing with the integral of CH<sub>2</sub>Br<sub>2</sub>. A <sup>13</sup>C NMR was also recorded to confirm the formation of benzene.

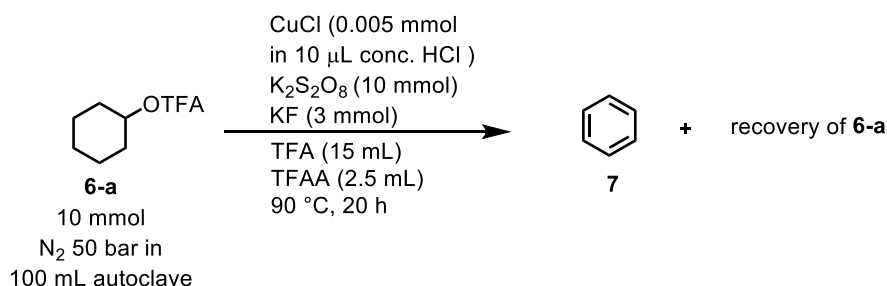


**Figure S23.** <sup>1</sup>H NMR spectrum of the reaction mixture of cyclohexane oxidation.

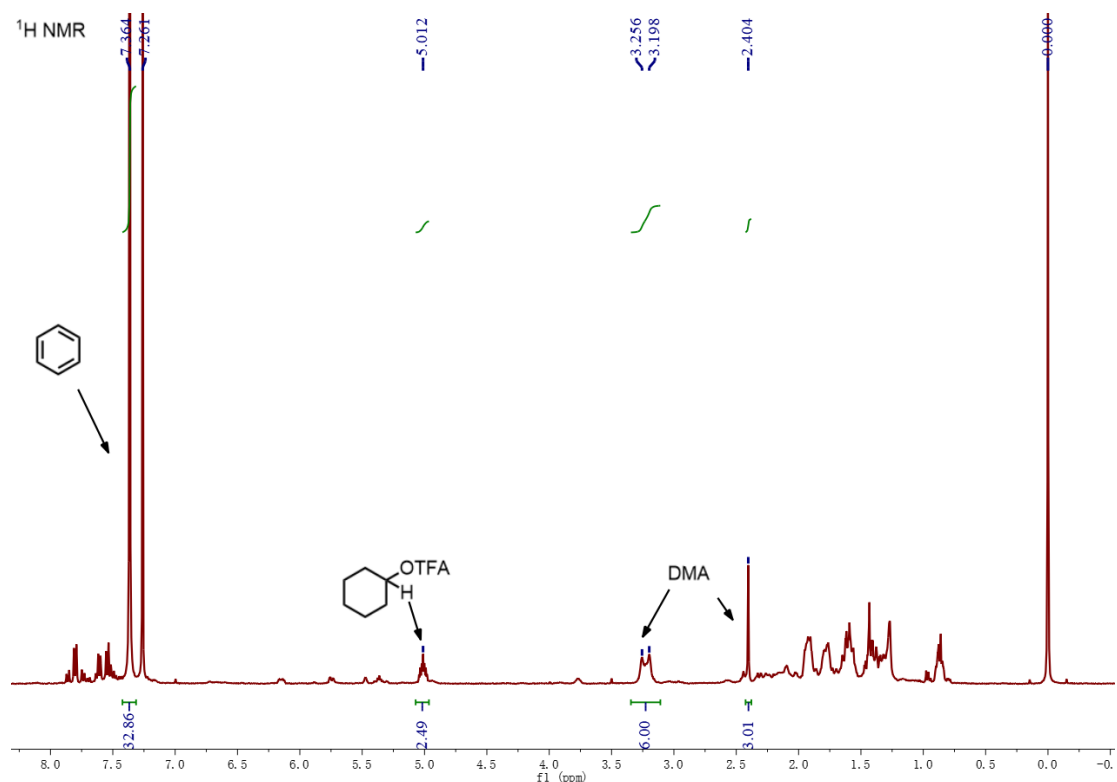


**Figure S24.** <sup>13</sup>C NMR spectrum of the reaction mixture of cyclohexane oxidation.

### 2.10.2 Oxidation of **6-a**

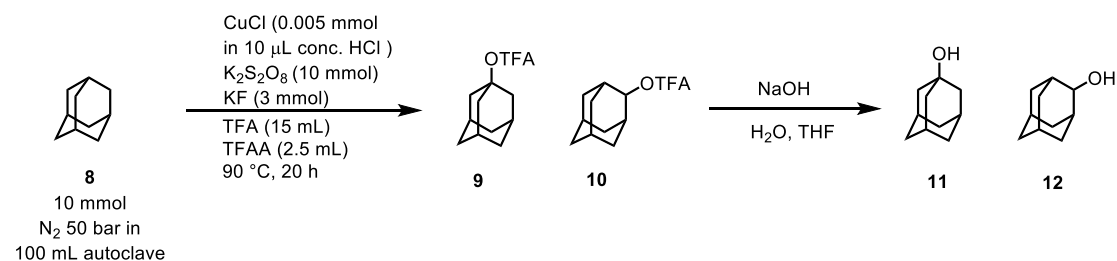


A 100 ml autoclave with PTFE lining was added **6-a** (10 mmol, 1962 mg), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mmol, 2.703 g), KF (3 mmol, 174 mg), TFA (15 mL), TFAA (2.5 mL), CuCl (0.5 M in conc. HCl, 10 μL, freshly prepared by dissolving 9.9 mg of CuCl in 200 μL conc. HCl with 30 s sonication). The autoclave was sealed and filled with 50 bar N<sub>2</sub>. After stirring for 20 h at 90 °C, the autoclave was cooled with cryostat at -15 °C. The autoclave was opened, the internal standard (DMA, 93 μL) was added and the mixture was stirred for 2 minutes, then several drops of reaction solution was mixed with CDCl<sub>3</sub> (1 mL) in an eppendorf tube and shaken for several seconds. The supernatant isolated by centrifugation was tested <sup>1</sup>H NMR to determine the yields (5.48 mmol, 54.8 % NMR yield with 2.49 mmol of **6-a** recovered) based on the integral of proton of these products as comparing with the integral of DMA. The crude <sup>1</sup>H NMR is as follow:



**Figure S25.**  $^1\text{H}$  NMR spectrum of the reaction mixture of **6-a** oxidation.

### 2.10.3 Oxidation of Adamantane



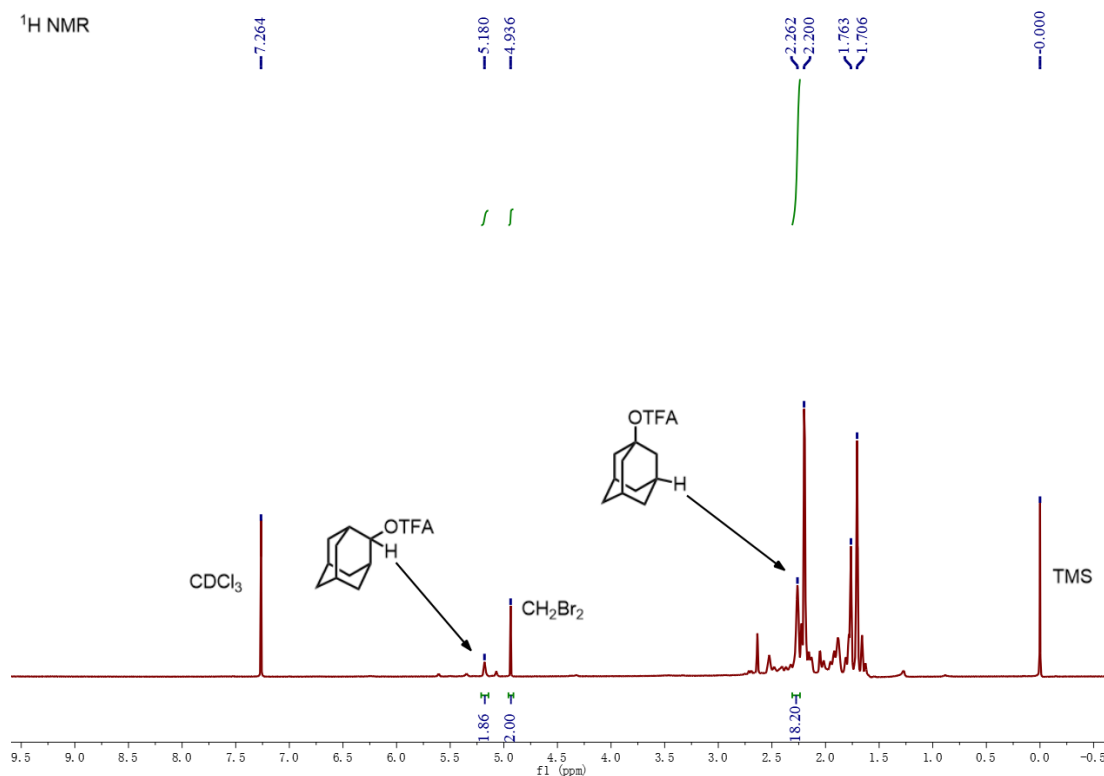
A 100 ml autoclave with PTFE lining was added adamantane **8** (10 mmol, 1.36 g),  $\text{K}_2\text{S}_2\text{O}_8$  (10 mmol, 2.703 g),  $\text{KF}$  (3 mmol, 174 mg), TFA (15 mL), TFAA (2.5 mL),  $\text{CuCl}$  (0.5 M in conc. HCl, 10  $\mu\text{L}$ , freshly prepared by dissolving 9.9 mg of  $\text{CuCl}$  in 200  $\mu\text{L}$  conc. HCl with 30 s sonication). The autoclave was sealed and filled with 50 bar  $\text{N}_2$ . After stirring for 20 h at 90 °C, the autoclave was cooled with cryostat at -15 °C. then the autoclave was opened and the internal standard ( $\text{CH}_2\text{Br}_2$ , 70  $\mu\text{L}$ ) was added. The mixture was stirred for 2 minutes, then several drops of reaction solution was mixed with  $\text{CDCl}_3$  (1 mL) in an eppendorf tube and shaken for several seconds. The supernatant isolated by centrifugation was tested  $^1\text{H}$  NMR to determine the yields of **9** (6.07 mmol, 60.7% NMR yield) and **10** (1.86 mmol, 18.6% NMR yield) which formed as the major products (**Figure S26**). Then, TFA and TFAA were evaporated under reduced pressure. **9** and **10** were isolated by flash column chromatography



over silica gel (hexanes) as a mixture (colorless oil). The trifluoroacetate **9** and **10** were hydrolyzed with NaOH (34 mmol, 1.36 g) in H<sub>2</sub>O/THF (25 mL /25 mL) overnight. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL × 3). Then the combined organic layer was washed with brine and dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated under reduced pressure. The products was purified by flash column chromatography over silica gel (30:1 n-pentane/EtOAc eluent) to afford 1-Adamantanol **11** (562 mg, 3.70 mmol, 37% yield) and 2-Adamantanol **12** (168 mg, 1.1mmol, 11.1% yield).

**11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.14 (s, 3H), 1.84(s,1H),1.72-1.68 (m, 6H), 1.62-1.57 (m, 6H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 68.27, 45.40, 36.16, 30.79.

**12**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.87 (s, 1H), 2.09-2.05 (m, 2H), 1.89-1.80(m, 6H), 1.72-1.68 (m, 5H), 1.56-1.50 (d, J = 12.7 Hz, 2H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 74.67, 37.72, 36.64, 34.67, 31.14, 27.65, 27.20.



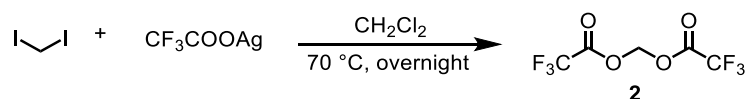
**Figure S26.** Crude <sup>1</sup>H NMR spectrum of the reaction mixture of adamantane oxidation.

## 2.11 Synthesis of 2, 3, 9 and 10 as Reference Compounds

To identify the products of methane oxidation, we synthesized compound **2** and **3** according to the literature.

### 2.11.1 Synthesis of 2 as Reference Compound

Compound **2** was prepared according to the reference: P. E. Aldrich, W. A. Sheppard, *J. Org. Chem.* **1964**, *29*, 11.

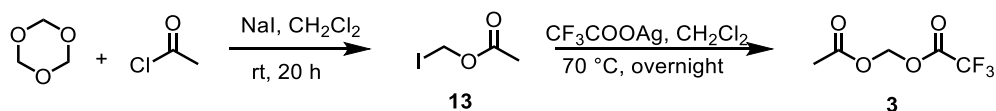


$\text{CH}_2\text{I}_2$  (1 mmol, 268 mg) was added to a stirred solution of  $\text{CF}_3\text{COOAg}$  (2.2 mmol, 486 mg) in  $\text{CH}_2\text{Cl}_2$  (5 mL) and the mixture was stirred at 70 °C overnight. The reaction mixture was filtrated through a pad of Celite and concentrated under reduced pressure to afford compound **2** without further purification.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.13 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.52, 156.07, 155.63, 118.35, 115.51, 112.68, 109.85, 82.03, 53.57.

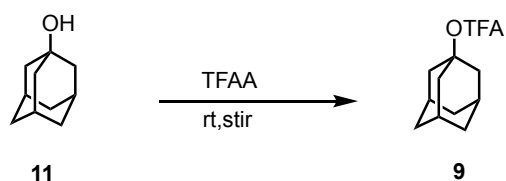
### 2.11.2 Synthesis of 3 as Reference Compound

Compound **13** was prepared according to the reference: J. D. Thomas, K. B. Sloan, *Synthesis*, **2008**, 272.



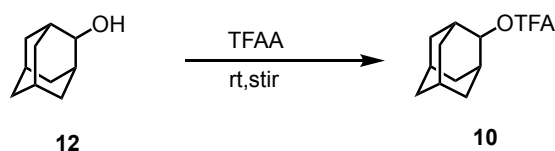
$\text{NaI}$  (33.6 mmol, 5.04 g) was added to a stirred solution of 1,3,5-trioxane (9.33 mmol, 840 mg) in  $\text{CH}_2\text{Cl}_2$  (60 mL) within a 150 mL sealed tube and the mixture was cooled to 0 °C. A solution of acetyl chloride (28 mmol, 1.19 mL) in  $\text{CH}_2\text{Cl}_2$  (25 mL) was added. Then the tube was covered with aluminum foil while the reaction was stirred at room temperature for 22 h. The mixture was washed with 10% aq  $\text{Na}_2\text{S}_2\text{O}_3$ , followed by brine. The organic phase was then dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under vacuum to give crude **13** (3.608 g, yield 64.4%). Then, **13** (2 mmol, 400 mg) was added to a solution of  $\text{CF}_3\text{COOAg}$  (2.5 mmol, 552 mg) in  $\text{CH}_2\text{Cl}_2$  (5 mL) within a 15 mL sealed tube and the mixture was stirred at 70 °C overnight. The reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure to afford compound **3** without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.94 (s, 2H),  $\delta$  2.18 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.39, 169.21, 156.61, 156.18, 118.55, 115.71, 112.88, 110.04, 90.52, 90.21, 89.03, 88.74, 87.56, 81.07, 79.47, 69.39, 53.56, 20.83, 20.56.

### 2.11.3 Synthesis of **9** and **10** as Reference Compounds



1-Adamantanol **11** (10.0 mg) and TFAA (0.5 ml) were added to a 15 mL sealed tube, the mixture was stirred for 4 hours at room temperature. Then, the mixture was concentrated under reduced pressure to afford compound **9** (12.8 mg, yield 78.5%) without further purification.

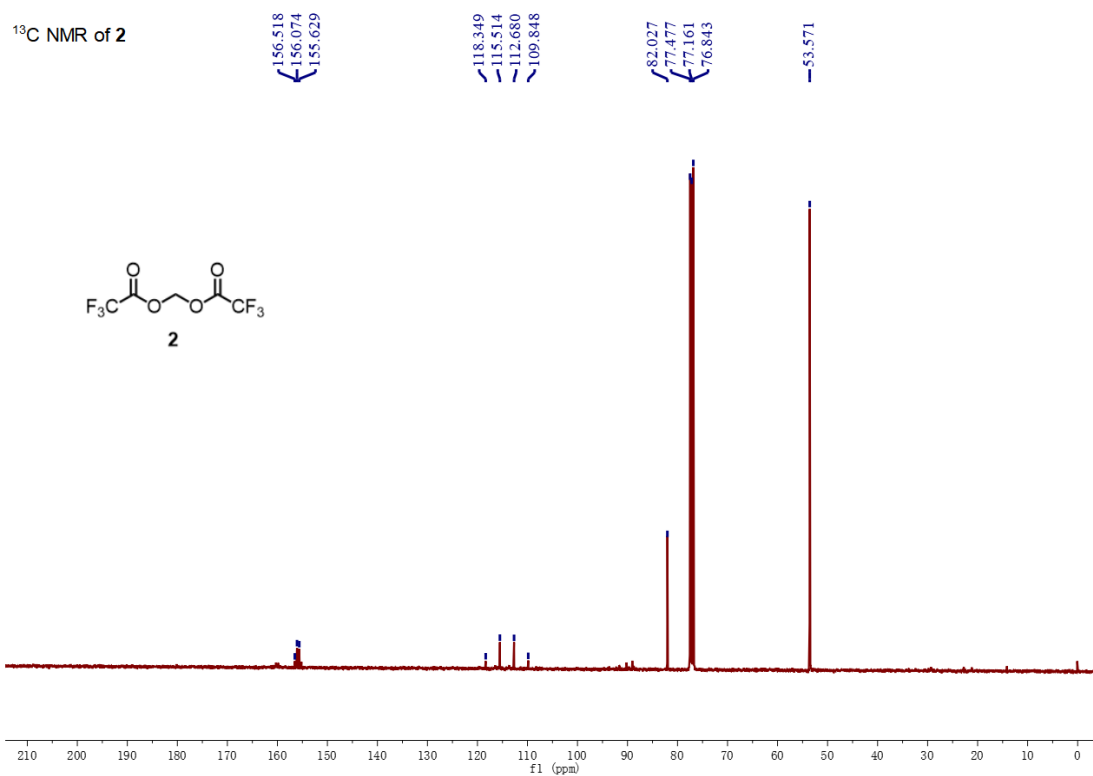
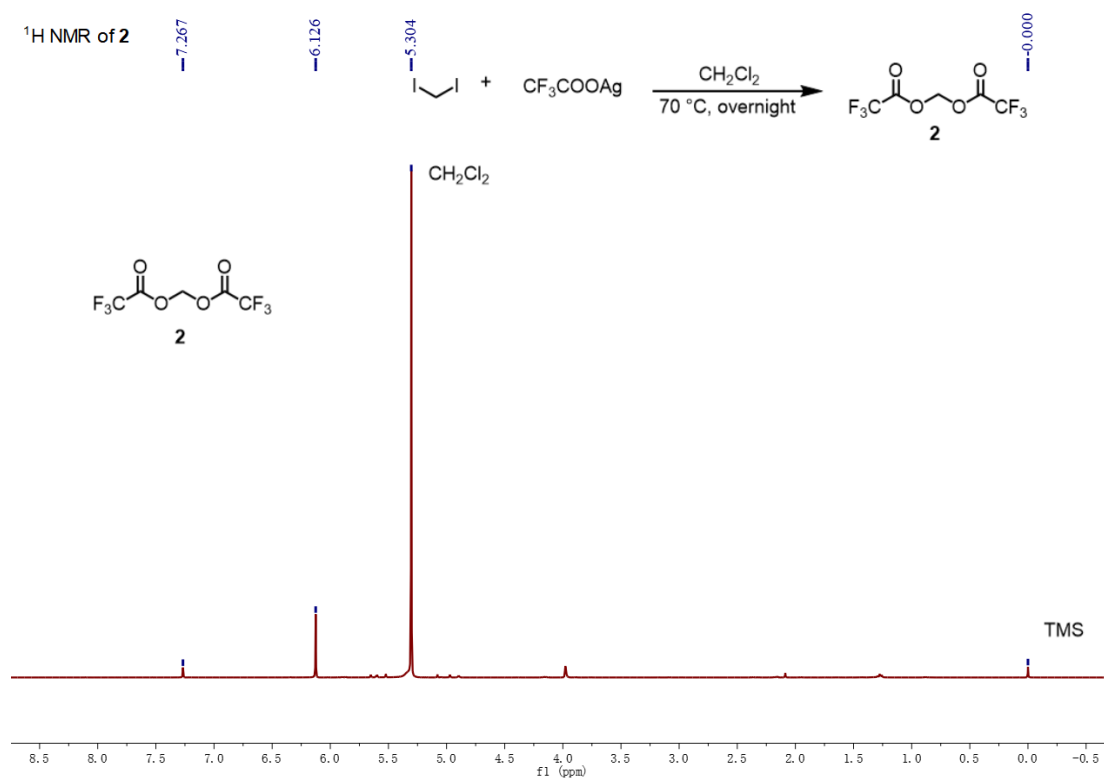
**9**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.24 (s, 3H), 2.19 (s, 6H), 1.69 (s, 6H).

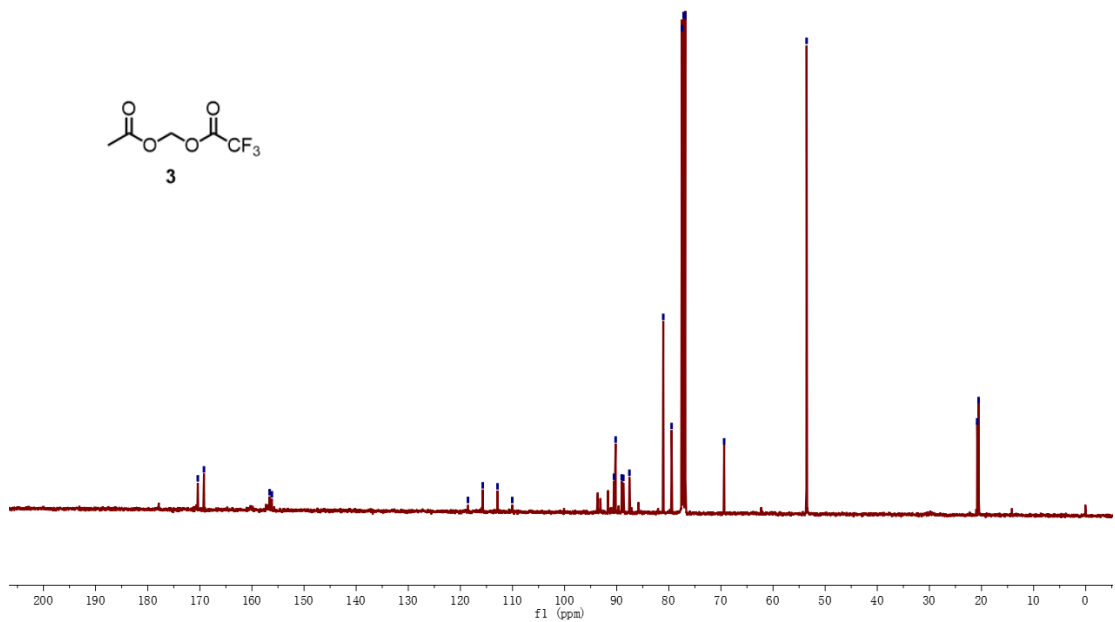
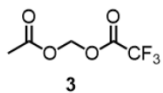
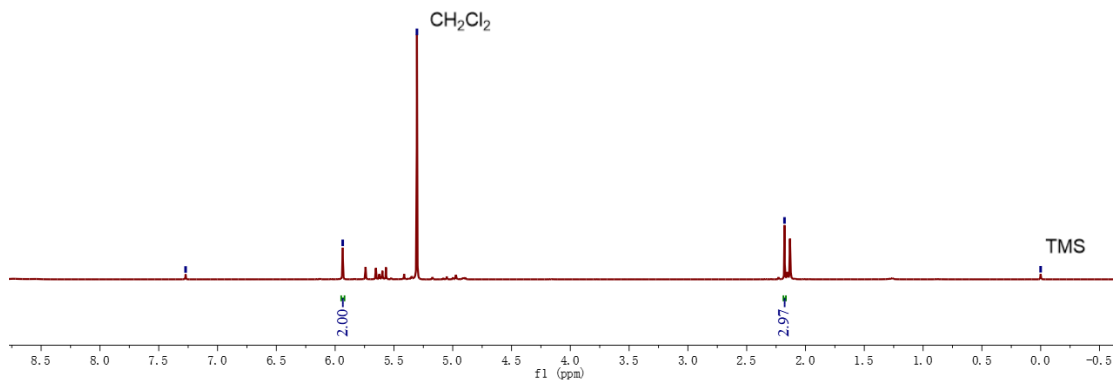
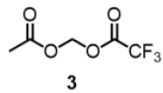
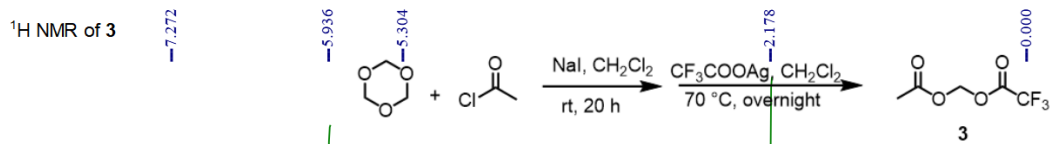


2-Adamantanol **12** (10.0 mg) and TFAA (0.5 ml) was added to a 15 mL sealed tube, the mixture was stirred for 4 hours at room temperature. Then, the mixture was concentrated under reduced pressure to afford compound **10** (14.8 mg, yield 90.7%) without further purification.

**10**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.14 (s, 1H), 2.12 (s, 2H), 2.03 (d,  $J = 12.9$  Hz, 2H), 1.92 (d,  $J = 13.6$  Hz, 4H), 1.79 (d,  $J = 13.9$  Hz, 4H), 1.62 (d,  $J = 12.5$  Hz, 2H).

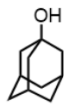
## 2.12 NMR spectra of Reference Compounds, 11 and 12





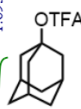
<sup>1</sup>H NMR of 9

7.263



2.244  
2.186

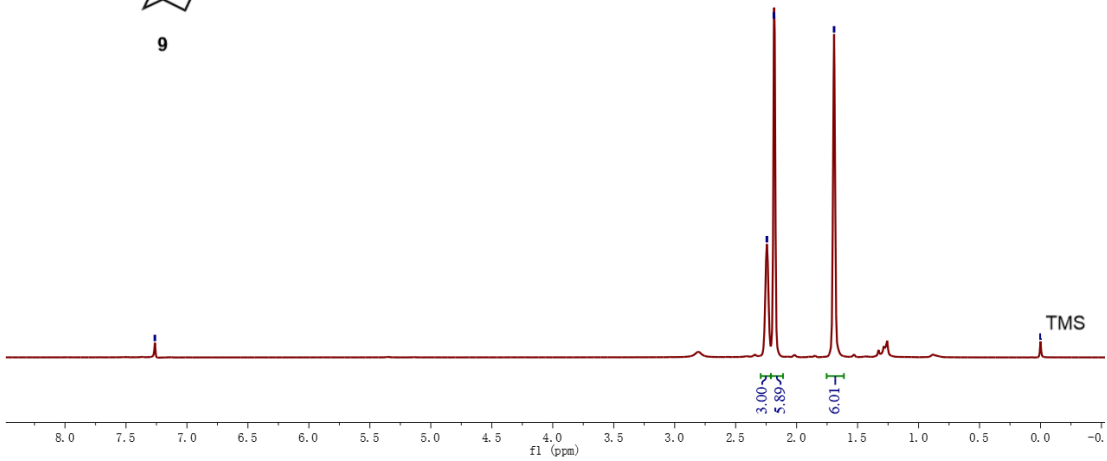
1.693



0.000

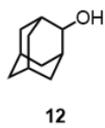


9



<sup>1</sup>H NMR of 10

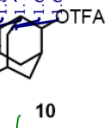
7.263



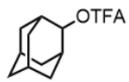
2.118  
2.043  
2.011

1.934  
1.900

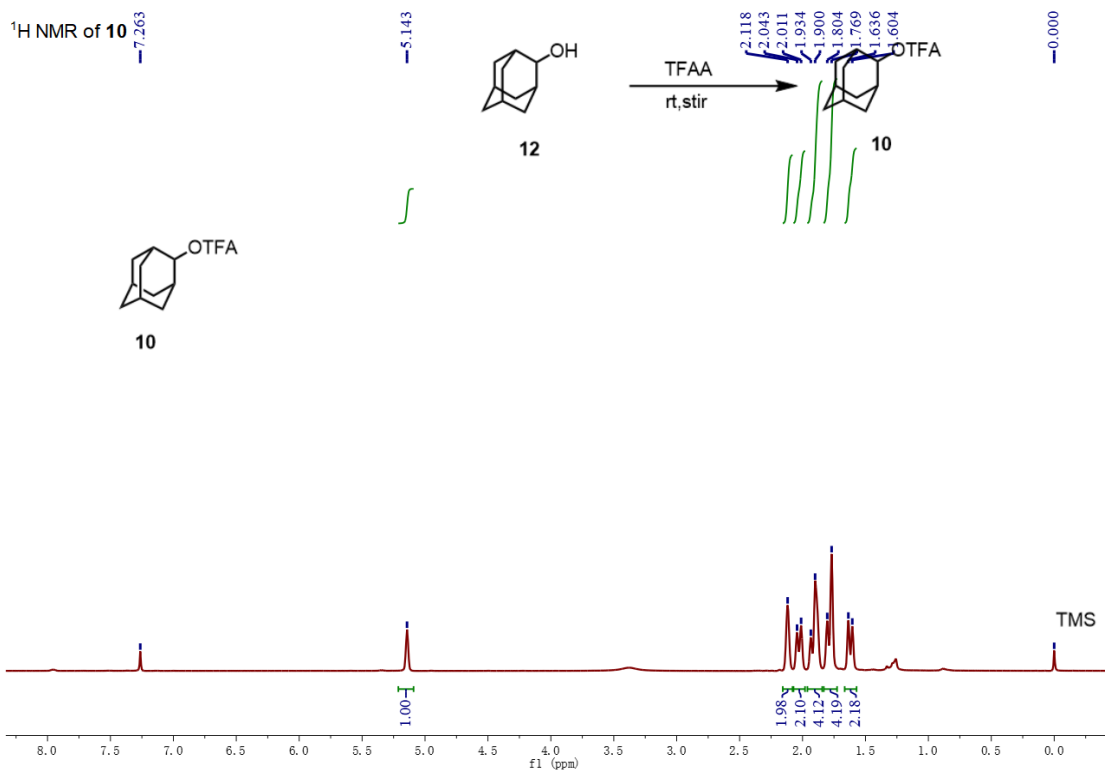
1.804  
1.769  
1.636  
1.604

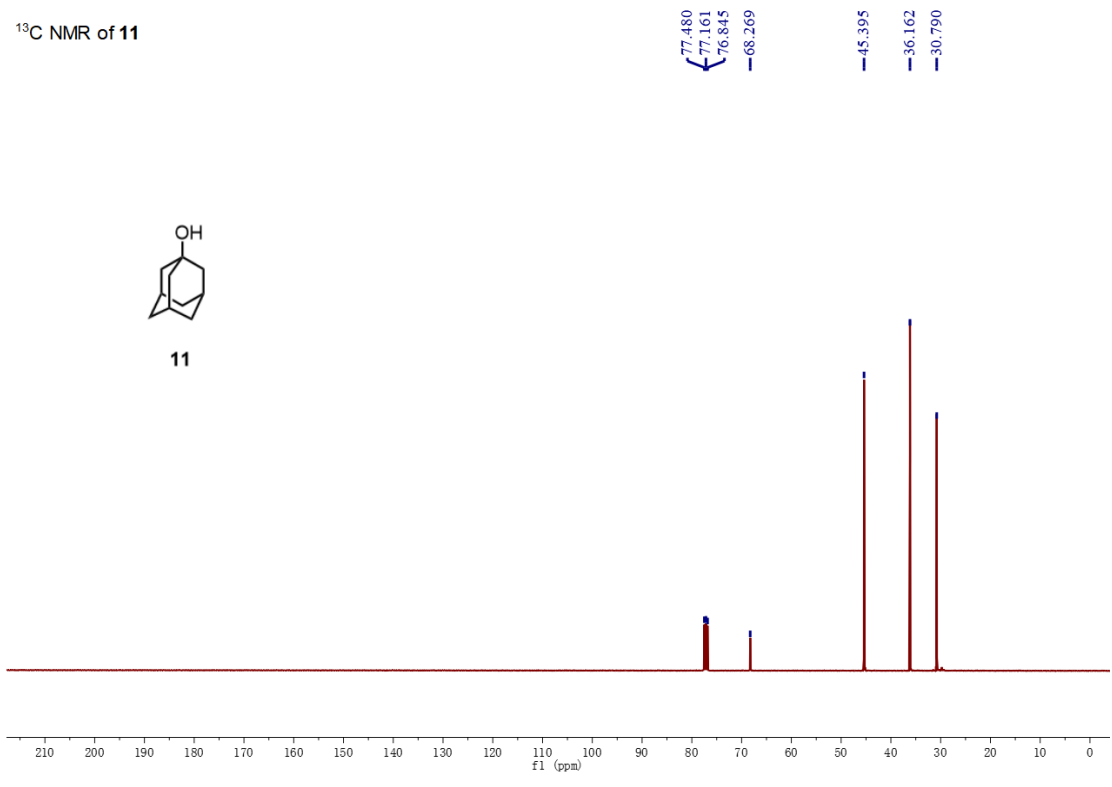
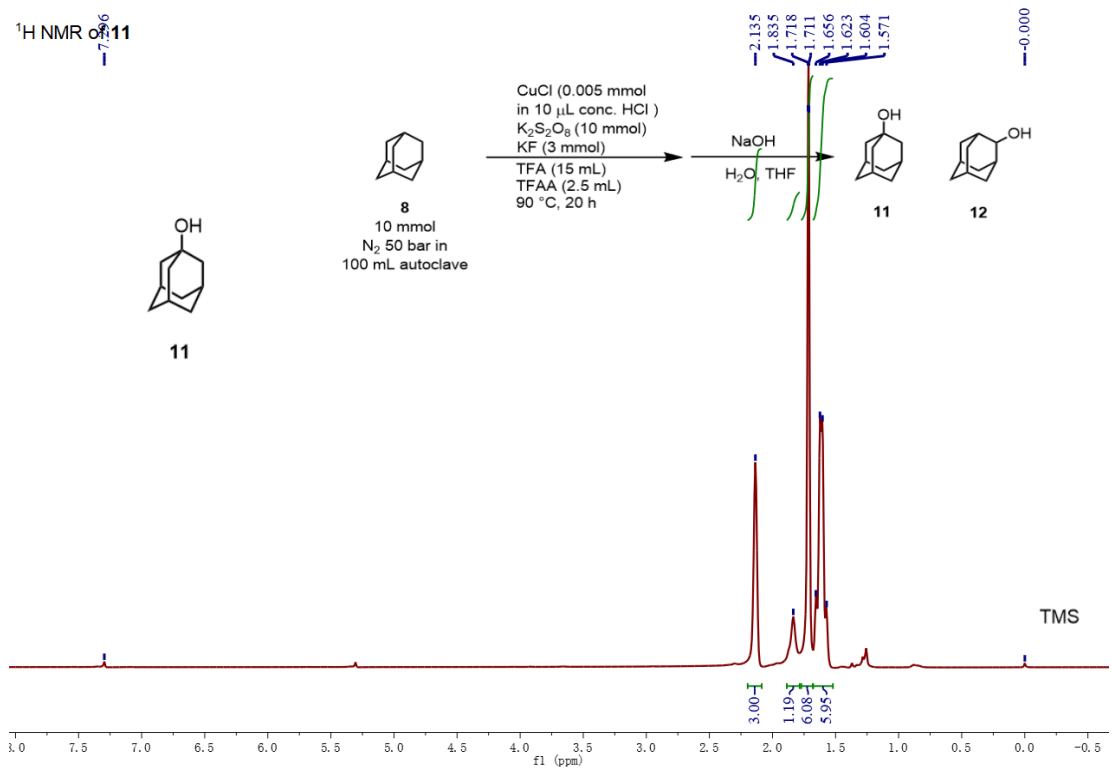


0.000

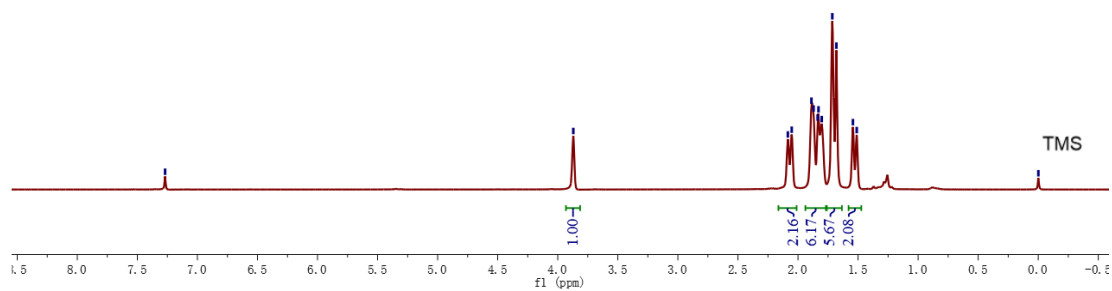
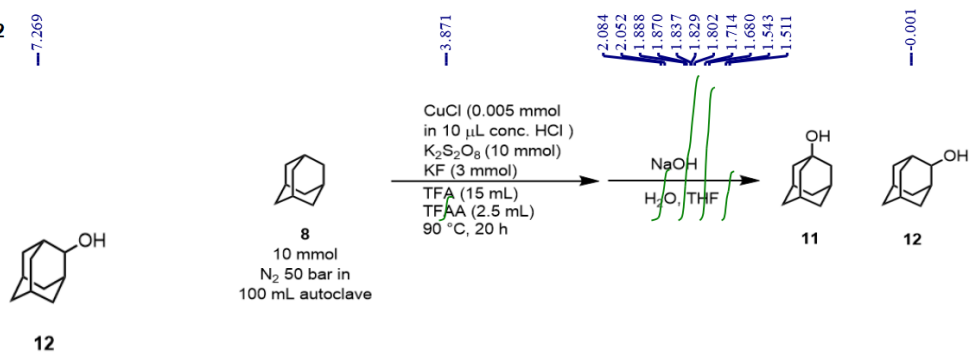


10

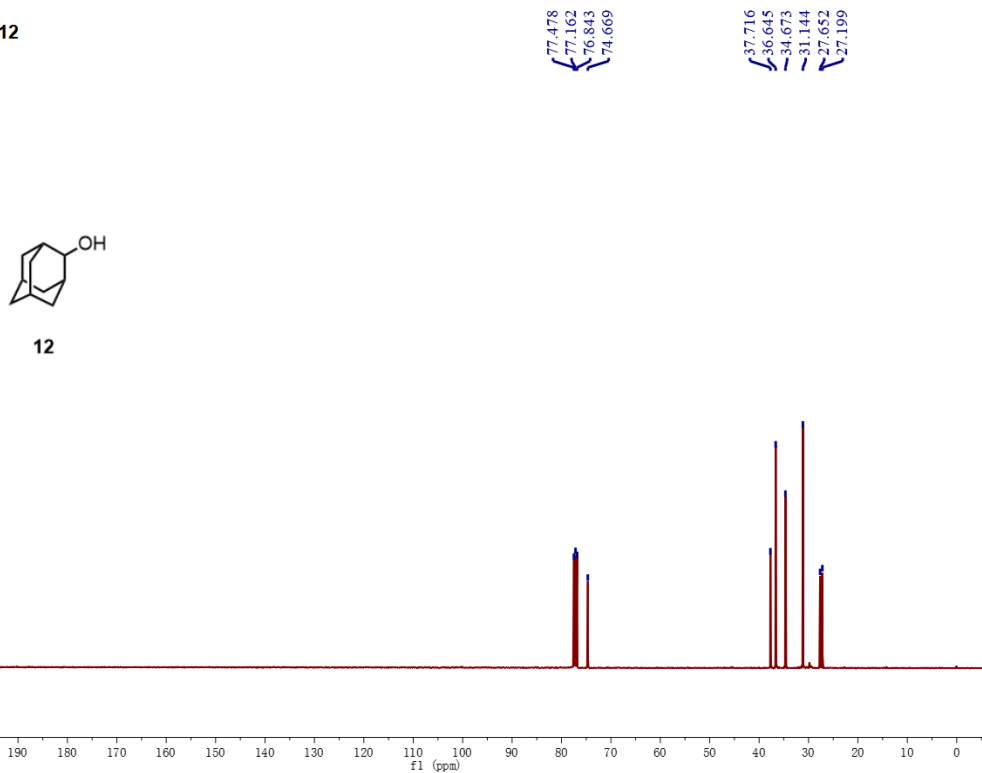




<sup>1</sup>H NMR of 12



<sup>13</sup>C NMR of 12





### **3. The Gas Phase Composition after Oxidation Reaction**

#### **All gas samples were tested in the following conditions:**

FID detector

Sample inject volume: 1.00 mL; column: GS-ALUMINA (length 50 m, diameter 0.53 mm); carrier gas: N<sub>2</sub> (8 mL/min).

TCD detector

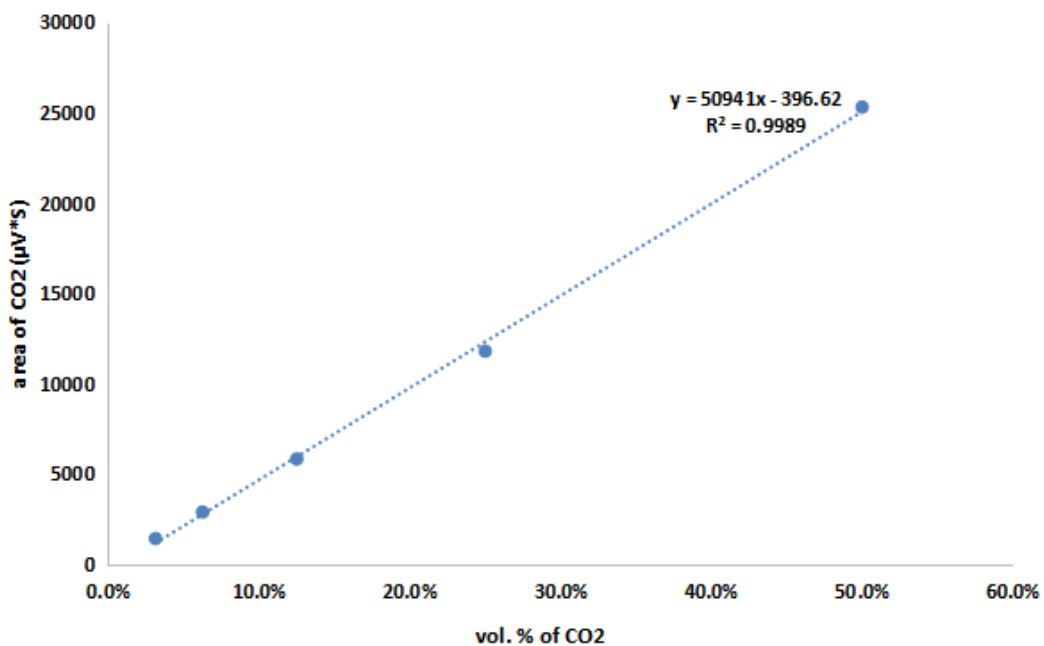
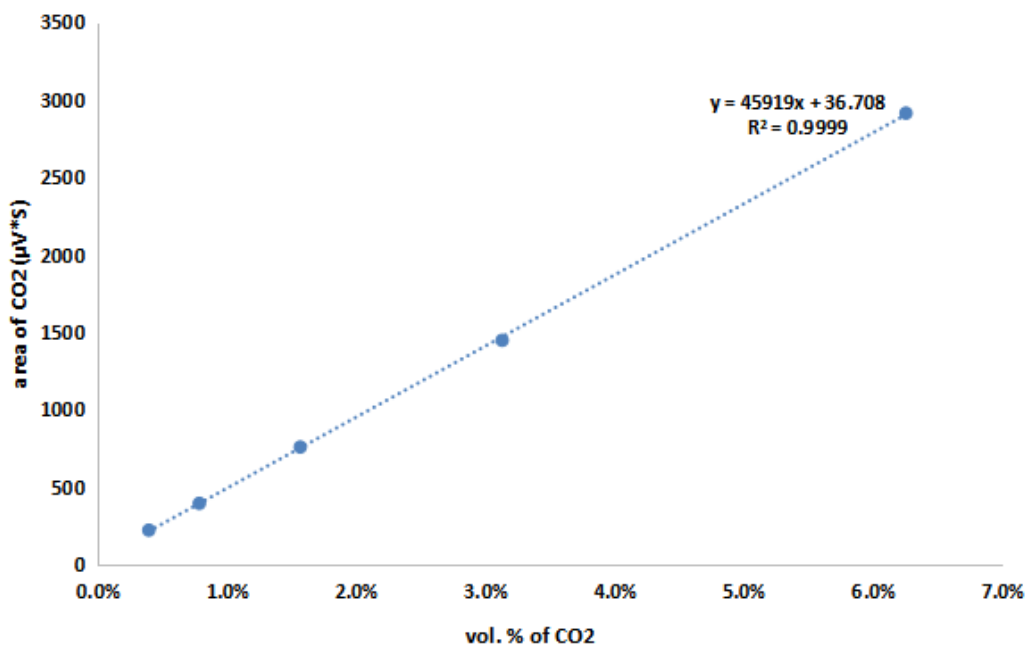
Sample inject volume: 0.25 mL; column: 8Ft 1/8 2mm Molsieve 5A 60/80 UM, 2Ft 1/8 2mm Unibeads 1S 60/80 UM, and 4Ft 1/8 2mm Unibeads 1S 60/80 UM; carrier gas: helium (5 PSI).

The same temperature program was used for both detectors.

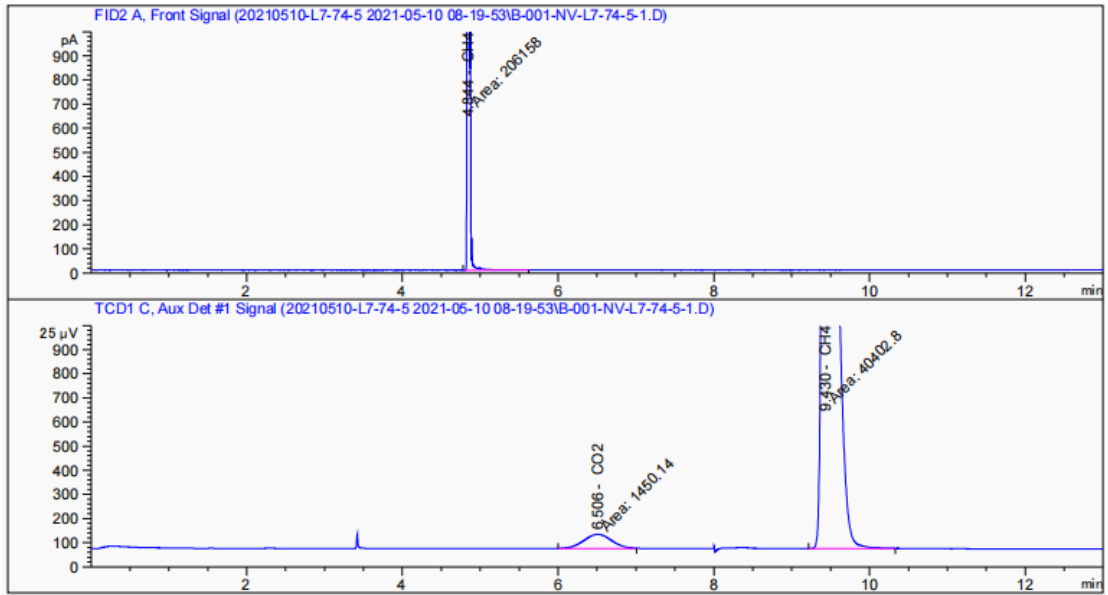
The oven temperature was initially kept at 70 °C for 8 min, then heated up to 190 °C (30 °C/min) and kept at 190 °C for 1 min. The FID detector was kept at 250 °C. The TCD detector was kept at 150 °C. The injection port was kept at 250 °C.

#### **The calibration curve of CO<sub>2</sub> volume content**

The calibration curve of CO<sub>2</sub> volume content was drawn according to the GC data of CO<sub>2</sub>/CH<sub>4</sub> with different concentrations. The different concentration of CO<sub>2</sub> in CH<sub>4</sub> was prepared as follow: 10 bar of CO<sub>2</sub> and 10 bar of CH<sub>4</sub> were filled into a 100 mL autoclave and stirred for 30 min. The gas mixture sample was tested on the GC instrument with FID detector for three times. The average area of CO<sub>2</sub> was corresponding to 50% volume content. Then half of the mixture was released when the pressure reduced to 10 bar. Another 10 bar of CH<sub>4</sub> were filled and the mixture was stirred for 30 min and tested for three times on the GC. Then the average area of CO<sub>2</sub> was corresponding to 25% volume content. Following the same procedure, the CO<sub>2</sub> in the autoclave was diluted to 12.5%, 6.25%, 3.125%, 1.5625%, 0.78125% volume content and the corresponding areas were measured on GC three times for each sample. Then the calibration curve of CO<sub>2</sub> volume content was draw according to the CO<sub>2</sub> volume content and corresponding average area of each gas sample on GC.



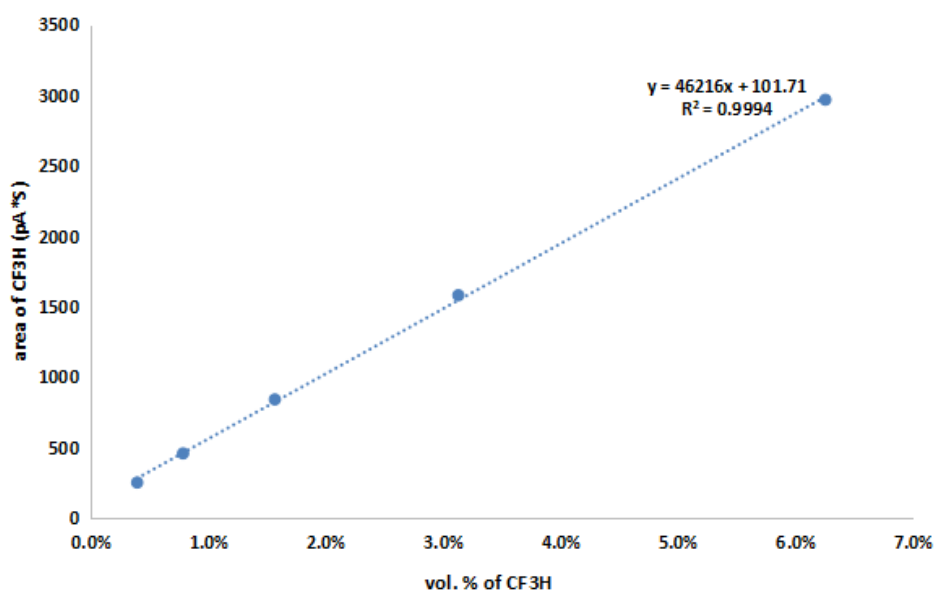
**Figure S27.** The calibration curve of CO<sub>2</sub> volume content ( $\leq 6.25\%$  and  $\geq 6.25\%$  are separated).



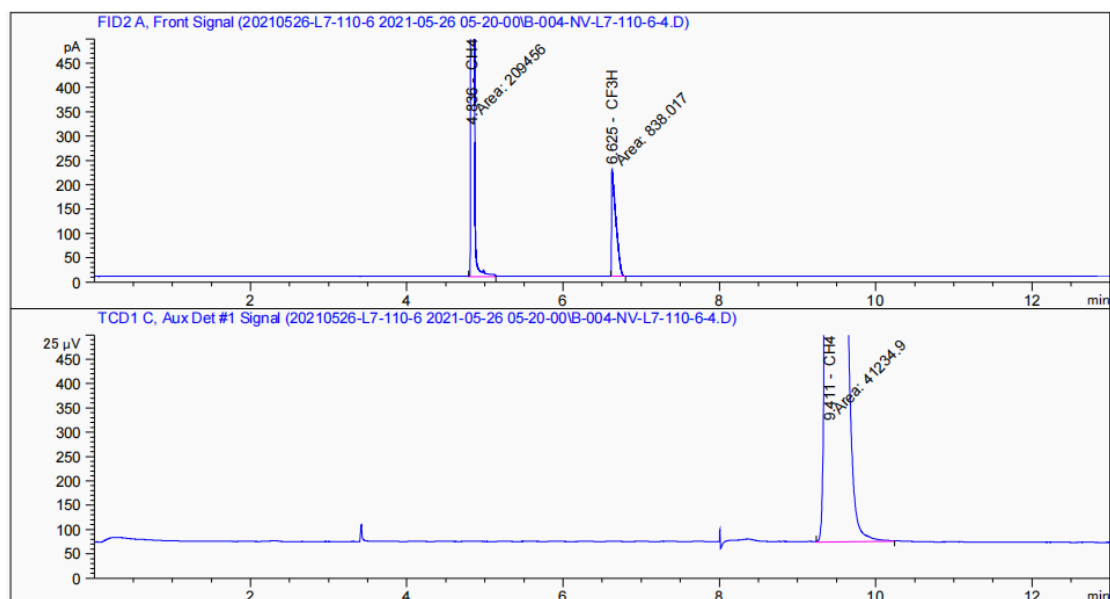
**Figure S28.** The Gas chromatogram of CO<sub>2</sub> in CH<sub>4</sub> (3.125% volume content) for the calibration curve of CO<sub>2</sub> volume content.

### The calibration curve of CF<sub>3</sub>H volume content

The curve was drawn according to the same procedure as CO<sub>2</sub>.



**Figure S29.** The calibration curve of CF<sub>3</sub>H volume content.



**Figure S30.** The Gas chromatogram of CF<sub>3</sub>H in CH<sub>4</sub> (1.5625% volume content) for the calibration curve of CF<sub>3</sub>H volume content.

### The calibration curve of C<sub>2</sub>F<sub>6</sub> volume content

The curve was drawn according to the same procedure as CO<sub>2</sub>.

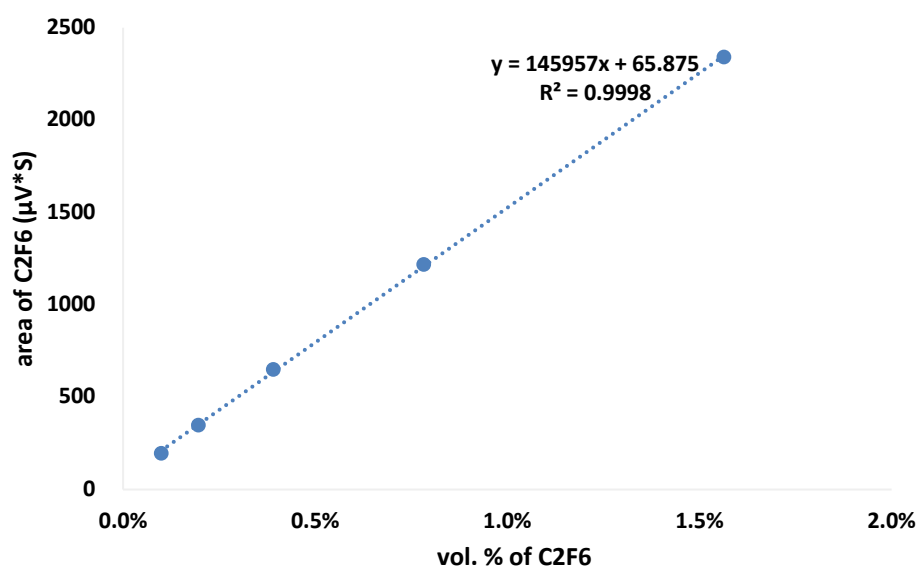


Figure S31. The calibration curve of C<sub>2</sub>F<sub>6</sub> volume content.

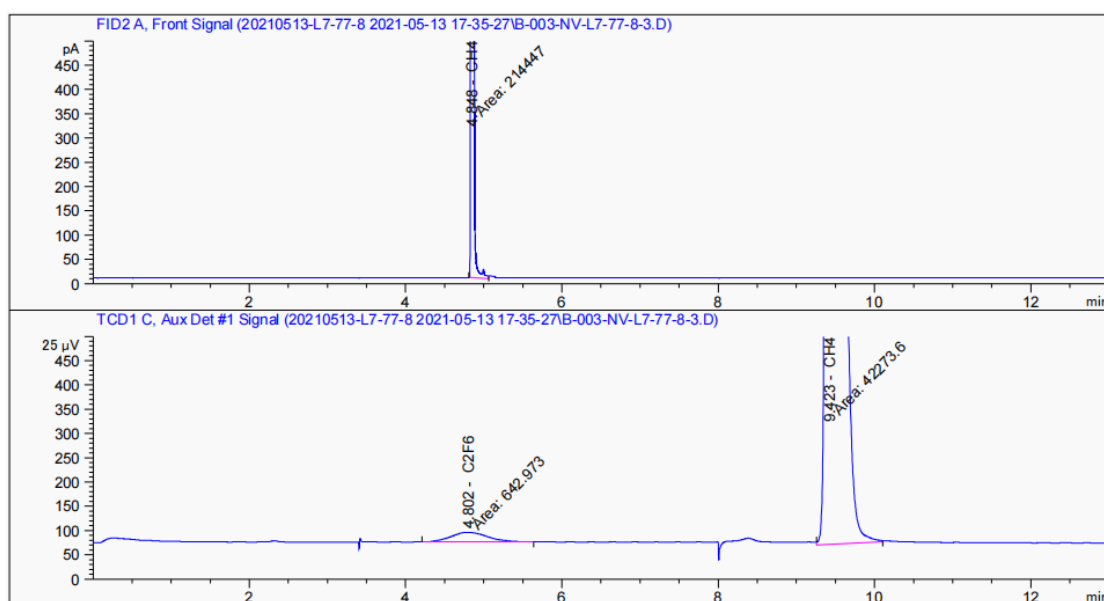
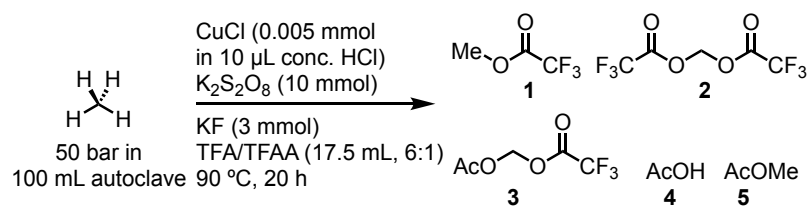
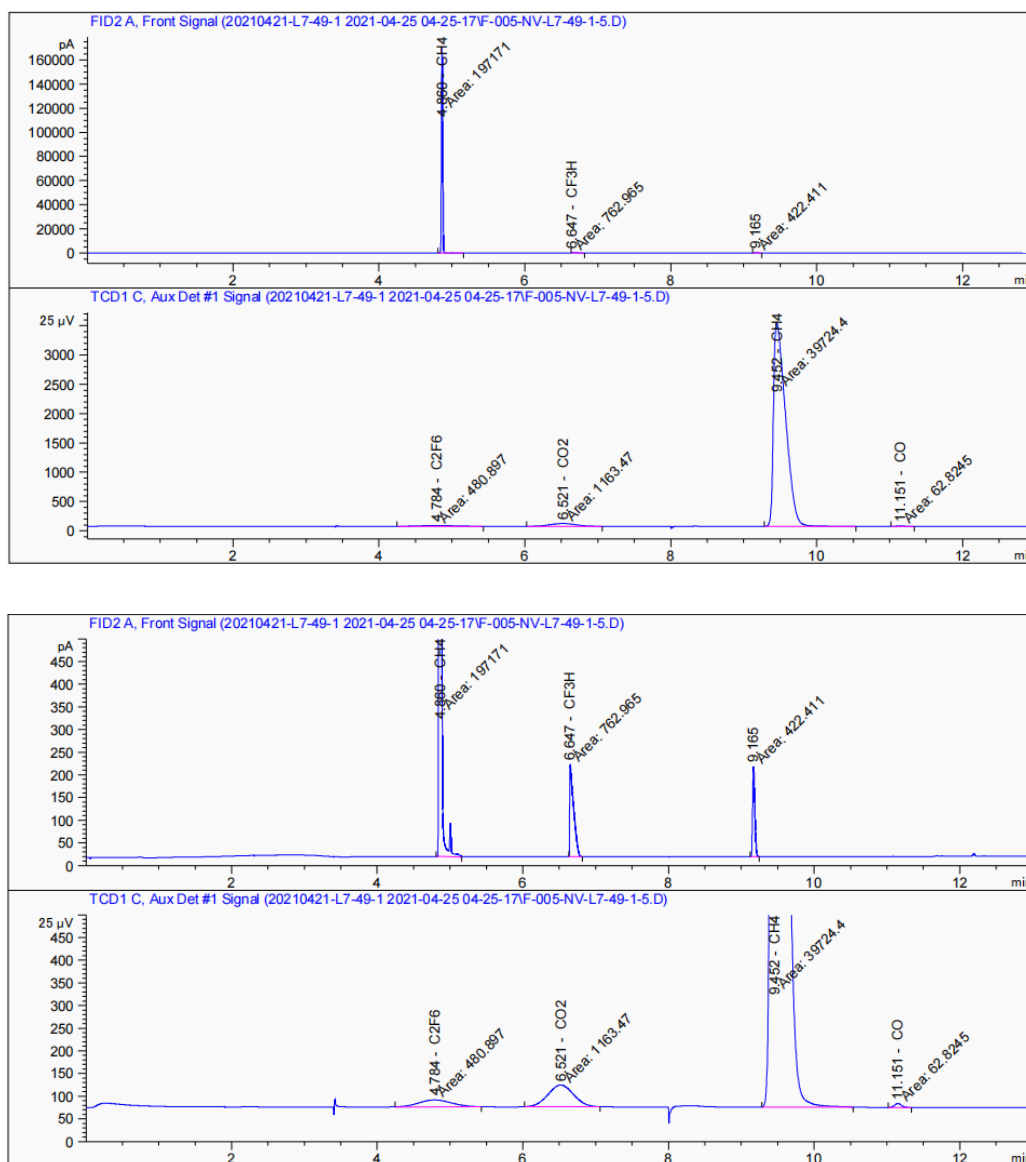


Figure S32. The Gas chromatogram of C<sub>2</sub>F<sub>6</sub> in CH<sub>4</sub> (0.390625% volume content) for the calibration curve of C<sub>2</sub>F<sub>6</sub> volume content.

### Gas Phase Composition Detection on GC after Oxidation Reaction (Table 3, entry 5)

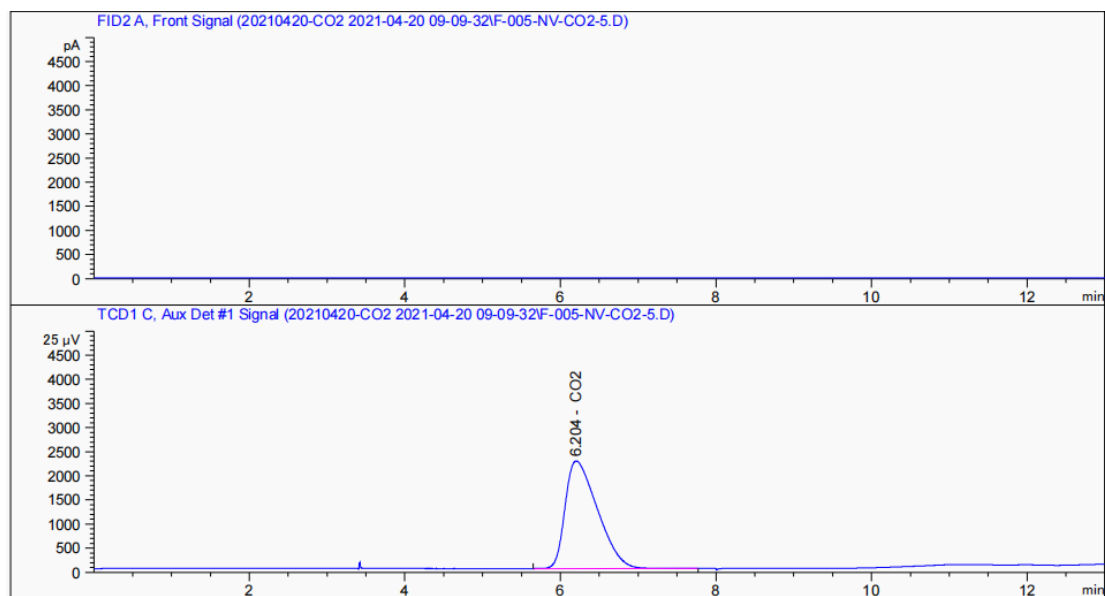


	Area	Vol. %
CO <sub>2</sub>	1163	2.45
CF <sub>3</sub> H	763	1.43
C <sub>2</sub> F <sub>6</sub>	481	0.28

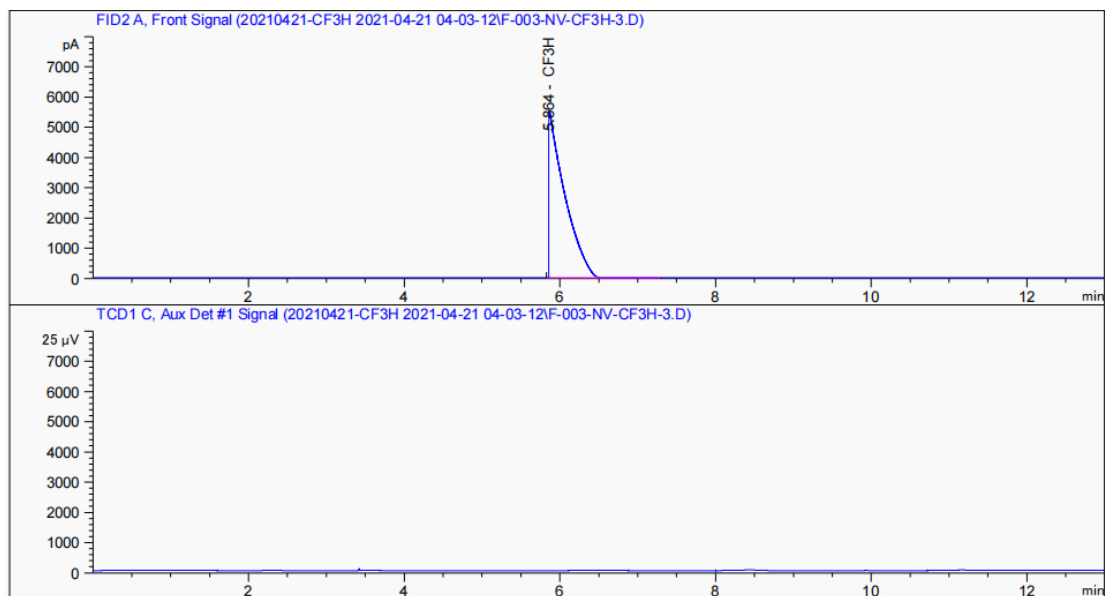


**Figure S33.** The Gas chromatogram of gas phase after oxidation reaction (Table 3, entry 5. Scaled up chromatogram is shown below).

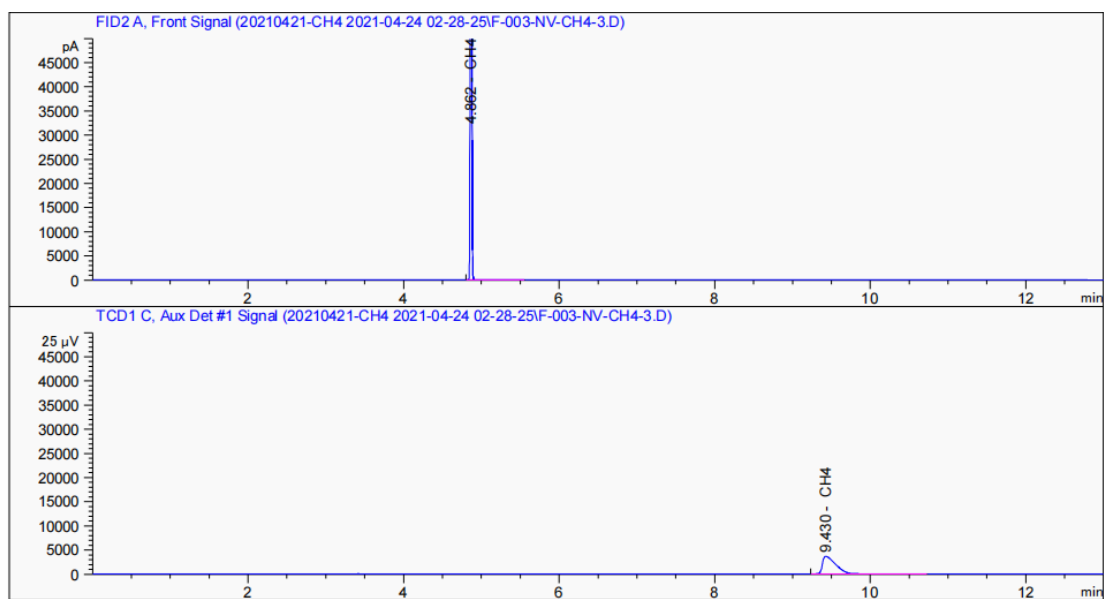
### Some GC Chromatogram of Standard Gases



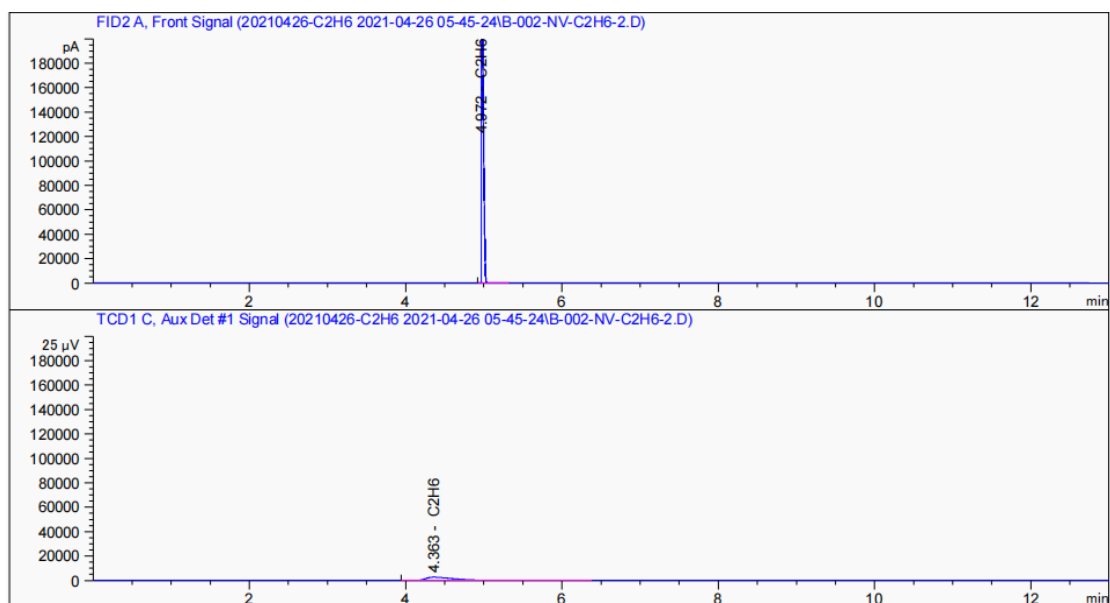
**Figure S34.** The Gas chromatogram of pure CO<sub>2</sub>.



**Figure S35.** The Gas chromatogram of pure CF<sub>3</sub>H.

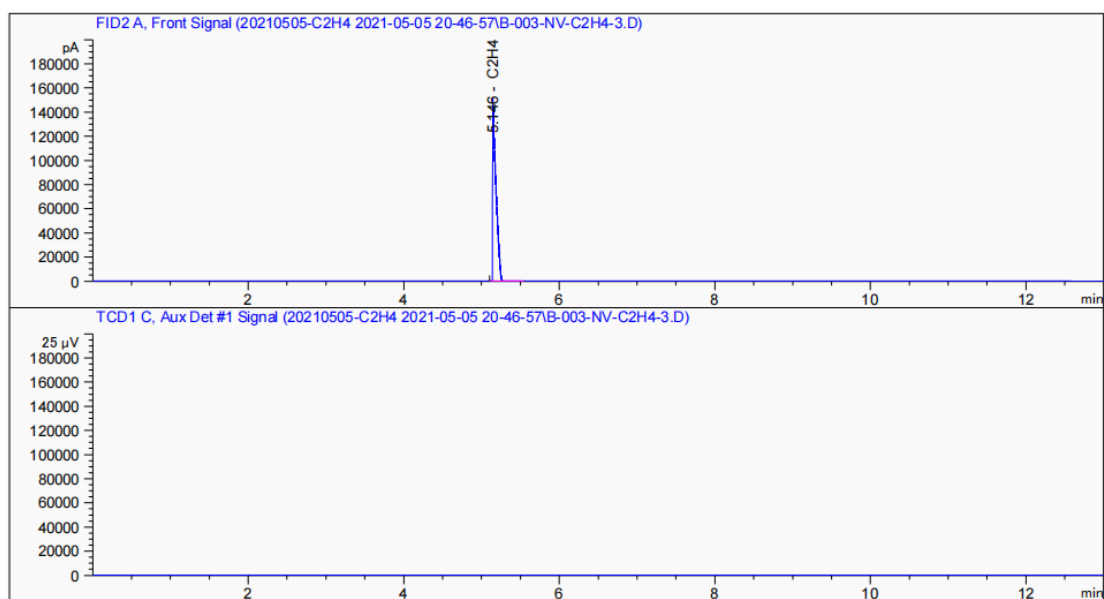


**Figure S36.** The Gas chromatogram of pure CH<sub>4</sub>.

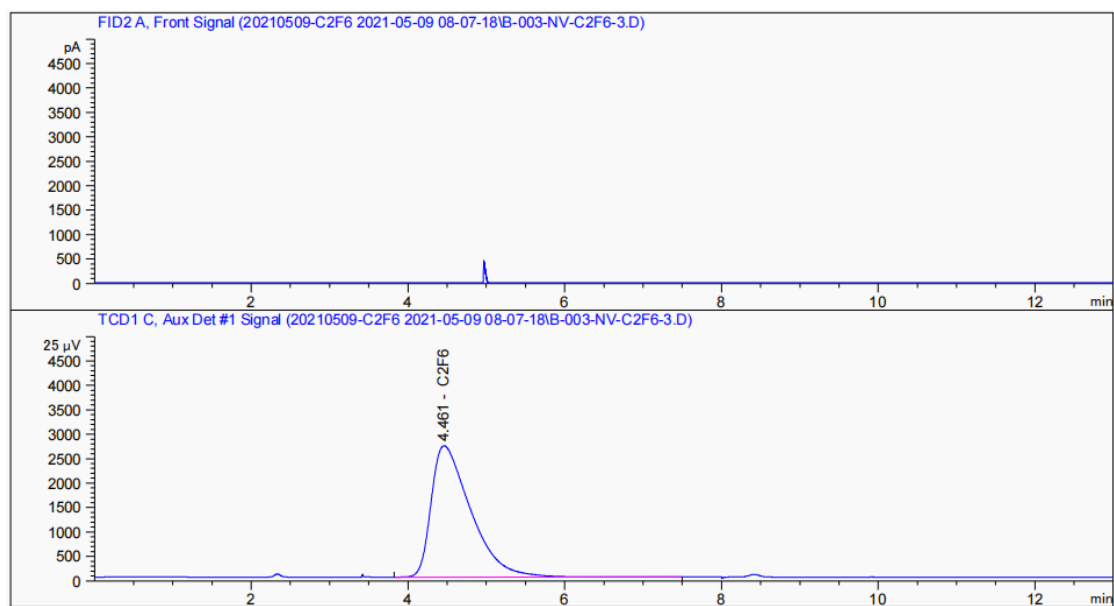


**Figure S37.** The Gas chromatogram of pure C<sub>2</sub>H<sub>6</sub>.

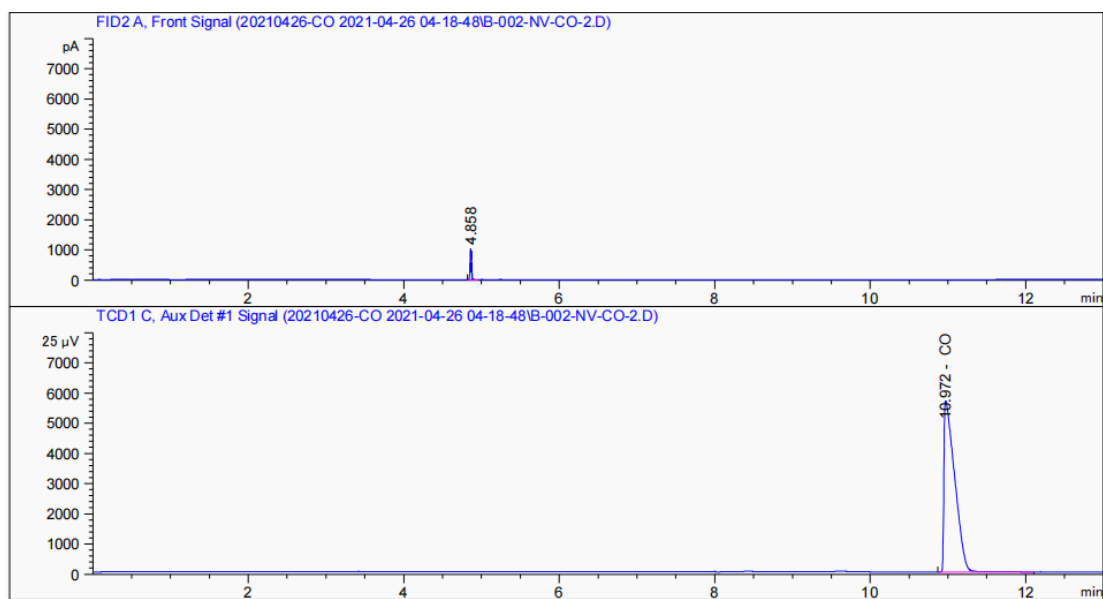




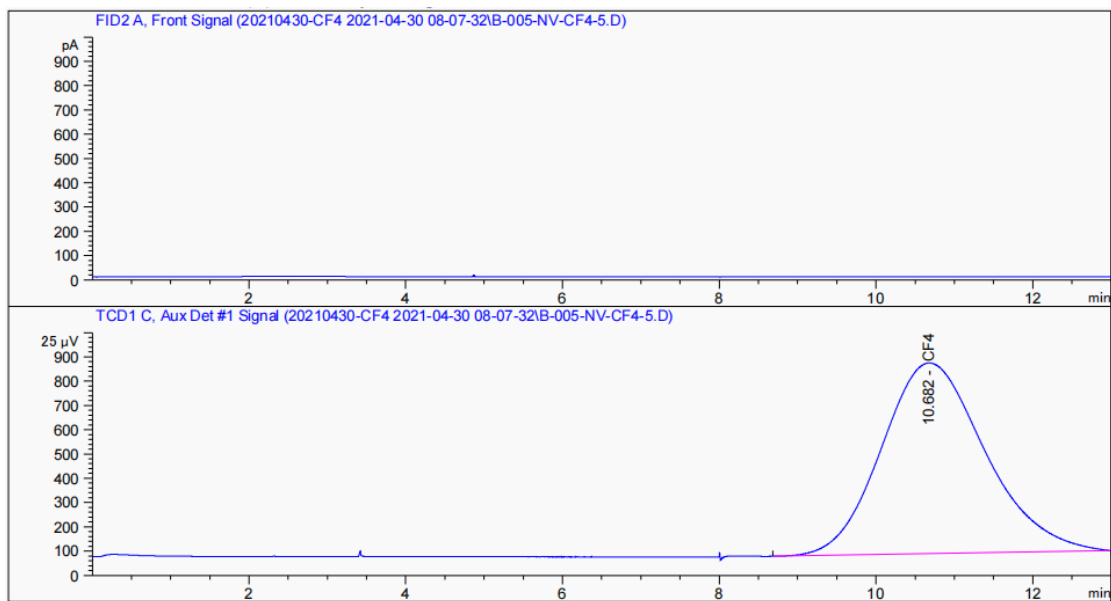
**Figure S38.** The Gas chromatogram of pure  $C_2H_4$ .



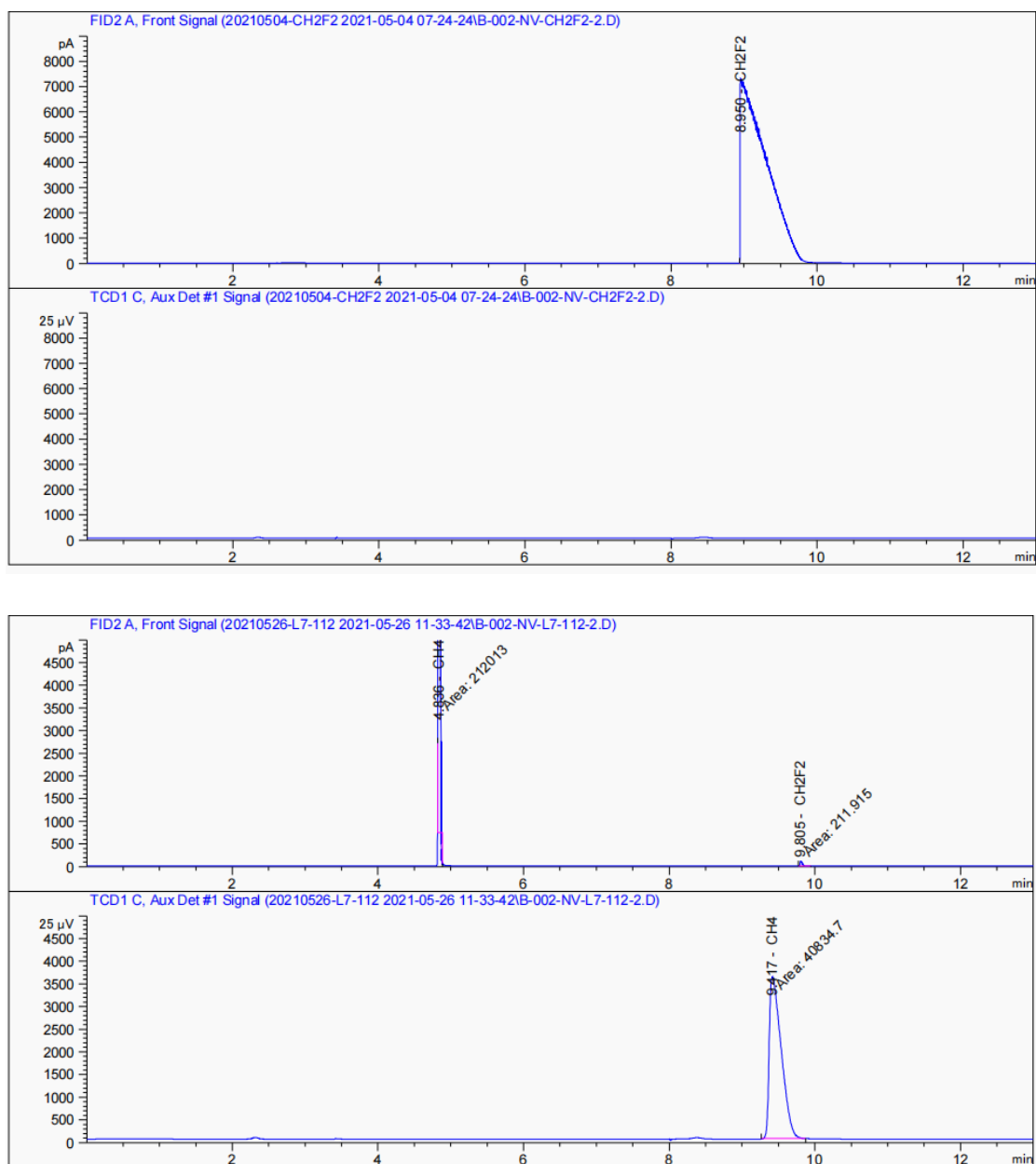
**Figure S39.** The Gas chromatogram of pure  $C_2F_6$ .



**Figure S40.** The Gas chromatogram of pure CO.



**Figure S41.** The Gas chromatogram of pure CF<sub>4</sub>.



**Figure S42.** The Gas chromatogram of CH<sub>2</sub>F<sub>2</sub>. Above: in pure form; Below: diluted in methane.