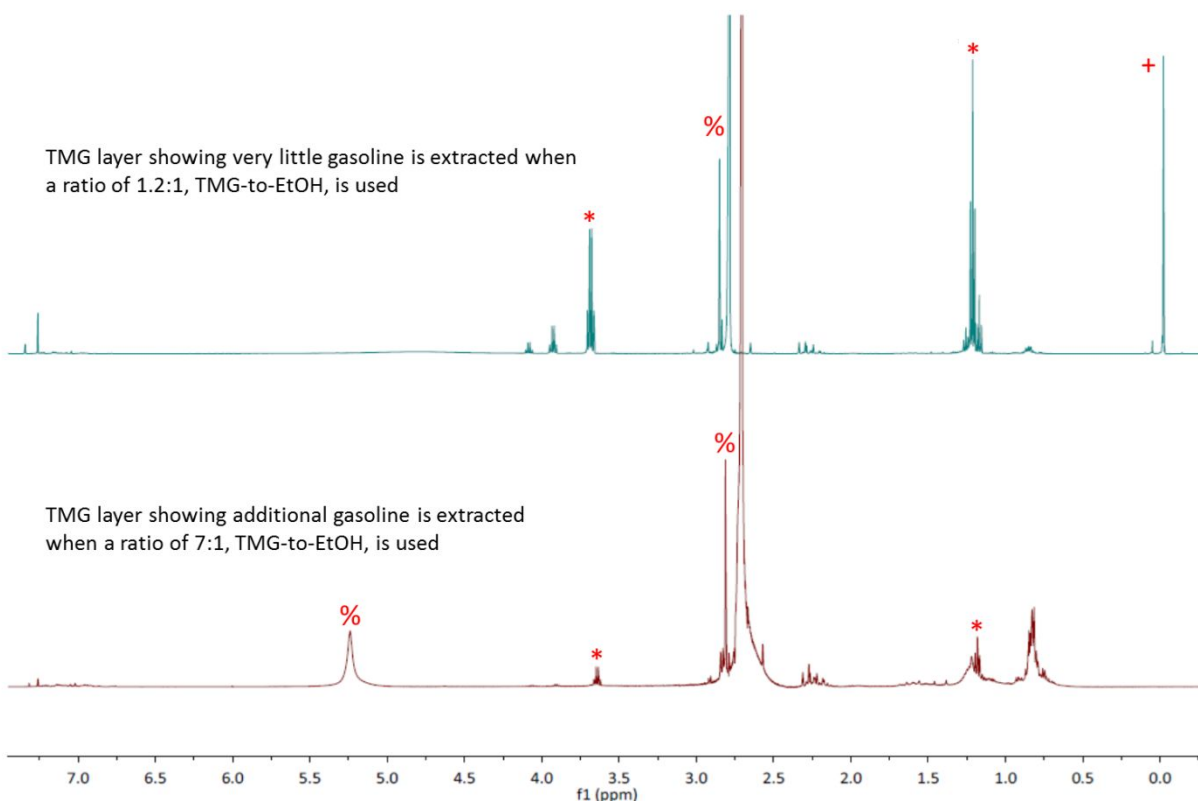


# Octane-on-Demand: Onboard Separation of Oxygenates from Gasoline

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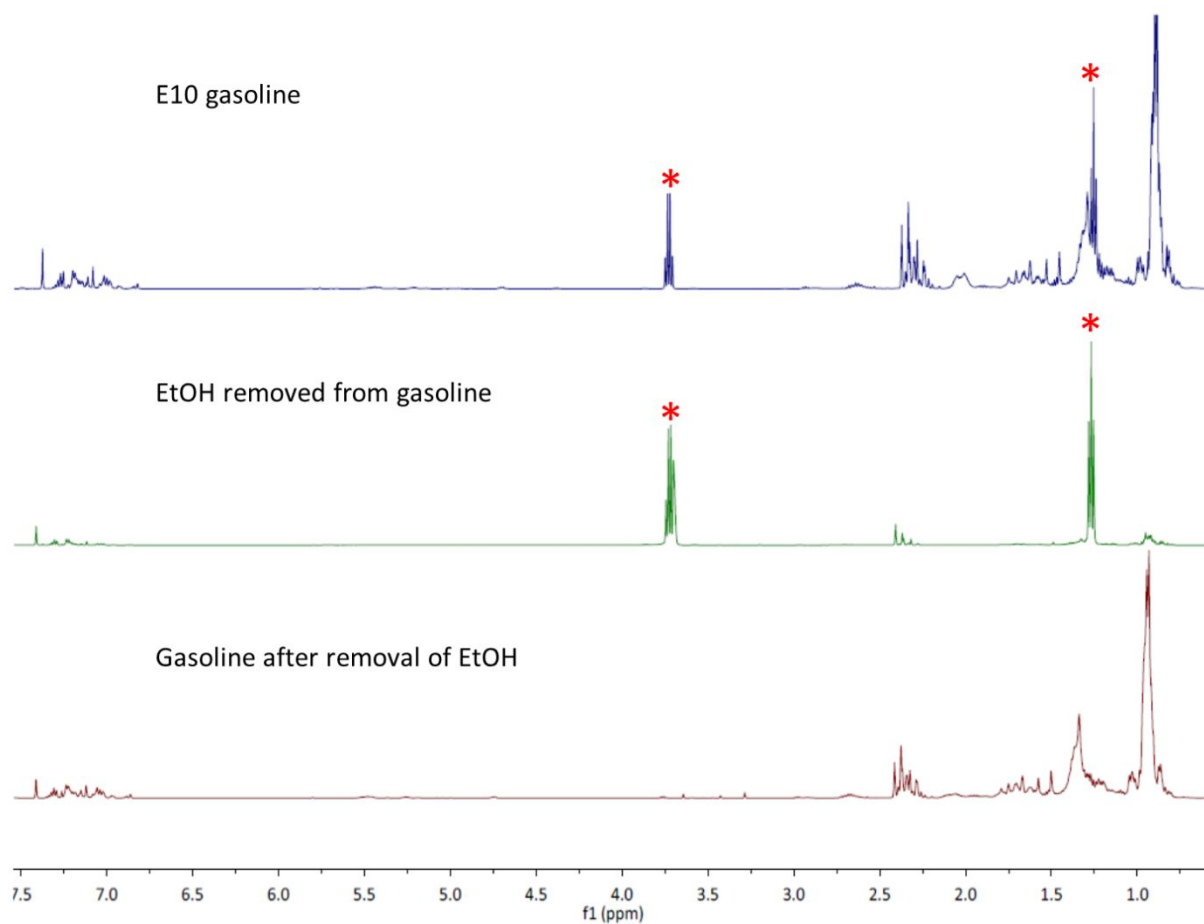
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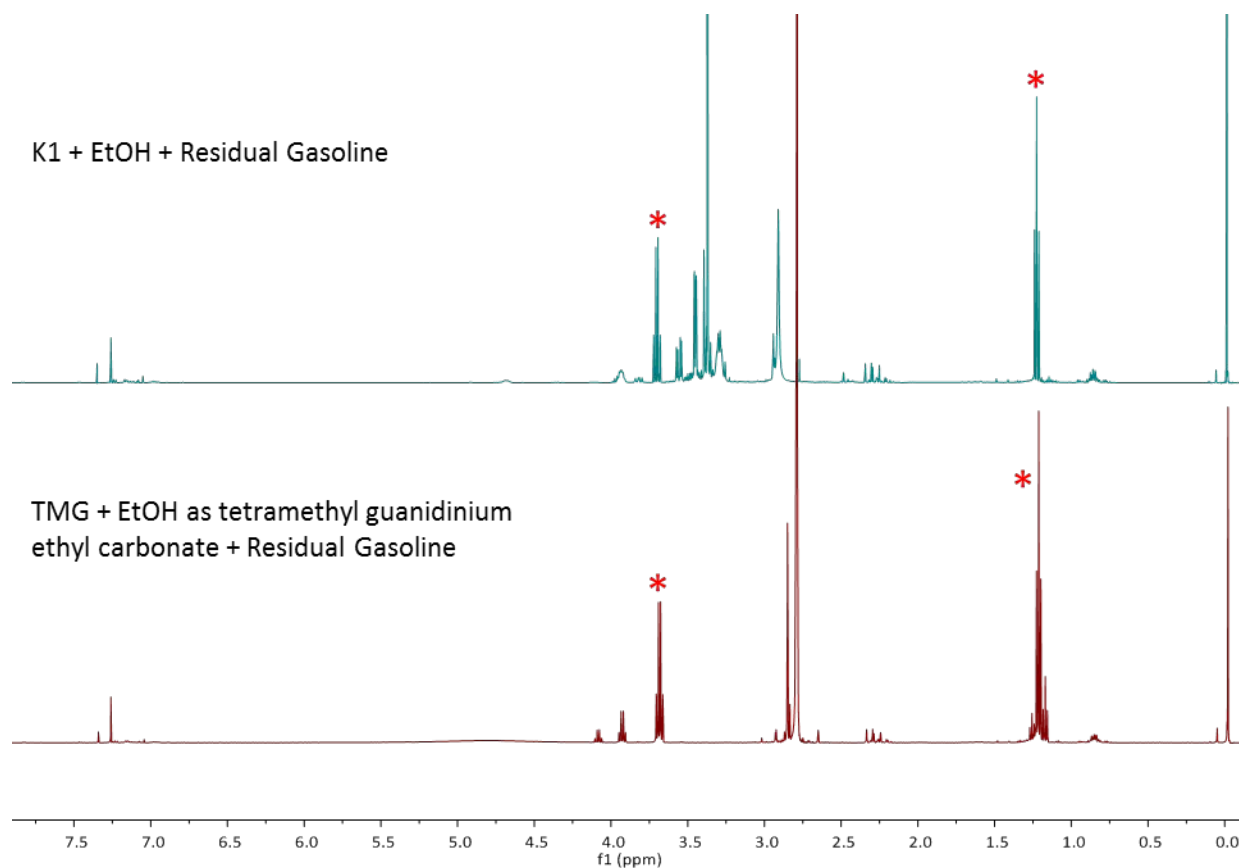


**Figure S1.** <sup>1</sup>H NMR spectra of two TMG-EtOH extractions showing that excess TMG facilitates the partitioning of gasoline into the TMG-Ethanol layer. Top: <sup>1</sup>H NMR of the mixture using the 1.2:1 ratio of TMG:EtOH (from the gasoline E10). Bottom: <sup>1</sup>H NMR of the mixture using the 7:1 ratio of TMG:EtOH (from the gasoline E10). Marked resonances denote the following: \* belong to EtOH, % belong to TMG, and + belongs to tetramethylsilane, a chemical shift reference. It is clearly visible that the extraction is cleaner in the case of the 1.2:1 ratio; less gasoline is pulled into the ionic liquid layer and the separation of EtOH is more efficient. Gasoline is denoted by the resonances in the proton NMR spectrum that are not otherwise designated.

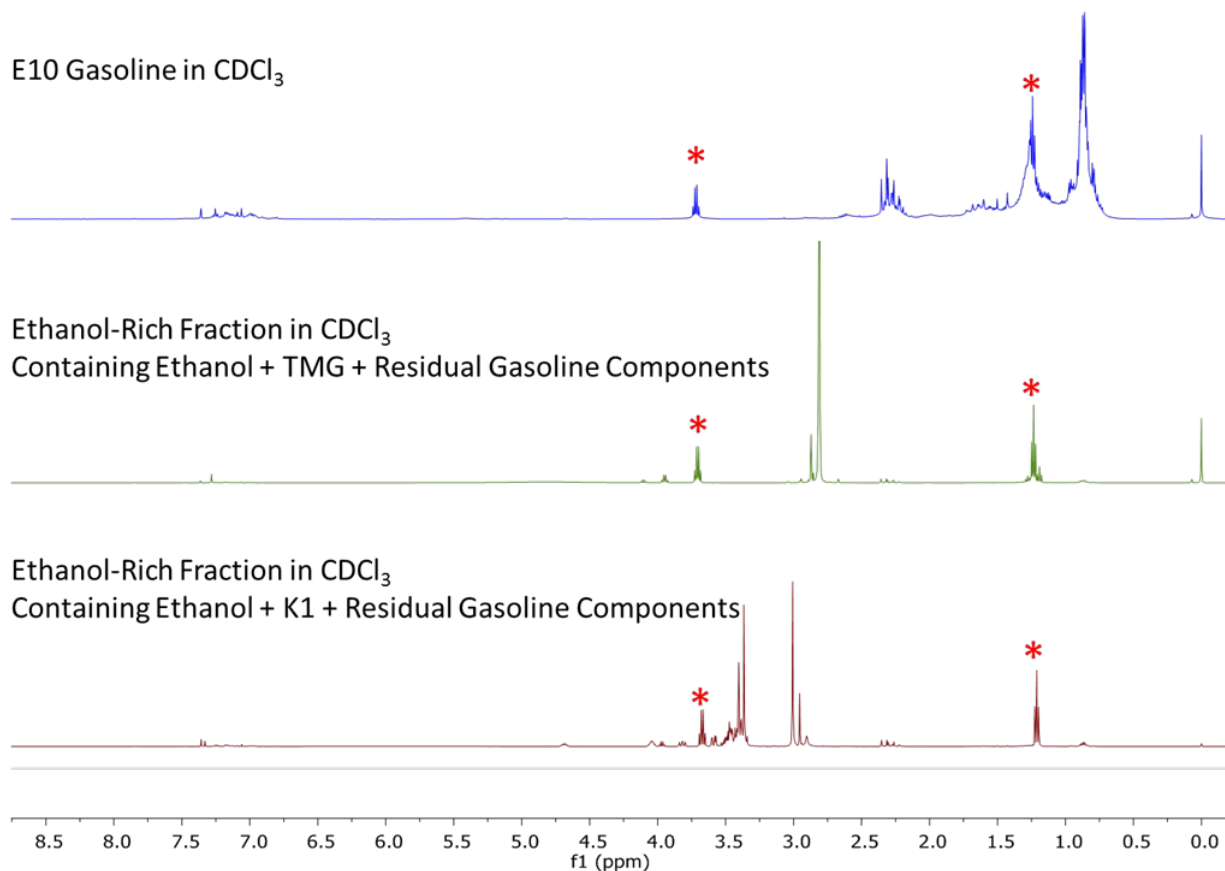
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**Figure S2.**  $^1\text{H}$  NMR series showing the separation of gasoline into two components, each having only minor contamination from the other component. Top:  $^1\text{H}$  NMR of the untreated gasoline E10; middle: removed and released EtOH fraction (after treatment of the E10 gasoline with 1.2 equivalents of K1 base); bottom:  $^1\text{H}$  NMR of the EtOH-lean gasoline, after EtOH removal using 1.2 equivalents of K1 base (per 1 equivalent of EtOH in the gasoline). \* denotes resonances belonging to EtOH.



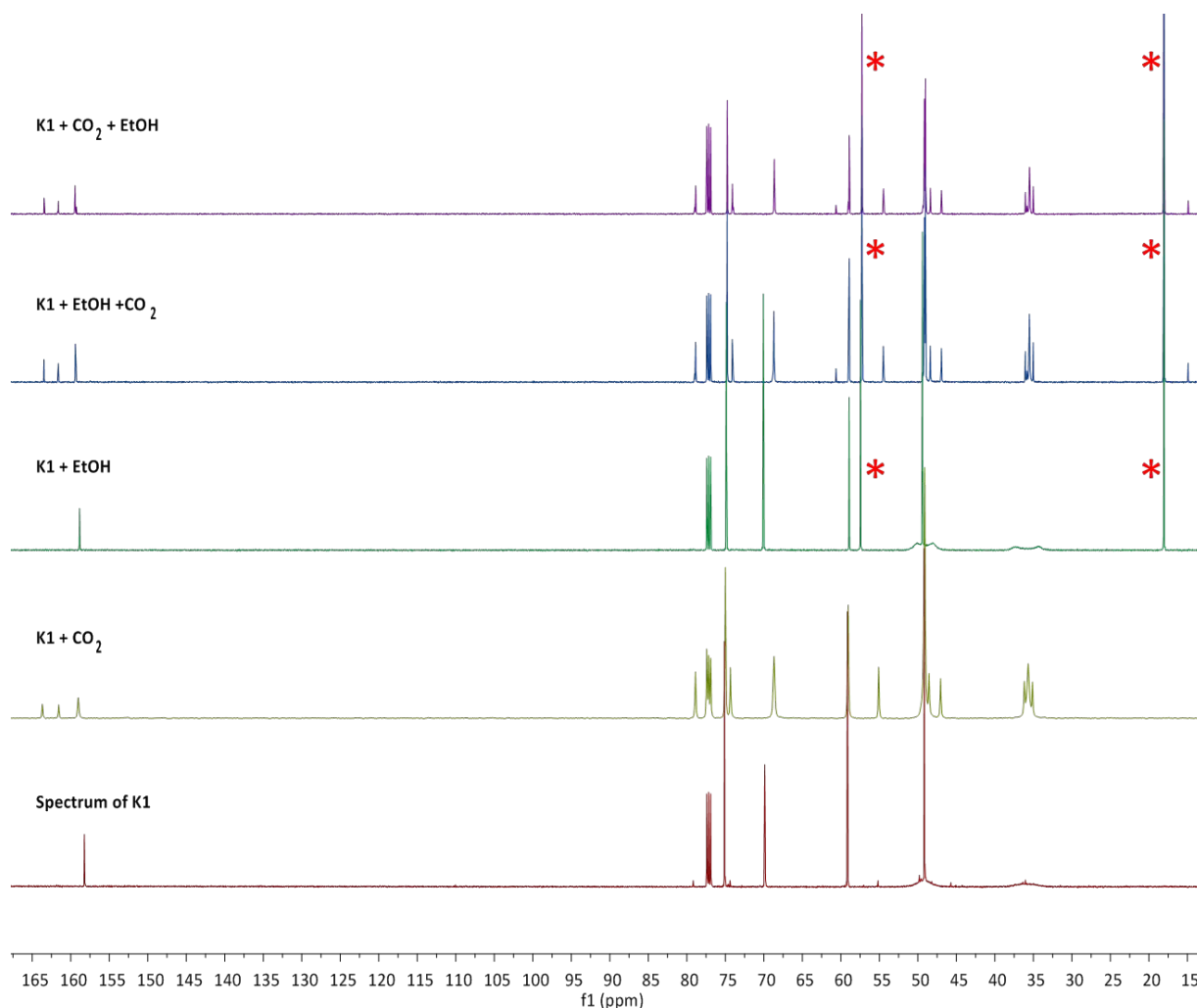
**Figure S3.** Comparative <sup>1</sup>H NMR spectra of the separated EtOH-rich layers of two switchable polarity solvents, K1 and TMG, showing only minor resonances from residual gasoline. Top: <sup>1</sup>H NMR of the K1 fraction containing EtOH (signals between 2.5ppm to 3.6 ppm belong to the K1 base); bottom: <sup>1</sup>H NMR of the TMG fraction containing EtOH, with two NMR resonances at about 2.7 ppm resulting from TMG. Other resonances present are from impurities in K1 or TMG and incidental gasoline captured by the sorbent material. \* denotes resonances belonging to EtOH.



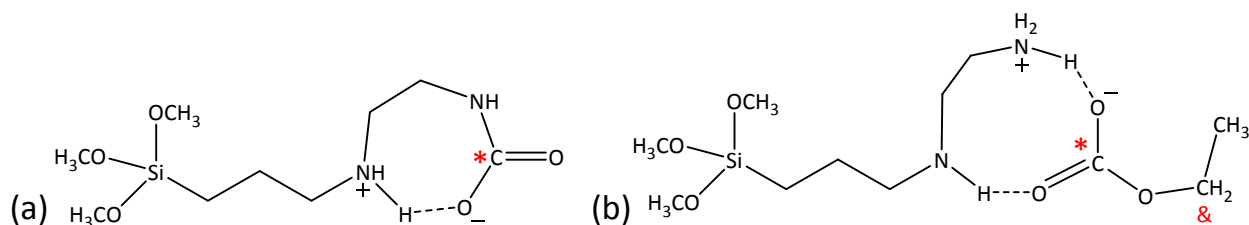
	Areas Normalized to Benzene			Area Compared to Methyl			Ratio Increase from Gasoline	
	E10 Gasoline	TMG- Ethanol Fraction	K1- Ethanol Fraction	E10 Gasoline	TMG- Ethanol Fraction	K1- Ethanol Fraction	TMG-Ethanol Fraction	K1-Ethanol Fraction
Naphthalene	0.43	0.64	0.35	0.000959	0.0366	0.0434	38	45
Partial Aromatic (7.20-6.8 ppm)	47.1	6.35	5.48	0.105	0.365	0.680	3.5	6.5
Methyl (1.0-0.5 ppm)	450	17.4	8.06					

**Figure S4.**  $^1\text{H}$  NMR spectra comparing E10 gasoline (top), and the materials extracted along with EtOH by TMG (middle) and K1 (bottom). Spectra were scaled to show equal intensity ethanol resonances (marked by the asterisks). The table at the bottom shows three integration regions, all normalized to the areas of the respective benzene resonances at 7.36 ppm, and then compared to the areas for the aliphatic methyl resonances. The results in the final two columns of the table show the increase in concentration of naphthalene and aromatic species with resonances from 7.20 to 6.80 ppm. That the values are different than one suggests that the aromatic species are not introduced by contamination during separation. Incidental increases in aromatic species in the ethanol fractions are also reported for pervaporation membranes.<sup>1-4</sup>

\* denotes resonances belonging to EtOH.

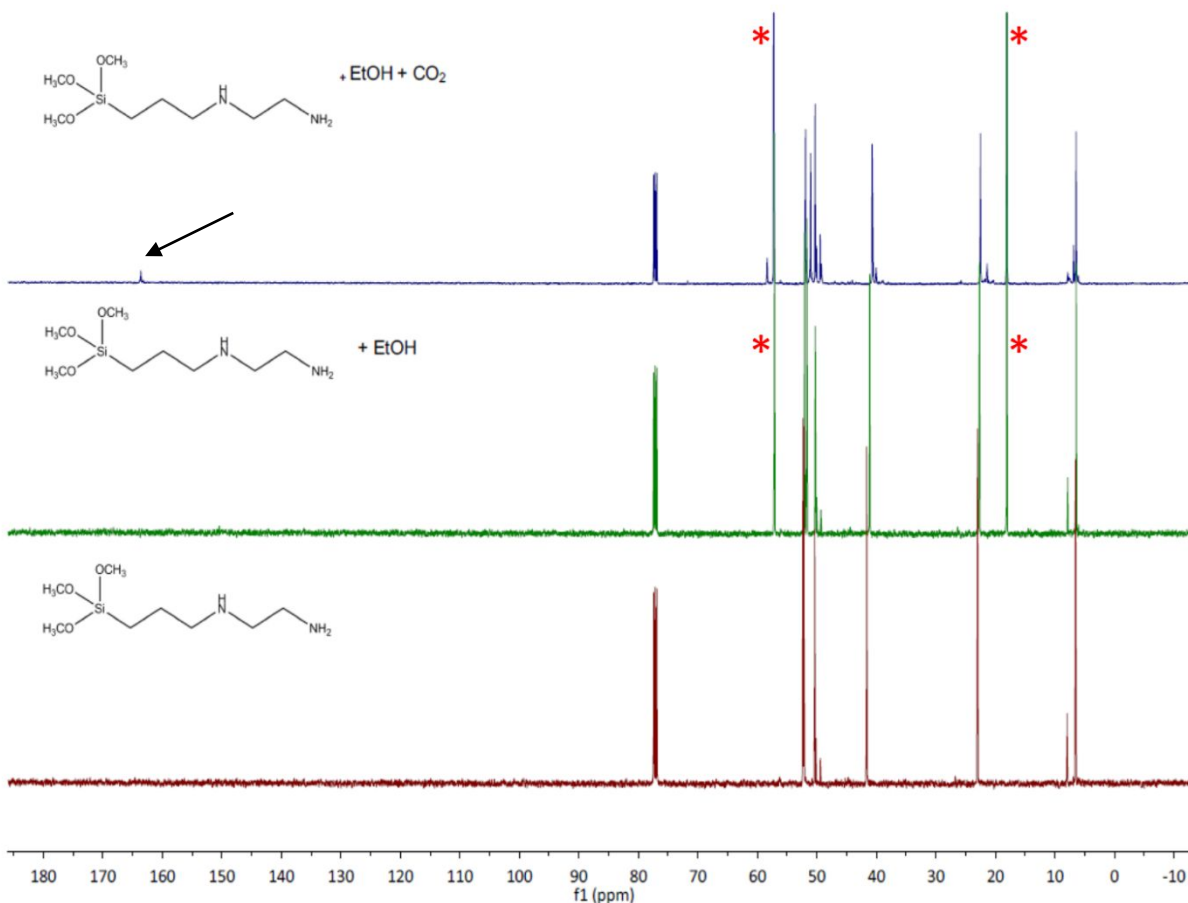


**Figure S5.** Sequence of spectra, bottom to top, showing the reaction of K1 with  $\text{CO}_2$  in  $\text{CDCl}_3$  is independent of the presence of EtOH.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the reference reactions with base K1 showing that the order of addition (alcohol vs.  $\text{CO}_2$ ) has no influence on the formation of the ethyl carbonate species. The formation of the carbonate is confirmed by the appearance of the signals in the range of 160 to 165 ppm; this is in agreement with published data.<sup>5</sup> \* denotes resonances belonging to EtOH.



**Figure S6.** Differentiation between two possible carbamate and carbonate structures.  
**(a)** Possible carbamate structure formed by reaction of  $N^1$ -(3-(trimethoxysilyl)propyl)ethane-1,2-diamine +  $\text{CO}_2$ . Ethanol is not needed to form a carbamate. **(b)** Possible carbonate structure

formed by the reaction of *N*<sup>1</sup>-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine + EtOH + CO<sub>2</sub>. \* indicates carbon that gives rise to the carbamate carbonyl resonance at 163.6 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR. The carbamate and carbonate resonances are not necessarily distinguishable by <sup>13</sup>C{<sup>1</sup>H} NMR, thus both are marked by \*. The NMR resonance that allows differentiation is the presence or absence of the methylene resonance (&) from the ethyl carbonate. In the <sup>13</sup>C{<sup>1</sup>H} NMR, the methylene resonance in free ethanol appears at about 58 ppm, while the methylene resonance in ethyl carbonate (&) appears at about 63 ppm.



**Figure S7.** Sequence of spectra, bottom to top, showing that in solution, a carbamate is formed preferentially over a carbonate when CO<sub>2</sub> is introduced to a solution of *N*<sup>1</sup>-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine + EtOH. Bottom: <sup>13</sup>C{<sup>1</sup>H} NMR of the *N*<sup>1</sup>-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine (model for the EDA-SAMMS); middle: <sup>13</sup>C{<sup>1</sup>H} NMR of the *N*<sup>1</sup>-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine + EtOH; top: <sup>13</sup>C{<sup>1</sup>H} NMR of the *N*<sup>1</sup>-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine + EtOH + CO<sub>2</sub>. The formation of the carbamate is confirmed by the appearance of the 163.6 ppm signal as indicated by the arrow in the top spectrum, and the absence of a resonance at 63 ppm, showing that there is no alcohol bound to the carbonate, as shown by a & in Figure S6. \* denotes resonances belonging to EtOH.

## References

1. Partridge, R. D.; Weissman, W.; Ueda, T.; Iwashita, Y.; Johnson, P.; Kellogg, G., Onboard Gasoline Separation for Improved Vehicle Efficiency. *SAE International Journal of Fuels and Lubricants* **2014**, 7 (2), 366-378.
2. Iwashita, Y.; Ueda, T.; Partridge, R. D.; Lucchesi, R.; Johnson, P. O.; Kellogg, G. L. Fuel separation method WO 2014/113020 A1, 2013.
3. Chishima, H.; Kuzuoka, K.; Kurotani, T.; Kudo, H., Study of Ethanol-Gasoline Onboard Separation System for Knocking Suppression, SAE Technical Paper 2015-01-1954. SAE International: 2015.
4. Mizuno, K.; Chishima, H.; Zhou, J.; Carpenter, B.; Wickert, P.; Welling, S.; Seitz, D. S., Study of Alcohol-Gasoline Separation Technology to Suppress Knock and Enable Higher Efficiency Engines, SAE Technical Paper 2018-01-0882. SAE International: 2018.
5. Malhotra, D.; Koech, P. K.; Heldebrant, D. J.; Cantu, D. C.; Zheng, F.; Glezakou, V. A.; Rousseau, R., Reinventing Design Principles for Developing Low-Viscosity Carbon Dioxide-Binding Organic Liquids for Flue Gas Clean Up. *Chemsuschem* **2017**, 10 (3), 636-642.