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Supporting Information
For

Partial Oxidation of Light Hydrocarbons using Periodate and Chloride Salts

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General Considerations. All reactions were setup in air. Trifluoroacetic acid, potassium periodate, ammonium iodate and potassium chloride were purchased from a commercial vendor and used as received. Methane, ethane and propane were purchased from GTS-Welco. ^{1}H NMR spectra were recorded on a Bruker 600 MHz, a Bruker 800 MHz or a Varian 500 MHz spectrometer. NMR spectra were taken in neat HTFA with a capillary of C_6D_6 as an internal lock reference. Chemical shifts for ^{1}H NMR are reported relative to the internal standards of HOAc (δ 2.04) or dichloromethane (DCM) (δ 5.03). All reactions were performed in house-built high-pressure reactors constructed primarily with stainless steel pieces from Swagelock. The reaction solutions were held in fabricated Teflon liners. The average volume of the reactors with the liner inserted is 16.1 mL. Reactions were stirred using 1.2 cm long rod-shaped stir bars. Reaction temperatures were maintained through inductive heat transfer from tight-fitting custom aluminum blocks. The initial moles of gas reported were determined by weighing the reactor before and after pressurization. Due to some variations, the mass of gas was averaged from at least 3 separate reactions. The exception to this procedure is when the mass of gas added is too small within the deviation of the balance used (See Determination of mmol Methane for 860 kPa below for more details, p. S10). All amounts of functionalized products are the result of averaging at least 3 independent runs.

General Procedure for Methane Functionalization with Periodate and Chloride. A stir bar, KIO_4, KCl and 8.0 mL HTFA were loaded into a tight-fitting Teflon liner. After the reactor was sealed and weighed, it was purged twice with CH_4 by pressurizing and slowly venting. The reactor was pressurized a third time with stirring for ~30 sec. After venting the reactor slowly, it was re-pressurized again with the appropriate pressure of CH_4 while stirring for 30 sec. The reactor was weighed again to quantify the mass of CH_4 added (for 860 kPa, the reactor was brought to a total pressure of ~3450 kPa using Ar at this point), and subsequently placed in a preheated aluminum block at the appropriate temperature. The reactor was stirred (800 rpm) at this temperature for 1 h. After this, it was removed from the heating block and placed in front of a fan for 30 min to cool to room temperature. The reactor was vented and then opened. HOAc was added as a standard and the contents were allowed to stir. An aliquot was removed, centrifuged, placed in an NMR tube containing a capillary filled with C_6D_6 and analyzed by ^{1}H NMR spectroscopy.

Data for Methane Functionalization with Periodate and Chloride

General Conditions:
Gas: Methane
HTFA (mL): 8.0
Stirring: 800 rpm
Time: 1 h

T (°C)	P (kPa)	KIO_4 (mmol)	KCl (mmol)	**MeTFA (mmol)**	**MeTFA (dev)**	**MeCl (mmol)**	**MeCl (dev)**	**N**
150	3450	7.7	.67	**.063**	**.0053**	**.056**	**.013**	**3**
160	3450	7.7	.67	**.12**	**.02**	**.14**	**.01**	**3**
170	3450	7.7	.67	**.34**	**.11**	**.12**	**.02**	**3**
180	3450	7.7	.67	**.81**	**.11**	**.10**	**.02**	**3**
190	3450	7.7	.67	**1.05**	**.16**	**.10**	**.003**	**3**
200	3450	7.7	.67	**1.55**	**.16**	**.10**	**.02**	**3**
210	3450	7.7	.67	**1.56**	**.20**	**0.09**	**.02**	**3**
220	3450	7.7	.67	**1.62**	**.13**	**.074**	**.005**	**3**
200	3450	7.7	0	**0.19**	**.06**	**n.d.**	**n.d.**	**3**
200	3450	7.7	.33	**.49**	**.05**	**.07**	**.006**	**3**
200	3450	7.7	1.0	**1.61**	**.27**	**.12**	**.04**	**3**
200	3450	7.7	1.3	**1.68**	**.44**	**.16**	**.04**	**4**
200	2070	7.7	.67	**1.24**	**.25**	**.096**	**.020**	**3**
200	4830	7.7	.67	**1.06**	**.20**	**.15**	**.01**	**4**
200	6200	7.7	.67	**1.11**	**.28**	**.17**	**.01**	**3**
200	3450	12	1.4	**2.25**	**.11**	**.19**	**.02**	**3**
200	3450	18	2.1	**2.49**	**.04**	**.16**	**.03**	**3**
200	2070	12	1.4	**1.33**	**.32**	**.15**	**.06**	**3**
200	3450	4.0	.47	**.90**	**.05**	**.074**	**.005**	**3**
200	860	12	1.4	**1.07**	**.14**	**.039**	**.021**	**3**
200	860	7.7	0.67	**1.18**	**.01**	**.03**	**0**	**3**
200	3450	15	1.8	**1.98**	**.54**	**.25**	**.05**	**3**

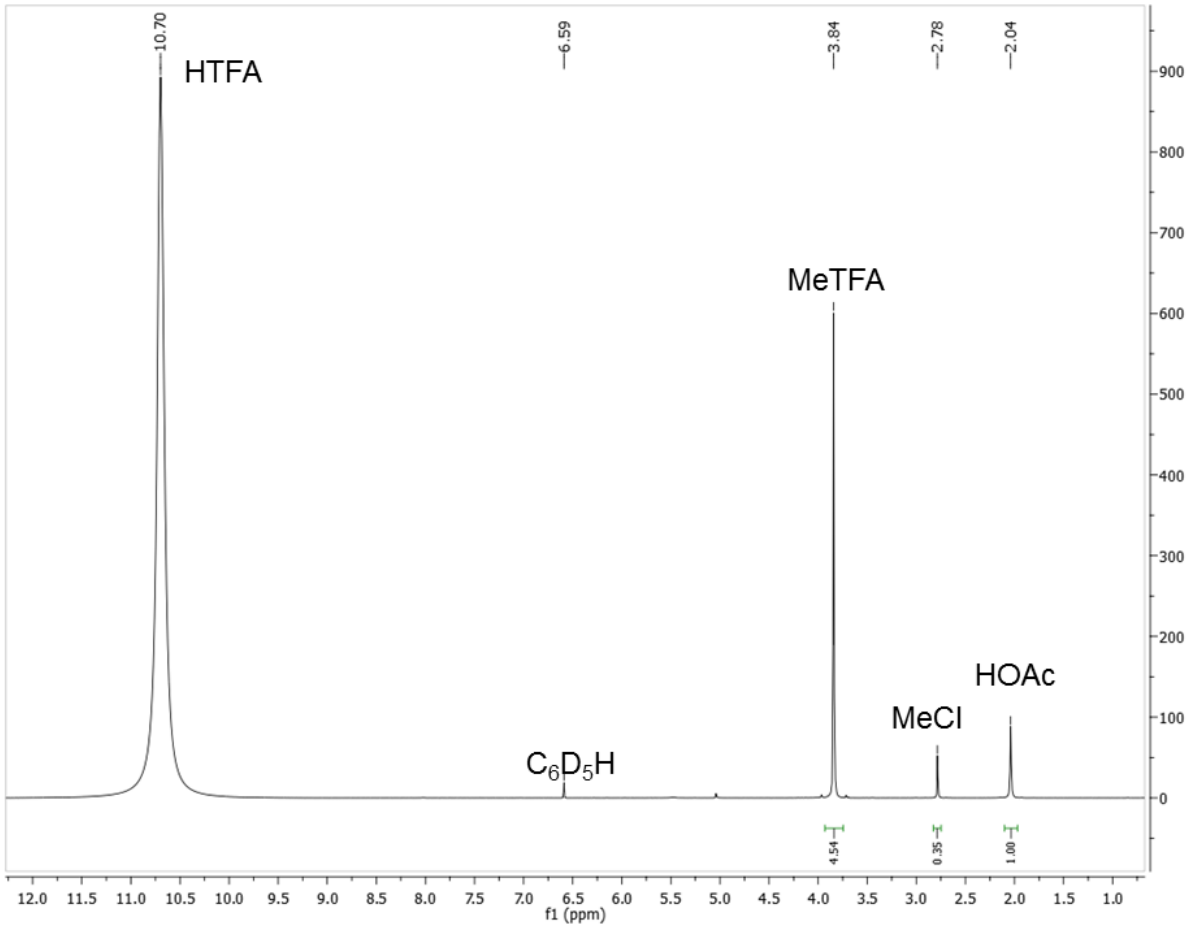

Figure S1. Sample ^{1}H NMR Spectrum with Assignments for Methane Functionalization with Periodate/Chloride.

General Procedure for Ethane Functionalization with Periodate and Chloride. A stir bar, KIO_4, KCl and 8.0 mL HTFA were loaded into a tight-fitting Teflon liner. After the reactor was sealed and weighed, it was purged twice with C_2H_6 by pressurizing and slowly venting. The reactor was pressurized a third time with stirring for ~30 sec. After venting the reactor slowly, it was re-pressurized again with the appropriate pressure of C_2H_6 while stirring for 30 sec. The reactor was weighed again to quantify the mass of C_2H_6 added, and subsequently placed in a preheated aluminum block at 200°C. The reactor was stirred (800 rpm) at this temperature for 1 h. After this, it was removed from the heating block and placed in front of a fan for 30 min to cool to room temperature. The reactor was vented and then opened. DCM was added as a standard and the contents were allowed to stir. An aliquot was removed, centrifuged, placed in an NMR tube containing a capillary filled with C_6D_6 and analyzed by ^{1}H NMR spectroscopy.

Data for Ethane Functionalization with Periodate/Chloride

General Conditions
Reaction Gas: Ethane
Pressure: 2070 kPa
Temp.: 200 °C
HTFA (mL): 8.0
Stirring: 800 rpm
Time: 1 h

KIO_4 (mmol)	KCl (mmol)	**EtTFA (mmol)**	**EtTFA (dev)**	**EtCl (mmol)**	**EtCl (dev)**	**Glycol (mmol)**	**Glycol (dev)**	**N**
7.7	.67	**0.95**	**.23**	**.29**	**.03**	**.022**	**.005**	**3**
12	1.4	**1.30**	**.33**	**.50**	**.15**	**.023**	**.004**	**3**

*Also observed trace (<0.02 mmol) 1,2-dichloroethane

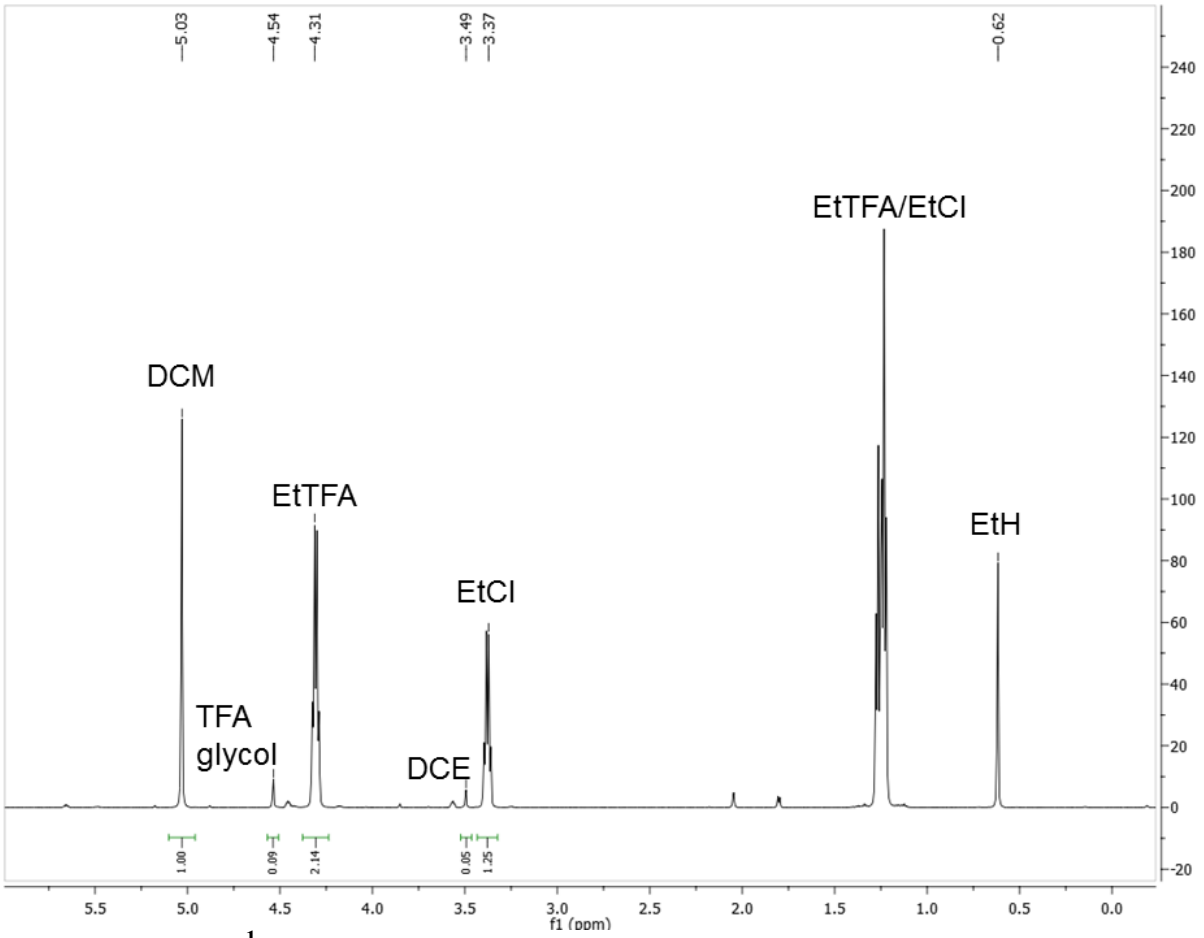

Figure S2. Sample ^{1}H NMR Spectrum with Assignments for Ethane Functionalization with Periodate/Chloride.

General Procedure for the Functionalization of Propane using Periodate and Chloride. A stir bar, KIO_4 (5.2 mmol), KCl (0.61 mmol) and 8.0 mL HTFA were loaded into a tight-fitting Teflon liner. After the reactor was sealed and weighed, it was purged twice with C_3H_8 by pressurizing and slowly venting. The reactor was pressurized a third time with stirring for ~10 sec. After venting the reactor slowly, it was re-pressurized again with 660 kPa of C_3H_8 while stirring for 10 sec. The reactor was weighed again to quantify the mass of C_3H_8 added. To the reactor was added Ar to bring the pressure to 2070 kPa. The reactor was subsequently placed in a preheated aluminum block at 200 °C. The reactor was stirred (800 rpm) at this temperature for 0.5 h. After this, it was removed from the heating block and placed in front of a fan for 30 min to cool to room temperature. The reactor was vented and then opened. HOAc was added as a standard and the contents were allowed to stir. An aliquot was removed, centrifuged, placed in an NMR tube containing a capillary filled with C_6D_6 and analyzed by ^{1}H NMR spectroscopy.

Data for Propane Functionalization with Periodate/Chloride

General Conditions
Reaction Gas: Propane
Pressure: 660 kPa
KIO_4(mmol): 5.2
KCl (mmol): 0.61
Temp.: 200 °C
HTFA (mL): 8.0
Stirring: 800 rpm
Time: 0.5 h

nPrTFA (mmol)	nPrTFA (dev)	iPrTFA (mmol)	iPrTFA (dev)	1,2-diTFA (mmol)	1,2-diTFA (dev)	nPrCl (mmol)	nPrCl (dev)	N
0.20	**.04**	**0.47**	**.10**	**.19**	**.05**	**.10**	**.01**	**3**

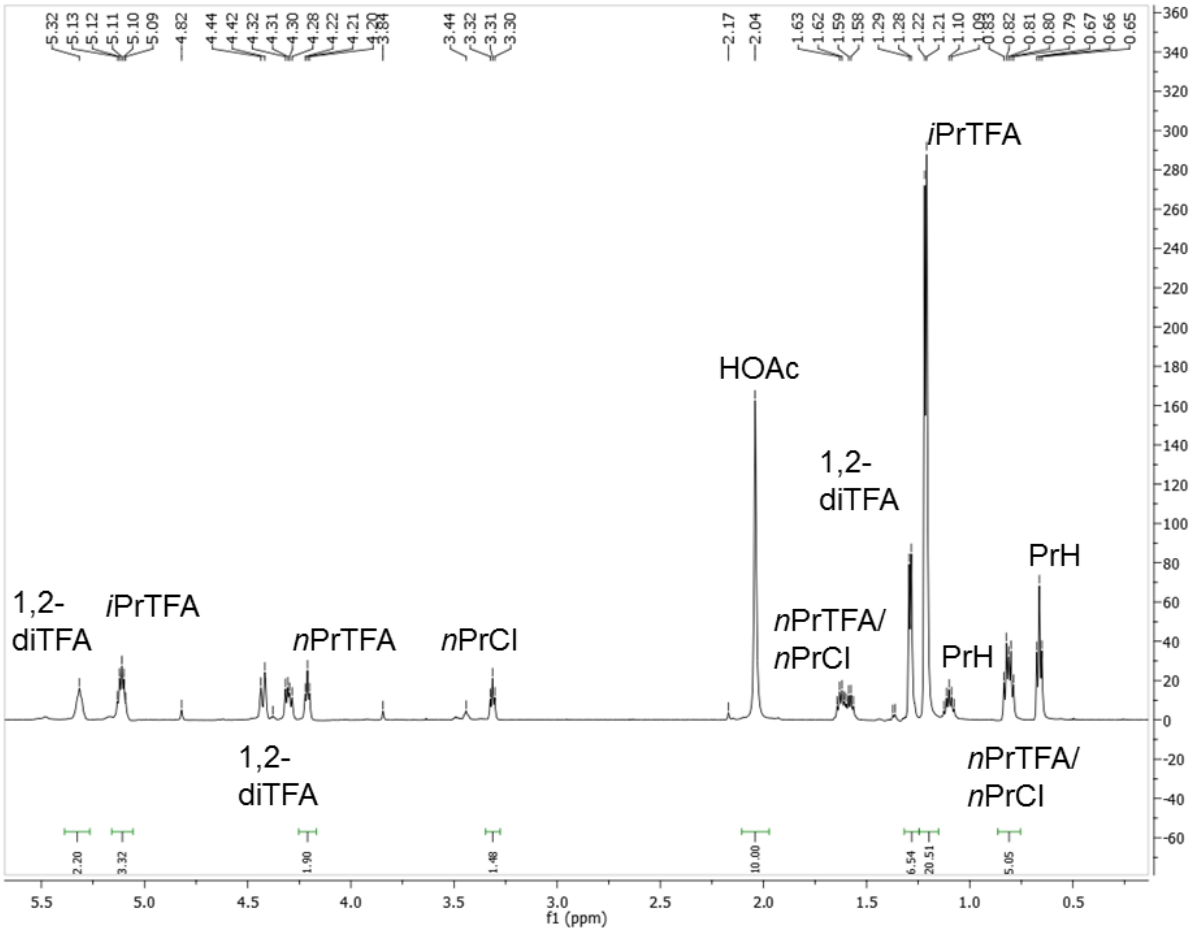

Figure S3. Sample ^{1}H NMR Spectrum with Assignments for Propane Functionalization with Periodate/Chloride.

General Procedure for Methane Functionalization with Iodate and Chloride. A stir bar, NH_4IO_3, KCl and 8.0 mL HTFA were loaded into a tight-fitting Teflon liner. After the reactor was sealed and weighed, it was purged twice with CH_4 by pressurizing and slowly venting. The reactor was pressurized a third time with stirring for ~30 sec. After venting the reactor slowly, it was re-pressurized again with 3450 kPa of CH_4 while stirring for 30 sec. The reactor was weighed again to quantify the mass of CH_4 added, and subsequently placed in a preheated aluminum block at 200 °C. The reactor was stirred (800 rpm) at this temperature for 1 h. After this, it was removed from the heating block and placed in front of a fan for 30 min to cool to room temperature. The reactor was vented and then opened. HOAc was added as a standard and the contents were allowed to stir. An aliquot was removed, centrifuged, placed in an NMR tube containing a capillary filled with C_6D_6 and analyzed by ^{1}H NMR spectroscopy.

Data for Methane Functionalization with Iodate and Chloride

General Conditions
Reaction Gas: Methane
Temp.: 200 °C
HTFA (mL): 8.0
Stirring: 800 rpm
Time: 1 h

NH_4IO_3 (mmol)	KCl (mmol)	CH_4 (kPa)	**MeTFA (mmol)**	**MeTFA (dev)**	**MeCl (mmol)**	**MeCl (dev)**	**N**
7.7	.67	3450	**2.22**	**.10**	**.054**	**.008**	**3**
12	1.4	3450	**2.41**	**.15**	**.063**	**0**	**3**
7.7	.67	862	**0.80**	**0.03**	**0.02**	**0.003**	**3**

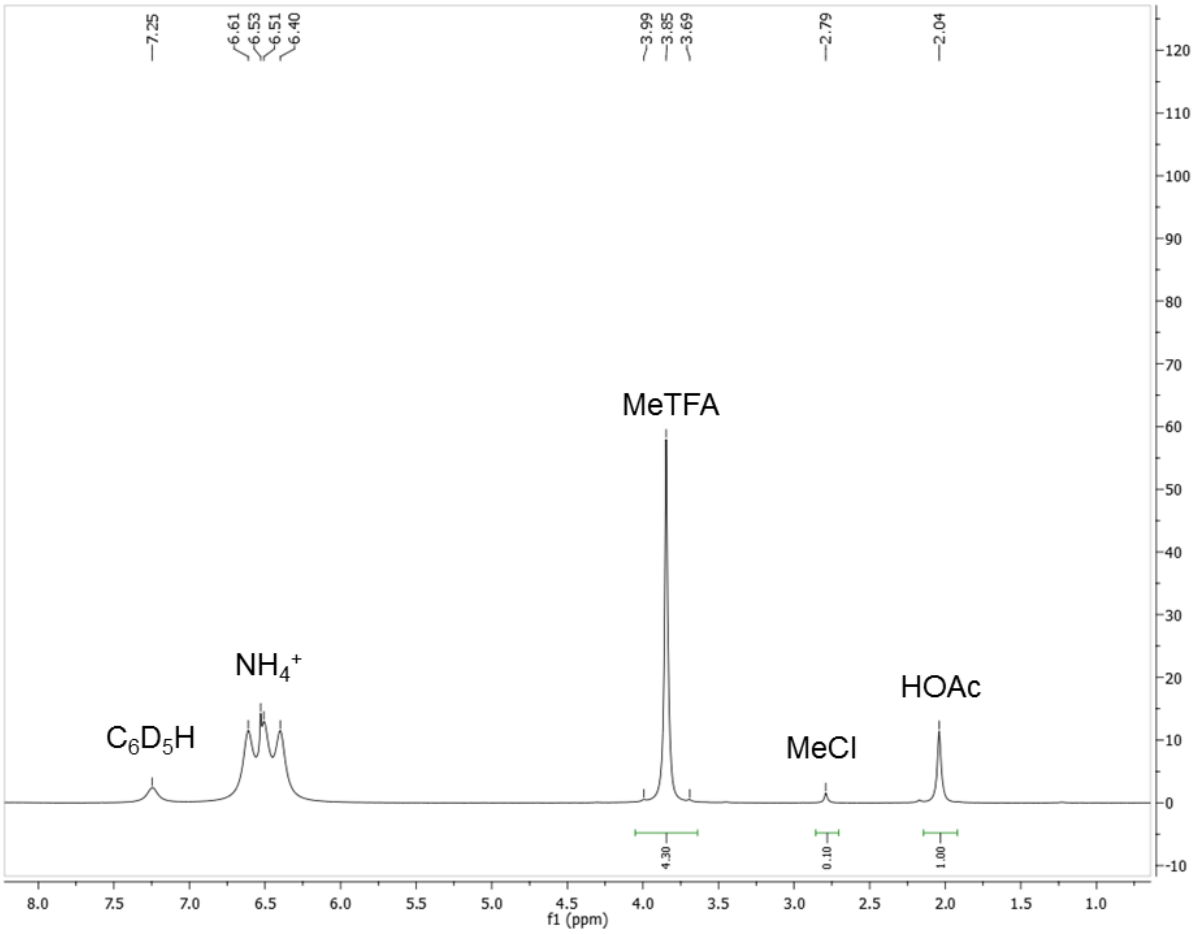

Figure S4. Sample ^{1}H NMR Spectrum with Assignments for Methane Functionalization with Iodate/Chloride.

Determination of mmol of Methane for 860 kPa

Across the range of pressures used in this study, methane pressure appears to follow Henry's Law and the ideal gas law (Figure S5). Due to deviations in the balance for small differences in mass, the following graph (Figure S5) was used to calculate the mmol of methane (2.9 mmol) added for reactions with 860 kPa of methane. The trend line was forced through (0,0).

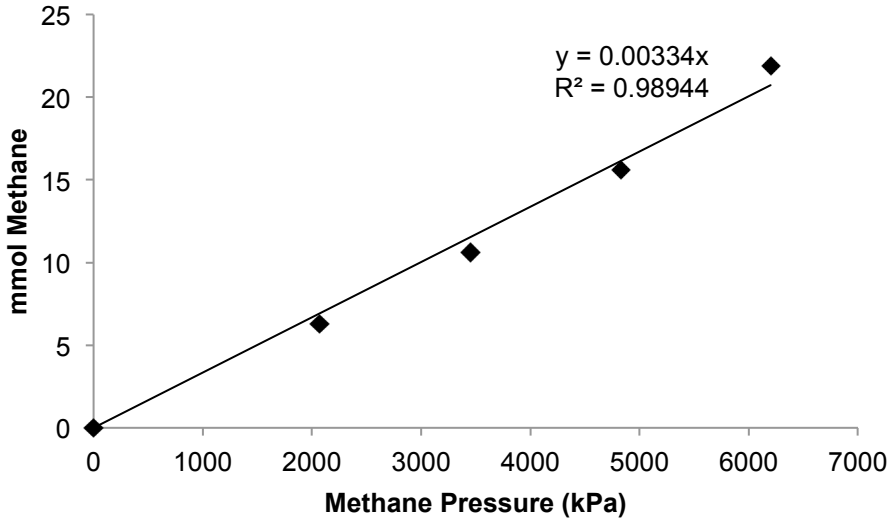

Figure S5. Plot of mmol of methane (as determined by mass) vs initial methane pressure.