Supporting Information to Investigation of Partial Oxidation of Methane in a Cold Plasma Reactor with Detailed Product Analysis

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1 Numerical Data

Table S 1 lists the process parameters and the electrical parameters of all individual experiments conducted in this work and the corresponding conversions X_j of methane (CH_4) and oxygen (O_2). Table S 2 lists the corresponding C-selectivities $S_{i,C}$ to the product components carbon monoxide (CO), carbon dioxide (CO_2), formic acid (FAc), methanol (MeOH), methyl hydroperoxide (MeOOH), formaldehyde (FA), methyl formate (MeFo), ethane (C_2H_6), ethene (C_2H_4), acetic acid (HAc), ethanol (EtOH), methyl acetate (MeAc), ethylene glycol (EG), and acetone (Ace) as well as the H-selectivities $S_{i,H}$ to the product components hydrogen (H_2) and water (H_2O).

Table S 1 Overview on specific energy input *SEI*, power *P*, residence time τ, feed temperature T^0, product stream temperature *T*, pressure *p*, and conversions X_j of CH_4 and O_2 of all individual experiments. The active volume *V* of the reactor was about 26.3 cm^3. In all experiments, the feed composition was 0.750 mol mol^{-1} argon (Ar), 0.167 mol mol^{-1} CH_4, and 0.083 mol mol^{-1} O_2. This corresponds to a molar reactant ratio (CH_4:O_2) in the feed of 2:1.

Exp.	*SEI*	*P*	τ	T^0	*T*	*p*	X_{CH4}	X_{O2}
	J cm^{-3}	W	s	K	K	mbar	mol mol^{-1}	mol mol^{-1}
1	0.3	18.3	0.5	294	310	984	0.052	0.044
2	0.4	20.3		294	315	970	0.049	0.036
3		21.0		294	315	982	0.047	0.038
4		21.0		294	315	987	0.046	0.034
5	0.5	27.2		295	310	985	0.060	0.059
6		27.8		294	317	965	0.062	0.066
7		28.4		294	318	983	0.057	0.065
8	1.2	15.6	2.0	297	299	979	0.104	0.256
9	1.6	21.2		296	301	978	0.134	0.195
10	2.1	27.3		291	298	990	0.188	0.378
11	2.2	28.5		293	299	997	0.204	0.369
12	2.4	30.9		296	303	977	0.157	0.401
13	3.0	16.7	4.7	296	299	981	0.185	0.661
14	3.7	20.5		292	[a]	985	0.308	0.642
15		22.7	4.3	295	299	973	0.270	0.761
16	3.8	21.0	4.7	294	298	987	0.275	0.709
17	4.1	23.2		297	302	997	0.195	0.753
18	4.2	23.3		[a]	[a]	984	0.317	0.793
19	4.3	24.1		292	297	986	0.354	0.770
20	4.9	27.4		296	303	977	0.253	0.849
21	5.0	27.9		294	300	990	0.311	0.875
22	5.1	28.4		294	300	975	0.343	0.894
23	6.0	33.3		296	300	984	0.320	1.000

[a] temperature was not recorded due to a software failure

Table S 2 Overview on C-selectivities $S_{i,C}$ to CO, CO_2, FAc, MeOH, MeOOH, FA, MeFo, C_2H_6, C_2H_4, HAc, EtOH, MeAc, EG, and Ace as well as the H-selectivities $S_{i,H}$ to H_2 and H_2O of all individual experiments. All values are given in mol mol^{-1}.

Exp.	$S_{CO,C}$	$S_{CO2,C}$	$S_{FAc,C}$	$S_{MeOH,C}$	$S_{MeOOH,C}$	$S_{FA,C}$	$S_{MeFo,C}$	$S_{C2H6,C}$	$S_{C2H4,C}$	$S_{HAc,C}$	$S_{EtOH,C}$	$S_{MeAc,C}$	$S_{EG,C}$	$S_{A,C}$	$S_{H2,H}$	$S_{H2O,H}$
1	0.318	0.093	0.017	0.066	0.027	0.023	0.011	0.029	0.019	0.001	0.001	0.000	0.0000	0.0000	0.080	0.200
2	0.286	0.096	0.033	0.073	0.033	0.019	0.023	0.029	0.025	0.002	0.001	0.000	0.0000	0.0000	0.000	0.205
3	0.279	0.127	0.022	0.074	0.027	0.019	0.016	0.030	0.025	0.002	0.001	0.001	0.0000	0.0000	0.000	0.232
4	0.301	0.137	0.019	0.025	0.013	0.009	0.007	0.032	0.027	0.003	0.001	0.000	0.0000	0.0000	0.000	0.252
5	0.280	0.099	0.047	0.038	0.007	0.018	0.023	0.027	0.021	0.004	0.001	0.002	0.0001	0.0000	0.000	0.238
6	0.271	0.114	0.018	0.031	0.008	0.015	0.011	0.027	0.022	0.001	0.001	0.000	0.0000	0.0003	0.000	0.230
7	0.285	0.094	0.026	0.036	0.018	0.008	0.019	0.027	0.021	0.002	0.001	0.001	0.0000	0.0000	0.000	0.195
8	0.337	0.182	0.116	0.121	0.057	0.007	0.070	0.015	0.000	0.005	0.002	0.002	0.0005	0.0000	0.156	0.508
9	0.352	0.173	0.094	0.115	0.059	0.011	0.060	0.022	0.016	0.005	0.002	0.001	0.0003	0.0000	0.165	0.460
10	0.315	0.133	0.066	0.091	0.048	0.007	0.040	0.009	0.004	0.002	0.001	0.000	0.0000	0.0001	0.108	0.367
11	0.268	0.124	0.042	0.090	0.036	0.013	0.031	0.008	0.004	0.003	0.001	0.001	0.0000	0.0000	0.118	0.318
12	0.451	0.160	0.071	0.132	0.066	0.005	0.051	0.012	0.000	0.004	0.002	0.001	0.0002	0.0001	0.153	0.484
13	0.453	0.287	0.125	0.085	0.042	0.008	0.057	0.022	0.010	0.006	0.002	0.001	0.0002	0.0001	0.233	0.508
14	0.296	0.177	0.030	0.050	0.021	0.005	0.015	0.010	0.003	0.002	0.001	0.000	0.0000	0.0000	0.120	0.248
15	0.367	0.204	0.071	0.081	0.022	0.006	0.037	0.017	0.007	0.005	0.002	0.002	0.0002	0.0000	0.238	0.371
16	0.335	0.160	0.034	0.102	0.043	0.005	0.026	0.014	0.005	0.002	0.001	0.000	0.0000	0.0000	0.234	0.267
17	0.544	0.276	0.094	0.098	0.035	0.008	0.051	0.024	0.011	0.006	0.003	0.002	0.0002	0.0000	0.289	0.525
18	0.333	0.200	0.060	0.055	0.013	0.007	0.027	0.013	0.005	0.005	0.002	0.002	0.0000	0.0000	0.186	0.362
19	0.291	0.161	0.034	0.052	0.019	0.004	0.019	0.008	0.002	0.002	0.001	0.001	0.0000	0.0000	0.094	0.257
20	0.505	0.250	0.073	0.076	0.027	0.004	0.040	0.021	0.008	0.005	0.003	0.001	0.0003	0.0001	0.241	0.518
21	0.408	0.223	0.037	0.112	0.052	0.005	0.025	0.016	0.006	0.004	0.002	0.001	0.0000	0.0000	0.199	0.406
22	0.355	0.196	0.038	0.084	0.038	0.003	0.026	0.015	0.005	0.002	0.001	0.000	0.0000	0.0000	0.175	0.248
23	0.417	0.241	0.052	0.019	0.005	0.003	0.009	0.020	0.004	0.006	0.001	0.000	0.0006	0.0001	0.180	0.345

2 NMR Spectroscopy

2.1 Acquisition Parameters

Quantitative NMR spectra were recorded with a ^{1}H standard sequence and ^{13}C inverse-gated ^{1}H-decoupled (hereafter referred to as ^{13}C) pulse sequence. These sequences ensure that the peak areas are proportional to the mole numbers of the corresponding functional groups. Table S 3 lists the NMR acquisition and processing parameters used in this work.

Table S 3 Acquisition and processing parameters of the quantitative NMR experiments.

	^{1}H	^{13}C
Acquisition parameters		
Temperature / K	303.15	303.15
Pulse program	zg	zgig
Decoupling sequence	-	Waltz16
Number of scans	8 … 32	400 … 1024
Flip angle / °	10	30
Excitation frequency offset / ppm	7	120
Sweep width / ppm	16	260
Relaxation delay / s	60	120
Acquisition time / s	5	2.6
Acquired size / kB	44	64
Processing parameters		
Apodization / Hz	none	0.3 … 1
Zero filling / kB	64	256

To ensure quantitative measurements, the sum of acquisition time and relaxation delay at a 90° flip angle should be five times the relaxation time. The longest relaxation time was measured for the carboxylate ester group of MeFo, which was about 8 s of the ^{1}H and about 30 s of the ^{13}C NMR experiment, such that quantitative measurement is ensured with the set relaxation delays and flip angles.

2.2 Structure Elucidation

The quantitative ^{1}H and ^{13}C NMR spectra for the cold trap sample (hereafter referred to as CT sample) of experiment 8 (see Table S 1) are presented in the main article. Four additional types of NMR spectra were acquired for the structure

elucidation of the products in the CT samples: ^{13}C DEPT-135; ^{13}C without ^{1}H decoupling; $^{1}H,^{13}C$ HSQC; and $^{1}H,^{13}C$ HMBC. Fig. S 1 to Fig. S 4 show the four additional NMR spectra of the CT sample of experiment 8. For an overview on labels and peak assignment to the components, see Table 3 in the main article. Peaks that have not been assigned to a component are labeled with a question mark (?) and peaks labeled with an asterisk (*) are ^{13}C satellites. 1,4-dioxane (S) is used as internal standard.

Fig. S 1 is a ^{13}C DEPT-135 (Distortionless Enhancement by Polarization Transfer) NMR spectrum. With the specific sequence of pulses used in this technique one can tell how many H atoms are bound to a C atom based on the peak intensity: a positive intensity corresponds to either a CH or a CH_3 group, a negative intensity corresponds to a CH_2 group. If the intensity equals zero in the spectrum, this corresponds to no H atom bound to the C atom. Fig. S 2 shows the ^{13}C NMR spectrum without ^{1}H-decoupling, where additionally C atoms are detected, which have no H atom. With this technique, the multiplicity of a peak depends on how many H atoms are directly bound to a C atom: a singlet corresponds to no H atom bound to the C atom, a doublet to one, a triplet to two and so forth. Fig. S 3 shows the $^{1}H,^{13}C$ HSQC (Heteronuclear Single Quantum Coherence) NMR spectrum. With this two-dimensional NMR technique $^{1}H,^{13}C$ single bond correlations are visualized topographically, so that one can tell which peaks in the ^{1}H and ^{13}C NMR spectra correspond to atoms that are only one bond length apart from each other in the same molecule. Fig. S 4 shows the $^{1}H,^{13}C$ HMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum. With this two-dimensional NMR technique one can tell which peaks in the ^{1}H and ^{13}C NMR spectra correspond to atoms that are two, three, and sometimes even four bonds apart from each other in the same molecule.

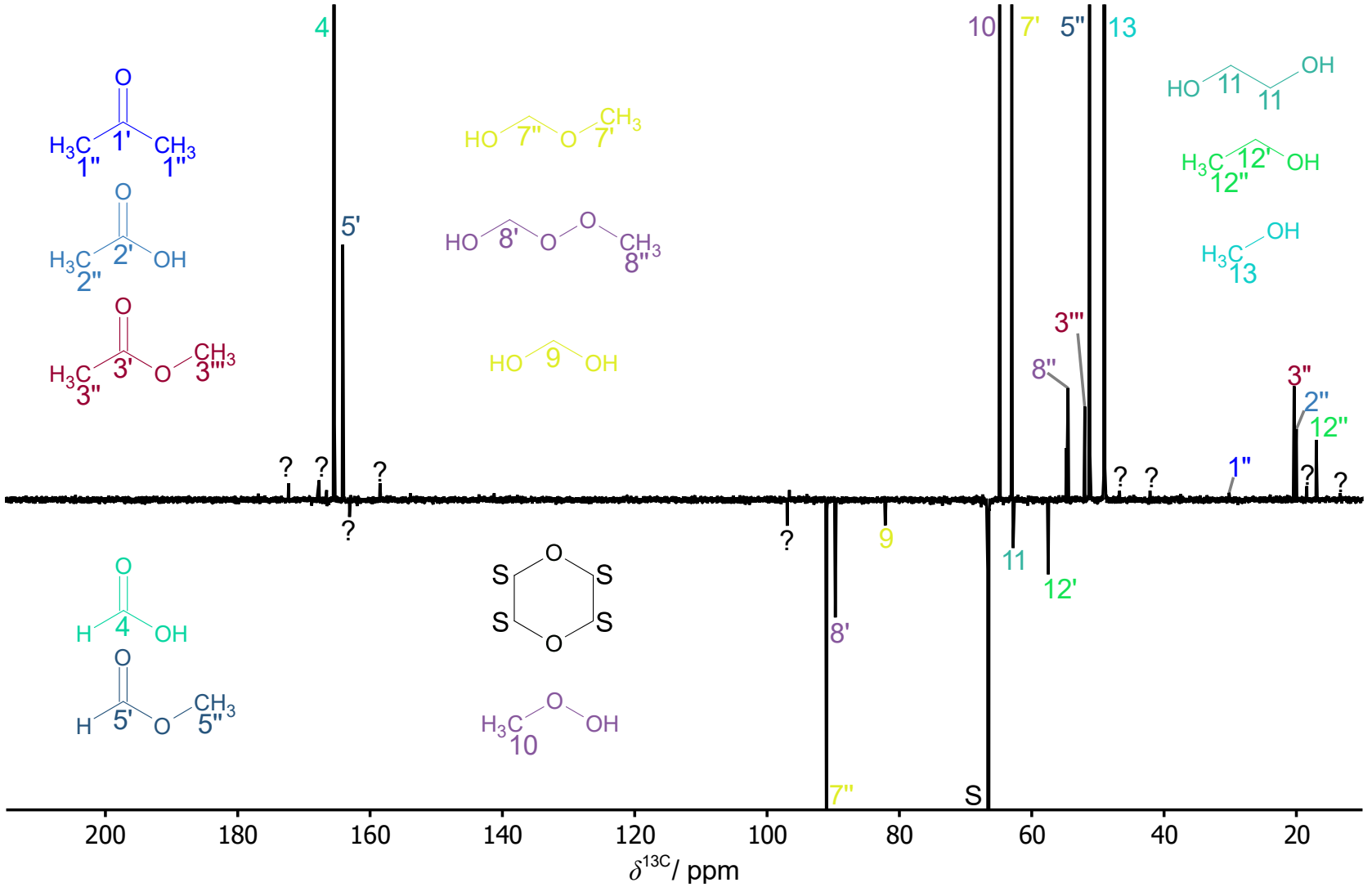

Fig. S 1 ^{13}C DEPT-135 NMR spectrum of the CT sample of experiment 8 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

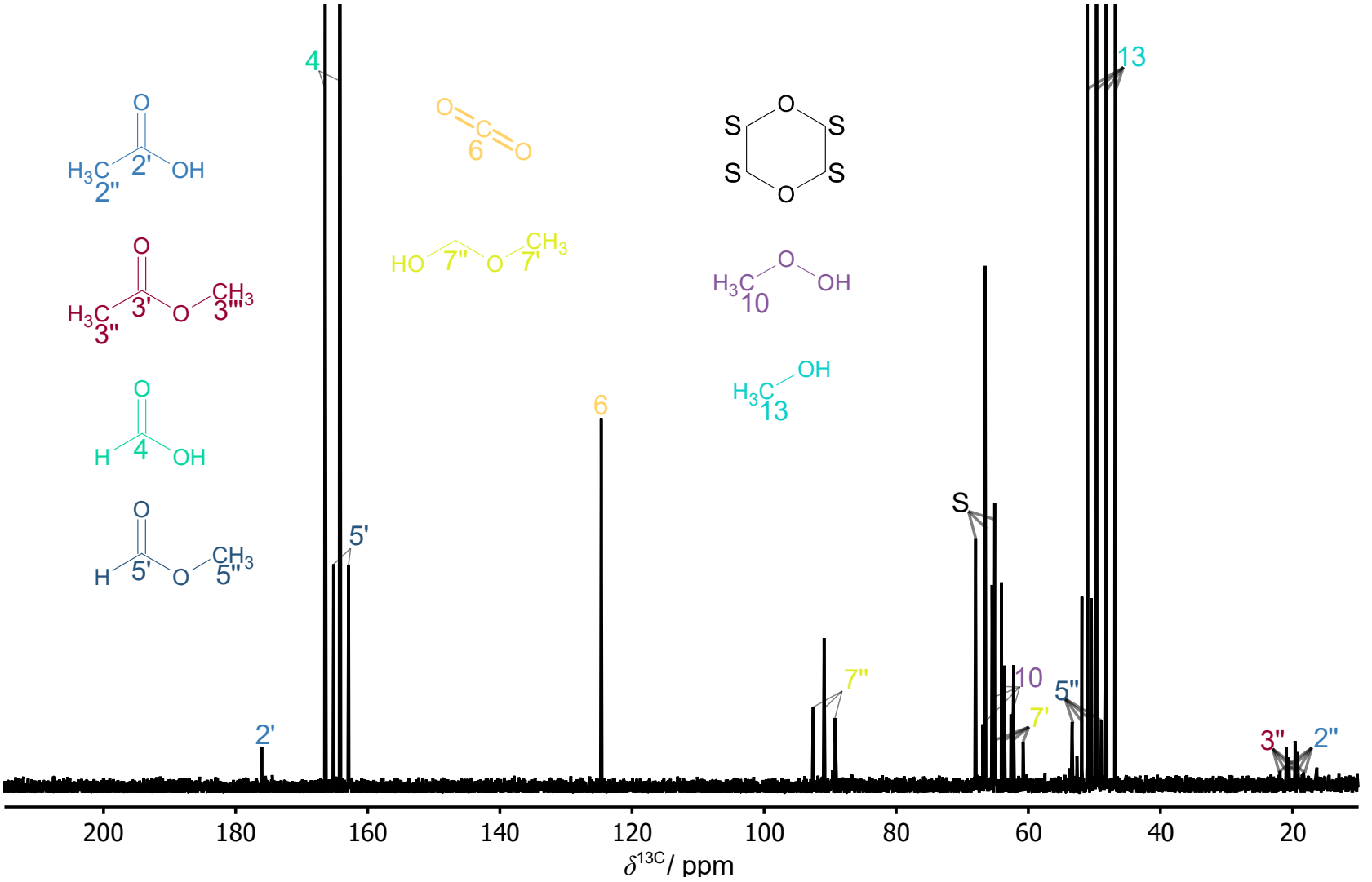

Fig. S 2 ^{13}C without ^{1}H decoupling NMR spectrum of the CT sample of experiment 8 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

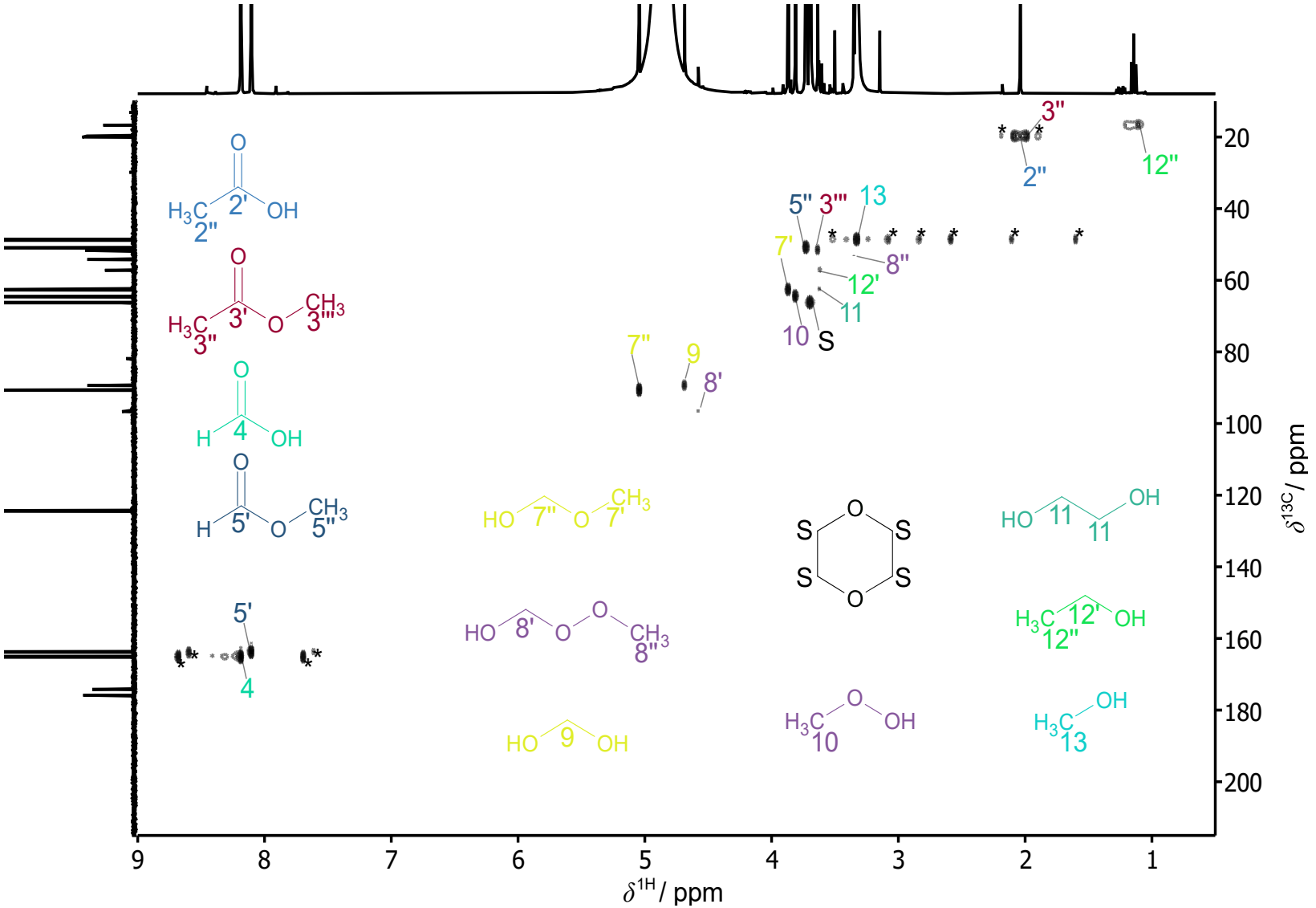

Fig. S 3 $^{1}H,^{13}C$ HSQC NMR spectrum of the CT sample of experiment 8 (see Table S 1).

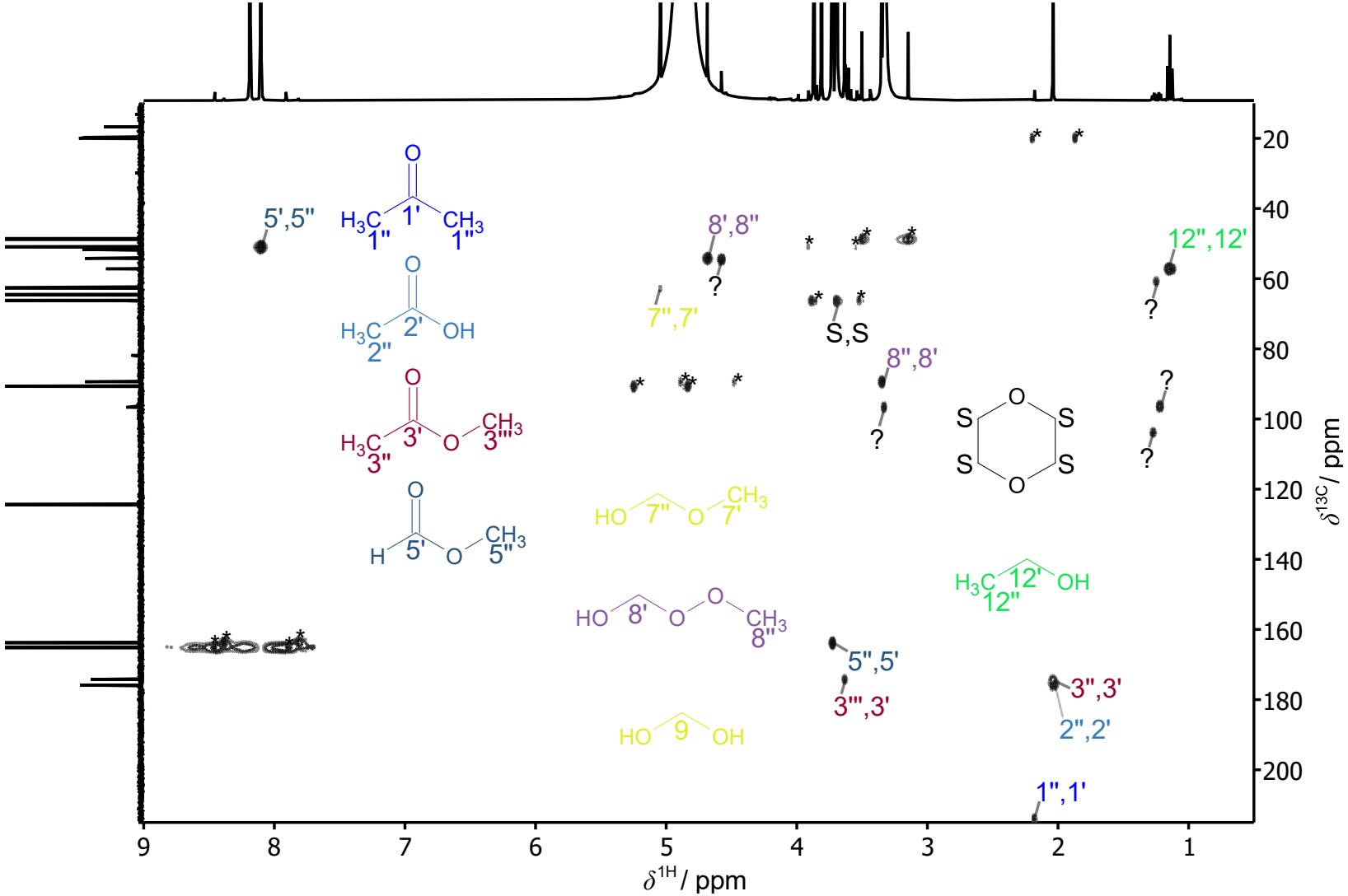

Fig. S 4 $^{1}H,^{13}C$ HMBC NMR spectrum of the CT sample of experiment 8 (see Table S 1).

As the spectra of the CT samples were sufficiently alike to assign the peaks alone from the ^{1}H and ^{13}C NMR spectra without the four additional types of NMR spectra, i.e., ^{13}C DEPT-135; ^{13}C without ^{1}H decoupling; ^{1}H,^{13}C HSQC; and ^{1}H,^{13}C HMBC, only ^{1}H and ^{13}C NMR spectra were acquired for the quantitative analysis. Here, two more sets of ^{1}H and ^{13}C NMR spectra are provided in Fig. S 5 to Fig. S 8. These spectra correspond to the CT samples of experiments 2 and 23 (see Table S 1). Again, an overview on labels and peak assignment to the components is presented in Table 3 in the main article. Peaks that have not been assigned to a component are labeled with a question mark (?) and peaks labeled with an asterisk (*) are ^{13}C satellites. 1,4-dioxane (S) is used as internal standard. It should be noted, that the -OH peak has shifted compared to other experiments, which may be due to a shift in pH value.

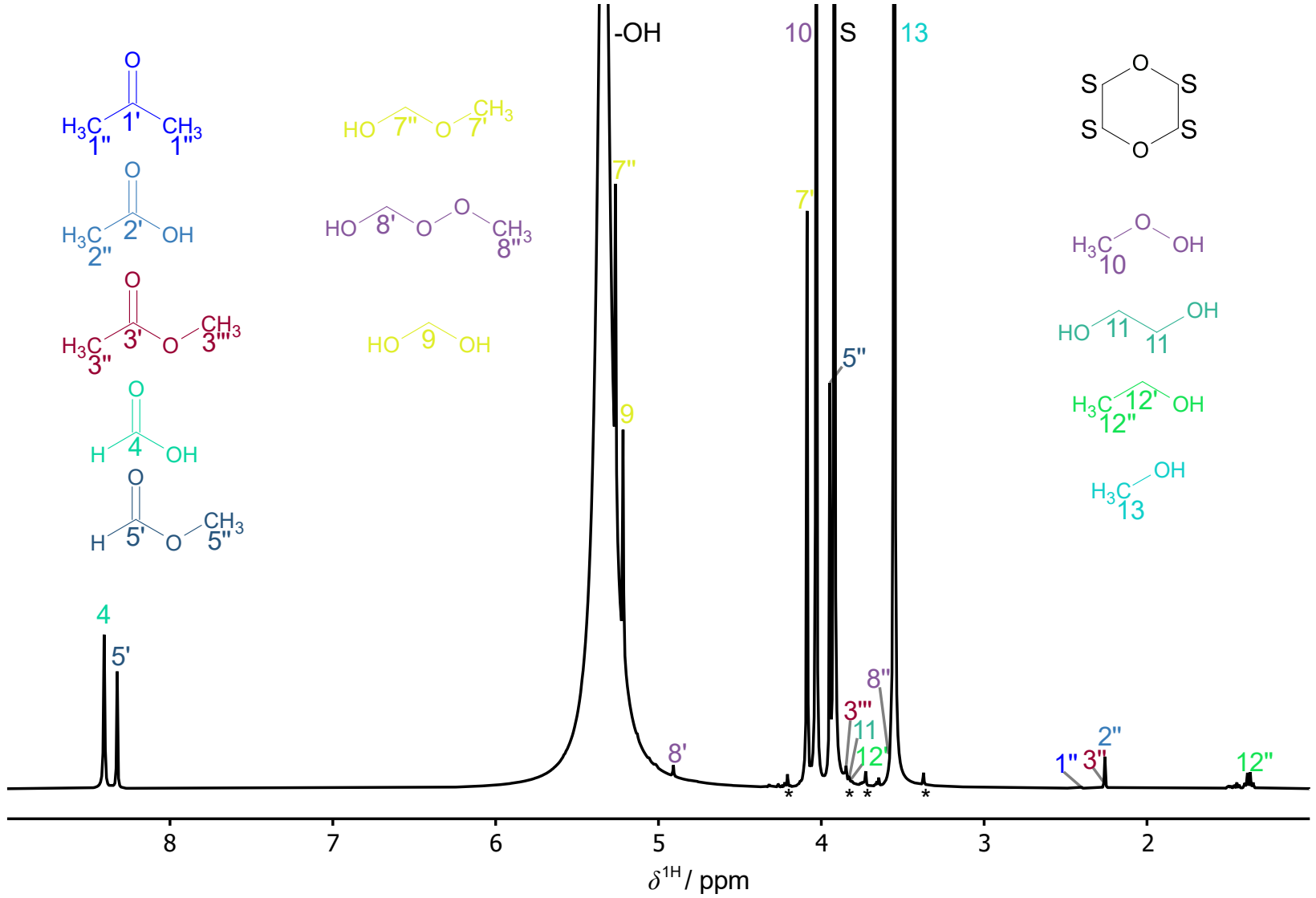

Fig. S 5 ^{1}H NMR spectrum of the CT sample of experiment 2 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

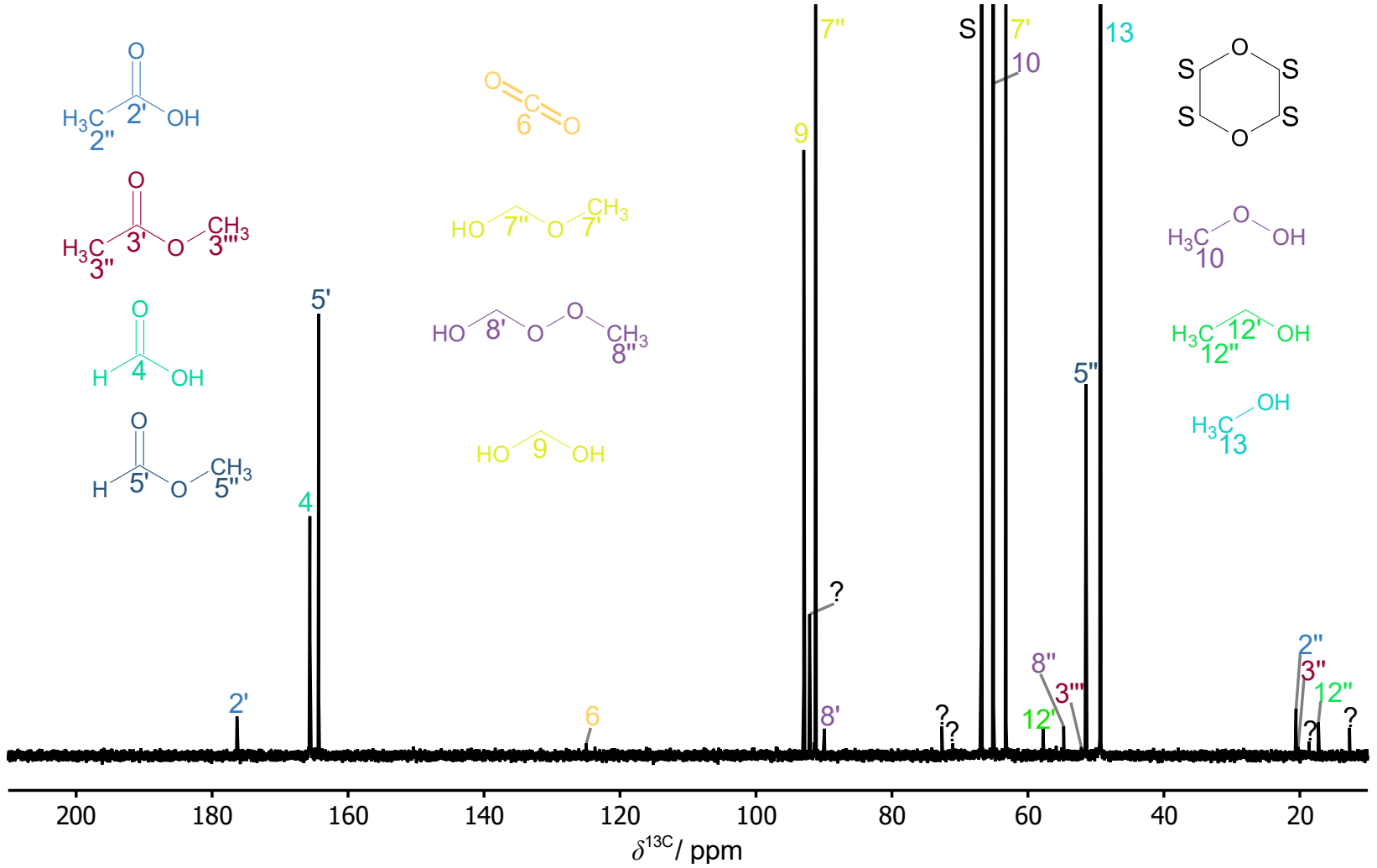

Fig. S 6 ^{13}C NMR spectrum of the CT sample of experiment 2 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

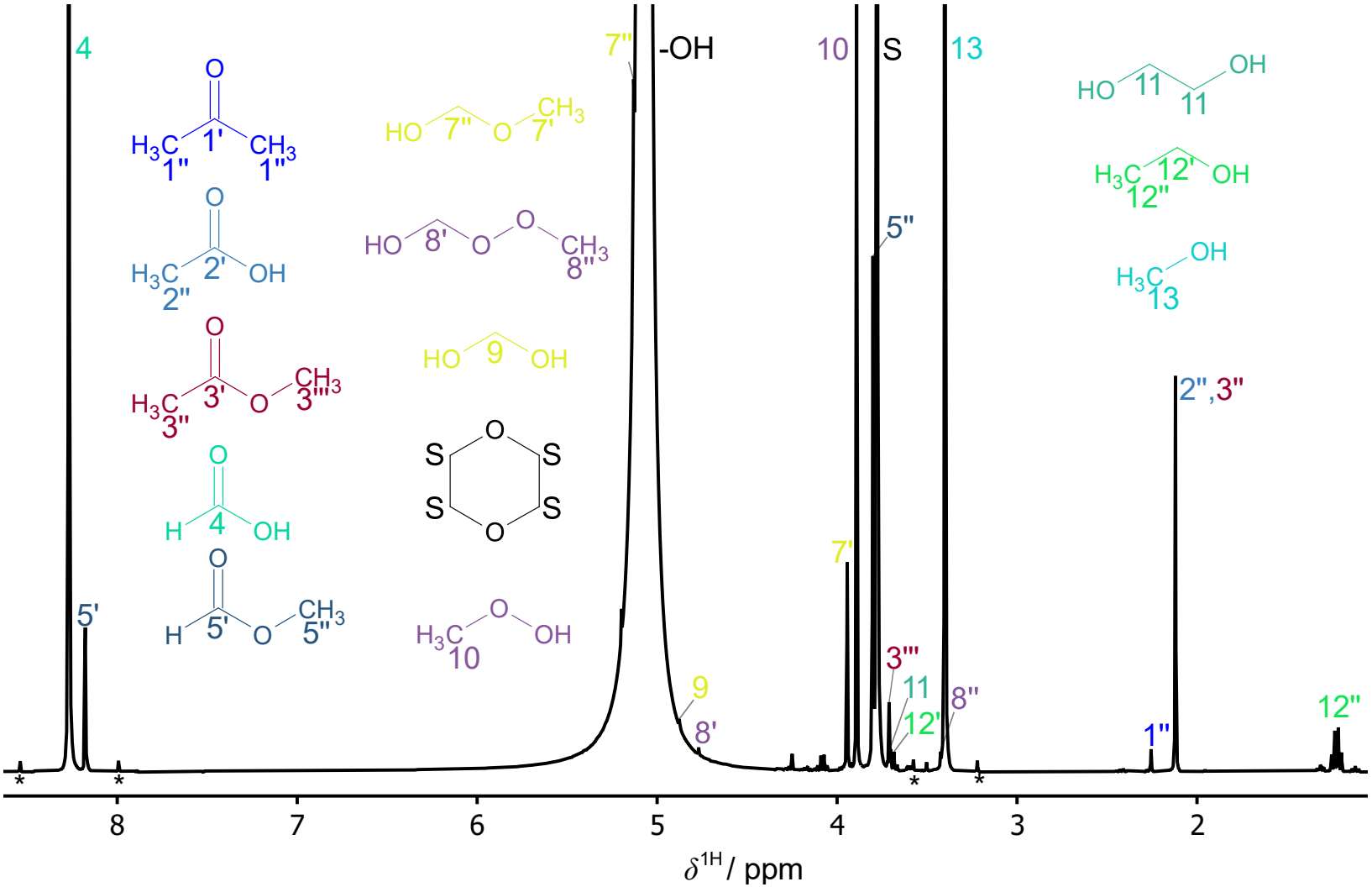

Fig. S 7 ^{1}H NMR spectrum of the CT sample of experiment 23 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

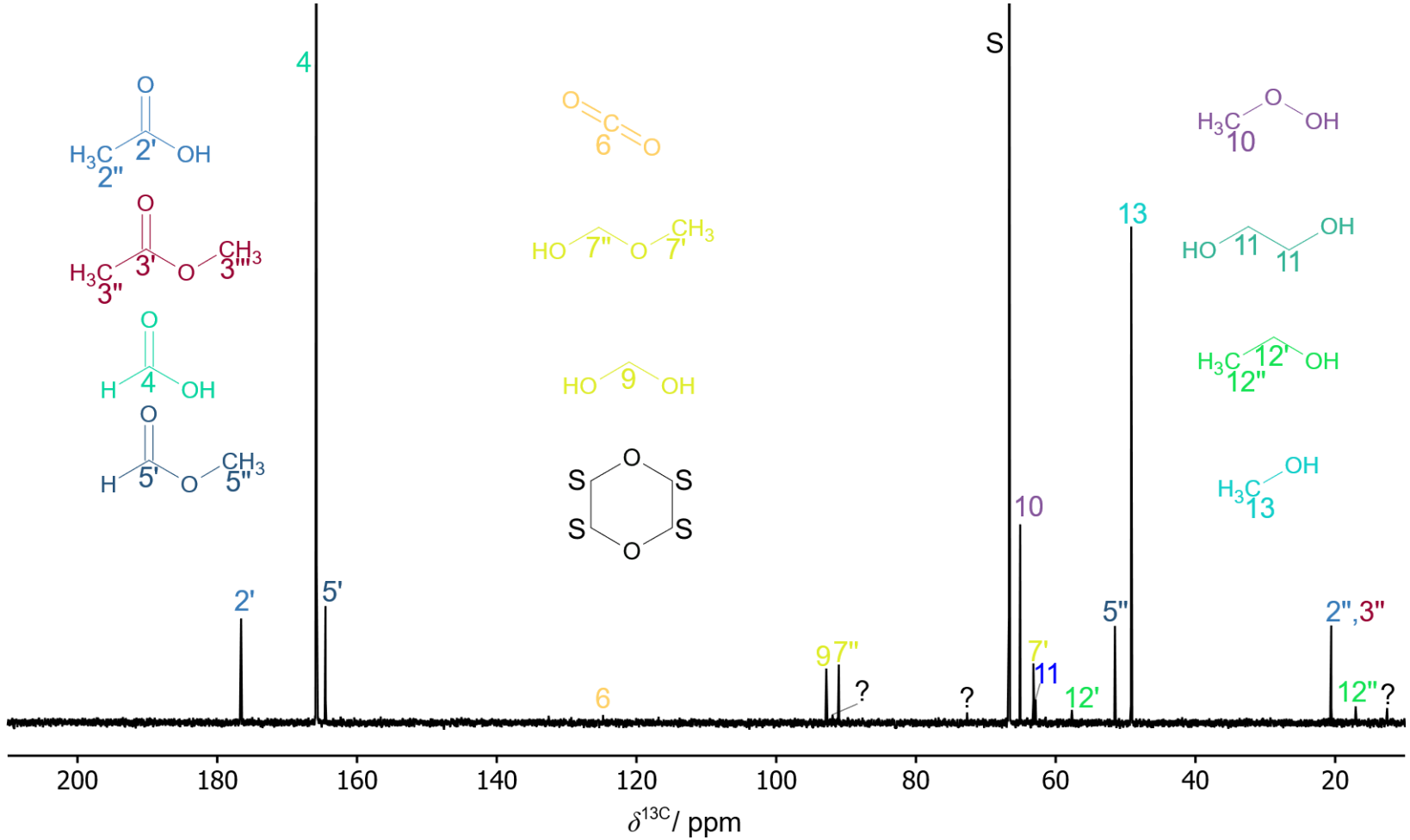

Fig. S 8 ^{13}C NMR spectrum of the CT sample of experiment 23 (see Table S 1), the full intensities of some peaks are truncated for better visibility.

3 Gas Chromatography

3.1 Acquisition Parameters

Table S 4 shows the acquisition parameters of Method 1 (carrier gas: He) and Method 2 (carrier gas: N_2) used on the gas chromatographic analysis of in this work.

Table S 4 Acquisition parameters of the gas chromatography methods.

Parameter	Method 1	Method 2
Carrier gas	He	N_2
Inlet temperature / K	423.15	423.15
Inlet pressure / bar	0.7	0.6
Total volume flow / ml min^{-1}	87	120
Split ratio	30:1	50:1
Initial oven temperature / K	313.15	313.15
Initial hold time / min	20	21
1^{st} oven temperature / K	333.15	-
1^{st} hold time / min	13.5	-
Detector temperature / K	473.15	523.15

3.2 Retention Times and Quantitative Evaluation

The retention times in the chromatograms were compared to the retention times of known components. External reference gases used in this work are CO_2, H_2, CO, C_2H_6, and C_2H_4. While calibrations of these components are conducted in *calibration* mode, the calibrations of the feed gases Ar, CH_4, and O_2 are conducted in *measurement* mode without operation of plasma.

Fig. S 9 and Fig. S 10 show the chromatograms and Table S 5 shows the corresponding retention times and assigned components from the GC analysis of the gaseous product stream obtained from experiment 8 (see Table S 1).

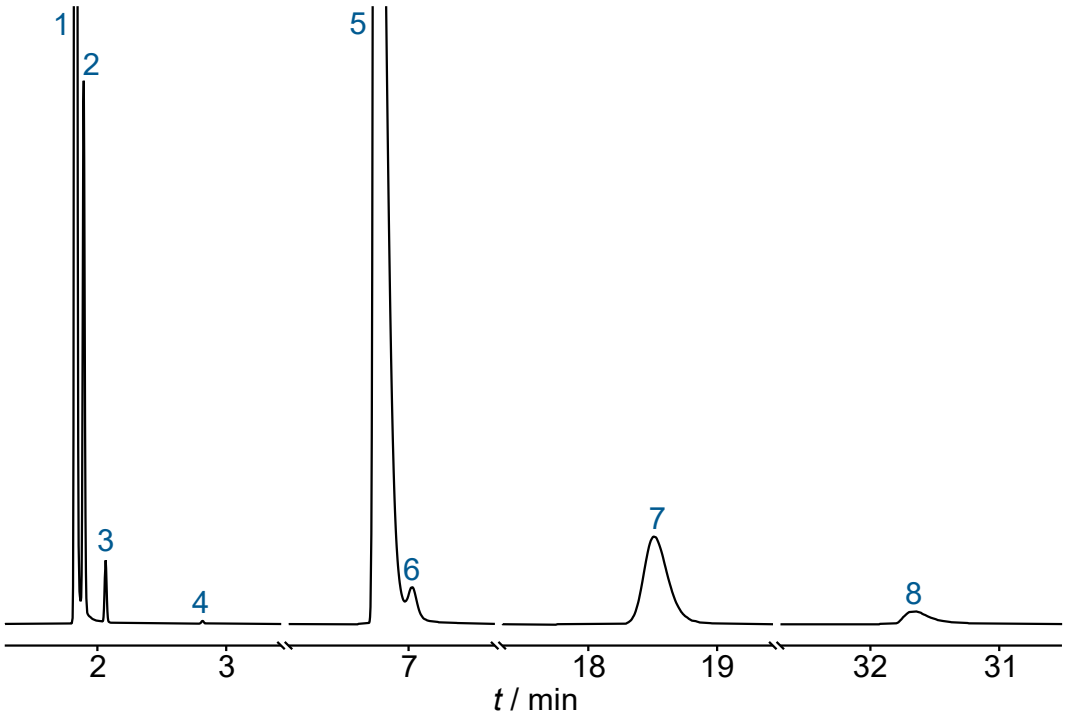

Fig. S 9 Chromatogram from Method 1 of the gaseous fraction of the product stream of experiment 8. The full intensities of some peaks are truncated for better visibility.

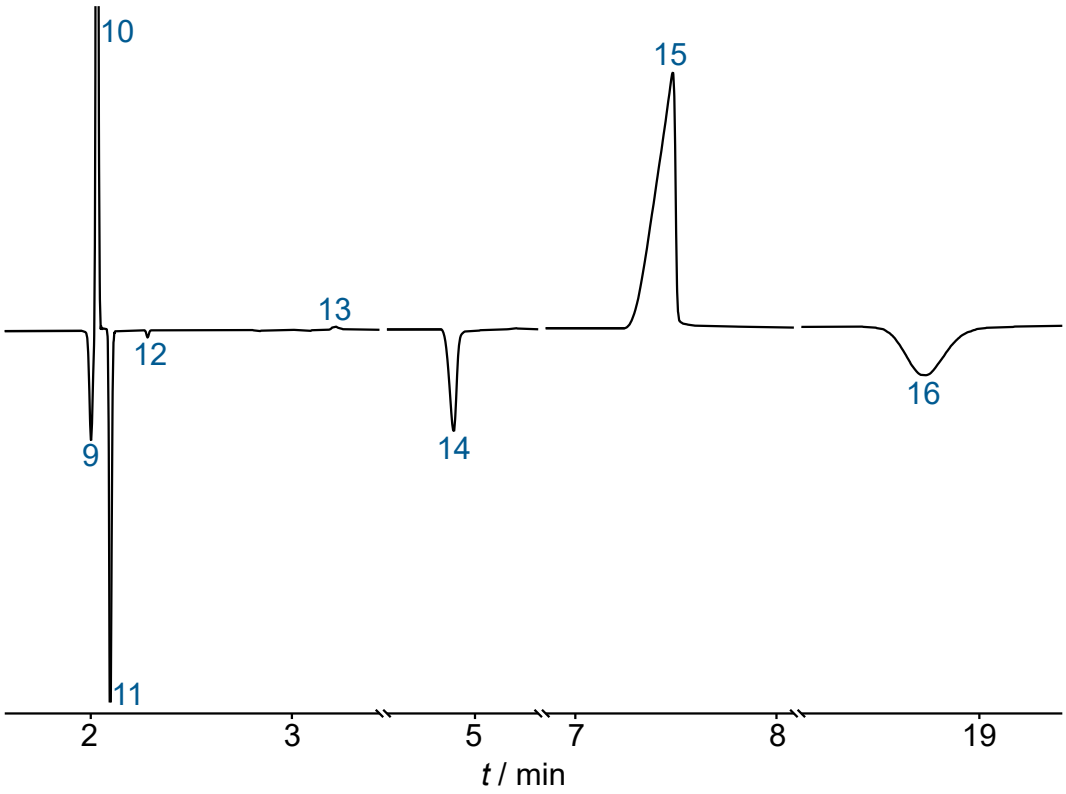

Fig. S 10 Chromatogram from Method 2 of the gaseous fraction of the product stream of experiment 8. The full intensities of some peaks are truncated for better visibility.

Table S 5 Overview on retention times, calibration factors k_i, and standard uncertainties of the determined partial pressure $u(p_i)$ of both methods. Unnumbered signals are not visible in the chromatograms shown in Fig. S 9 and Fig. S 10. Signals without calibration factor have not been evaluated quantitatively.

Signal	t / min	Component	k_i / mbar (µVs)$^{-1}$	$u(p_i)$ / mbar
Method 1				
1	1.8	H_2, O_2, Ar, CO	-	-
2	1.9	CH_4	-	-
3	2.1	CO_2	1.0	4.4
-	2.4	C_2H_4	1.0	0.2
4	2.8	C_2H_6	1.0	1.0
-	4.4	H_2	99.0	25.4
5	6.7	Ar	0.6	14.6
6	7.0	O_2	0.6	5.4
7	18.5	CH_4	0.8	6.6
8	31.3	CO	0.7	2.6
Method 2				
9	2.0	H_2, O_2	-	-
10	2.0	Ar	-	-
11	2.1	CH_4	-	-
12	2.3	C_2H_4	2.3	0.4
13	3.2	C_2H_6	0.5	1.1
14	4.7	H_2	0.3	2.9
15	7.5	Ar	2.2	19.0
-	7.6	O_2	9.1	22.2
16	18.7	CH_4	0.8	8.9

In general, there are two retention times per component and per method, as a double column was used in the analytical set-up. However, the components CO_2, C_2H_6, and C_2H_4 have only one retention time in each method since they do not elute from the Molsieve 5Å column but are adsorbed by it. The retention times of H_2, O_2, Ar, CO, and CH_4 coincide at about 2 min for both methods. For quantitative analysis of these components, only the areas of a higher retention time are used. When more than one area was available for quantitative evaluation, the average was calculated. This was except for O_2, for which the calibration factor in Method 2 was subject to significantly higher uncertainties than with Method 1. In Method 2, some areas were negative. Interestingly, the area of C_2H_6 changes from positive to negative at high concentrations. This phenomenon has already been described for hydrogen [1, 2]. For H_2, the results from Method 1 were exclusively

used for the quantification in experiments 2 to 7, as the detection limit was 0.02 mol mol^{-1}.

4 Individual Results

Fig. S 11 shows the individual results for the conversions X_j of CH_4 and O_2 as a function of the *SEI*. Fig. S 12 a) to e) shows the individual results for the C-selectivities $S_{i,C}$ to CO, CO_2, FAc, MeOH, MeOOH, FA, MeFo, C_2H_6, C_2H_4, HAc, EtOH, MeAc, EG, and Ace. Fig. S 13 a) shows the individual results for the H-selectivities $S_{i,H}$ to H_2O and H_2. Finally, Fig. S 13 b) shows the individual results for the molar ratios of (H_2:CO_2) and (H_2:CO). The error bars in Fig. S 11 to Fig. S 13 indicate the uncertainty calculated from the analytical uncertainties with error propagation.

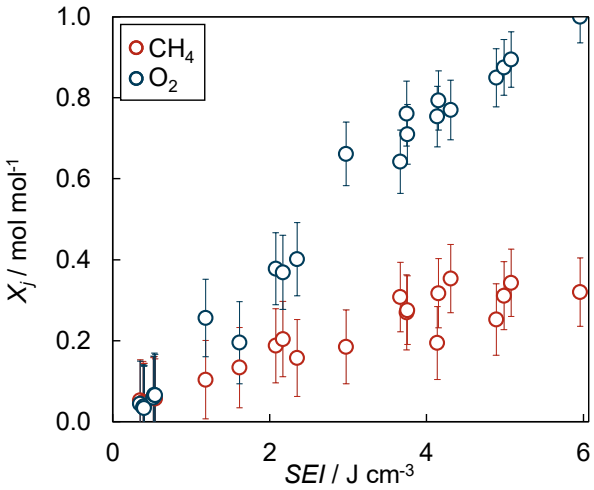

Fig. S 11 Conversions of CH_4 and O_2.

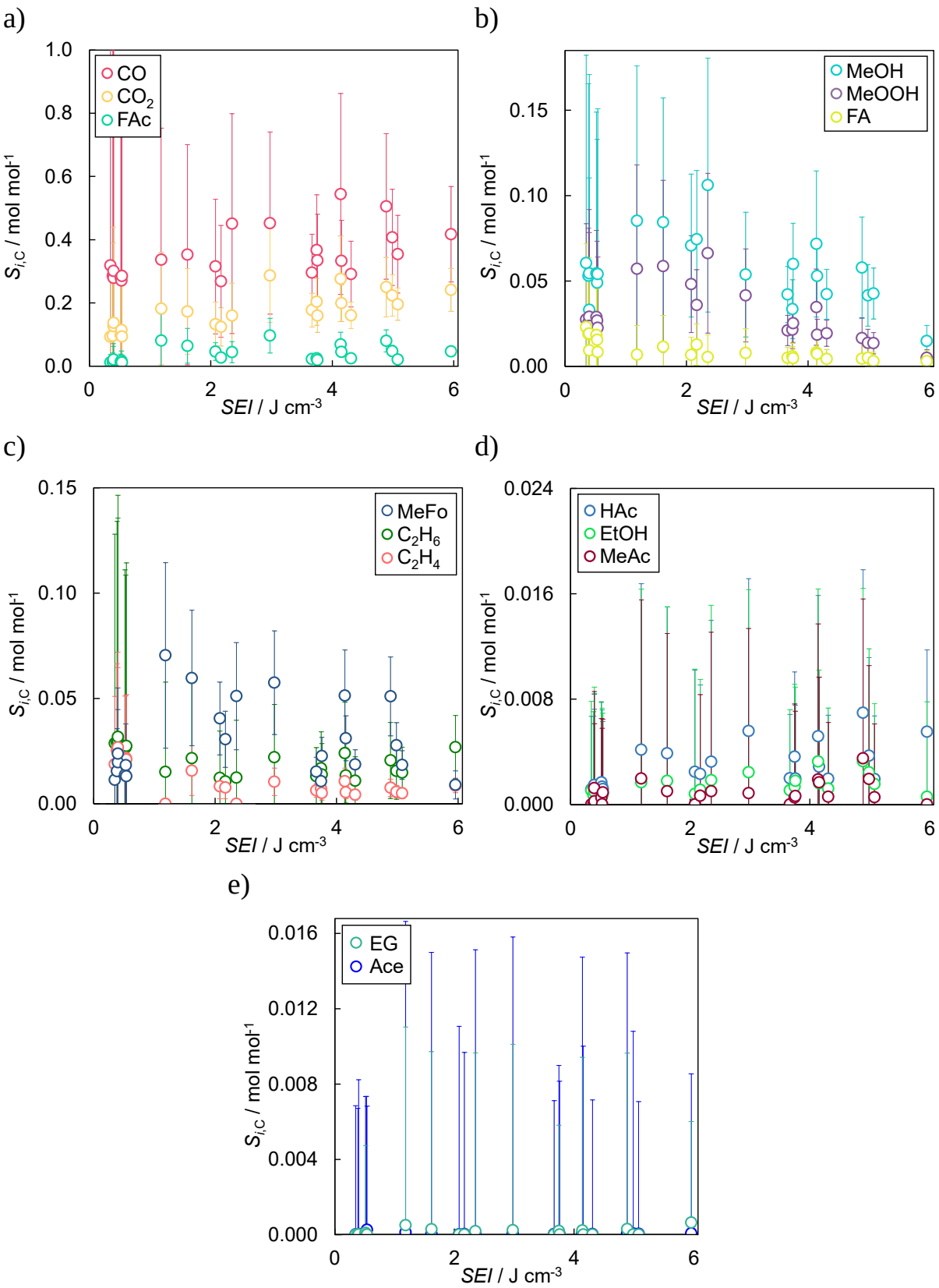

Fig. S 12 Individual C-selectivities to a) CO, CO_2, FAc; b) MeOH, MeOOH, FA; c) MeFo, C_2H_6, C_2H_4; d) HAc, EtOH, and MeAc; e) EG and Ace.

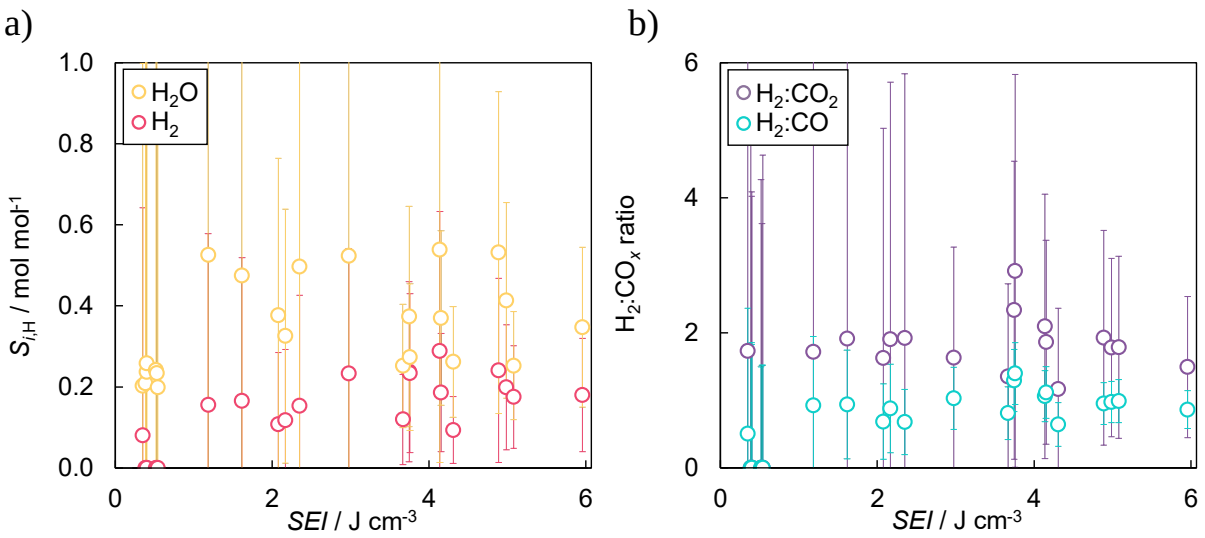

Fig. S 13 a) Individual H-selectivities to H_2O and H_2 and b) molar ratio of (H_2:CO_2) and (H_2:CO).

5 Element balance

Since atoms are preserved in the cold plasma reactions, the element balance is used to quantify the rest of C, H, and O atoms, that have not been detected by the analytical methods used in this work. Fig. S 14 shows the results for the individual experiments. The error bars indicate the uncertainty calculated from the analytical uncertainties with error propagation.

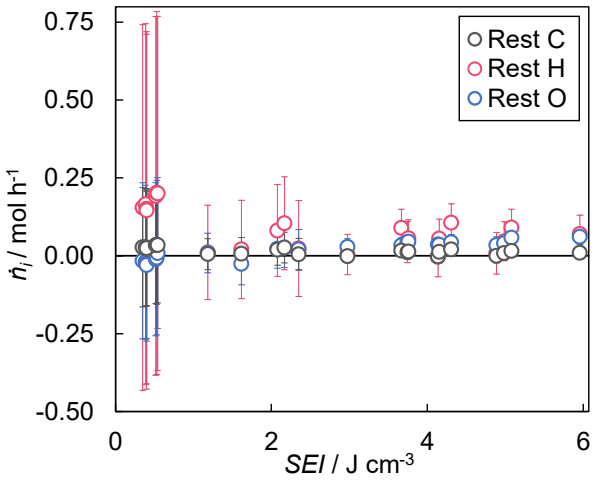

Fig. S 14 Rest of C, H, and O atoms calculated from the element balance.

References

1. Cowper CJ, Derose AJ (2013) The Analysis of Gases by Chromatography. Elsevier
2. Snavely K, Subramaniam B (1998) Thermal Conductivity Detector Analysis of Hydrogen Using Helium Carrier Gas and HayeSep® D Columns. J Chromatogr Sci 36:6