

Unveiling the nitrogen chemistry of Titan with the Dragonfly Mass Spectrometer: experimental focus on amines and amides

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Supporting Information

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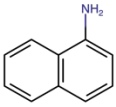
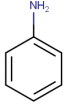
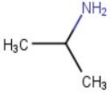
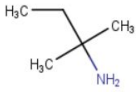
28 Fig. S5 – p. S7

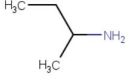
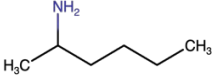
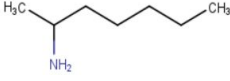
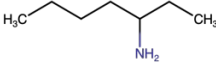
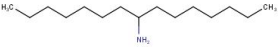
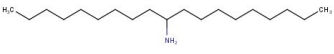
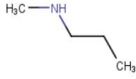

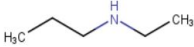
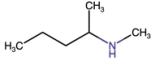
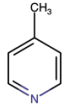
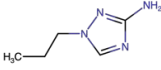

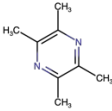
29 Supporting Information

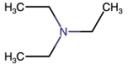
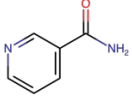
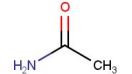
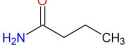
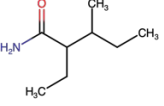
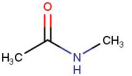
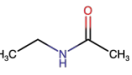
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31 **Table S1.** List of the compounds investigated in this study, their chemical families and types, and
32 their structures. In orange, the compounds that are chiral. In green, the compounds that were
33 investigated in LDMS.

34

Name	Type	Structure
Ethylamine	Aliphatic primary amines	$\text{H}_2\text{N}-\text{R}^1$ <p>R¹ corresponds to the length of the carbon chain</p>
Butylamine		
Pentylamine		
Hexylamine		
Octylamine		
Nonylamine		
Decylamine		
Dodecylamine		
Tetradecylamine		
Hexadecylamine		
Octadecylamine		
1-Naphthylamine	Aromatic primary amines	
Aniline		
Isopropylamine	Branched primary amines	
Tert-amylamine		

2-aminobutane		
2-aminopentane		
2-aminoheptane		
3-aminoheptane		
8-aminopentadecane		
10-aminononadecane		
N-methylpropylamine	Aliphatic secondary amines	
N-isopropylmethylamine		
N-ethyl-N-propylamine		
N-methyl-2-pentanamine		
1,2,4-Triazole		Aromatic secondary amines
4-methylpyridine	Tertiary amines	
1-propyl-1H-1,2,4-triazol-3-amine		
N-methylpyrrole		
2,3,5,6-tetramethylpyrazine		
Hexamethylenetetramine (HMT)		

Triethylamine		
Nicotinamide	Primary amides	
Acetamide		
Butyramide		
2-ethyl-3-methylpentamide		
N-methylacetamide	Secondary amides	
N-ethylacetamide		

35

36

37 **Table S2.** Retention time of underivatized and derivatized amines and amides (*cf.* material and
38 methods for experimental conditions)

39

Compound	Retention Time (min)	
	Pure compound	Derivatized compound
Pentylamine	2.84	7.96
Decylamine	9.95	14.54
N-ethyl-N-propylamine	2.18	Methylated: ND Dimethoxymethylated: 6.00 Formylated: 7.52
Aniline	7.01	12.92
Butyramide	6.40	12.20

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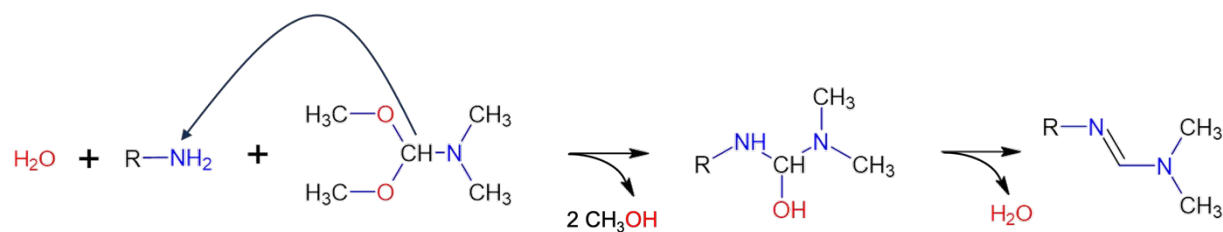
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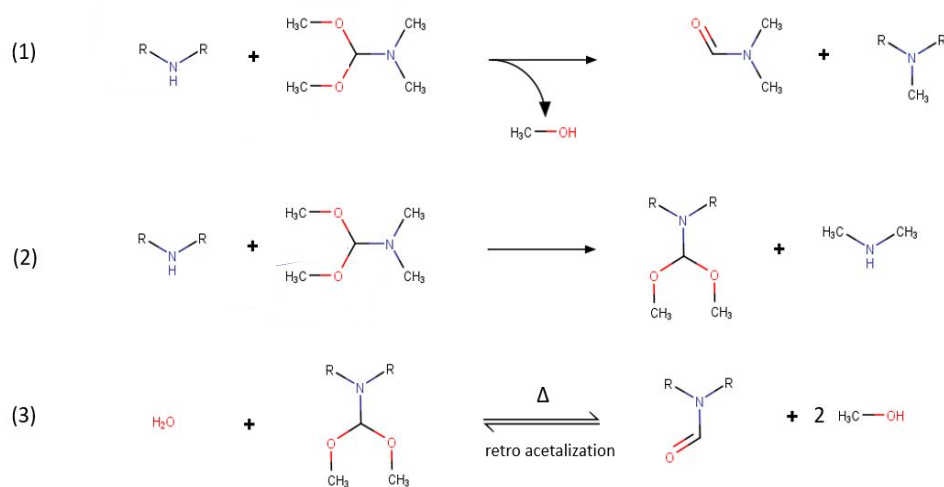
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50 **Figure S1.** Proposed mechanism of DMF-DMA derivatization on primary amines:
51 dimethylformamidination is observed.

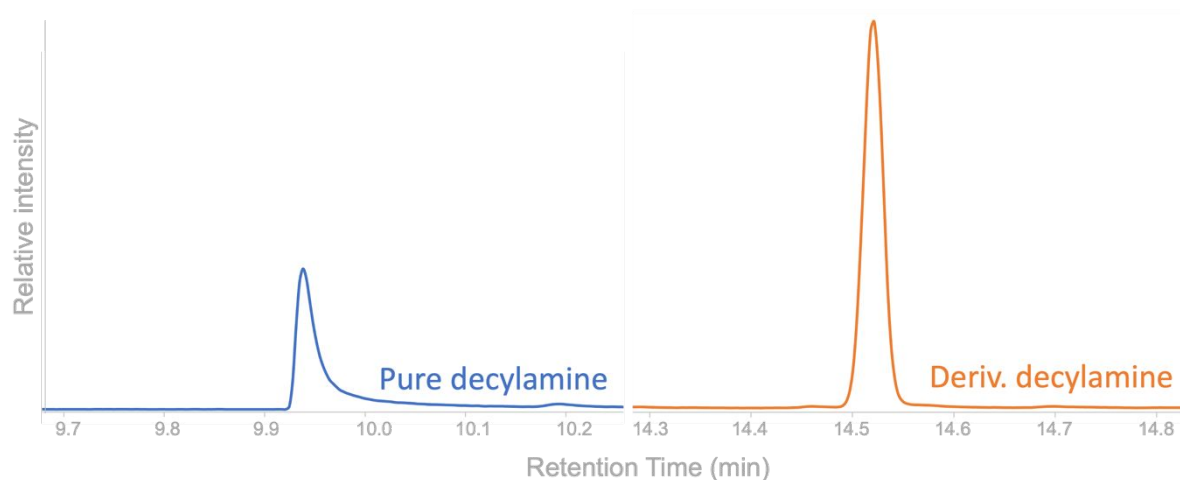
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64

65 **Figure S2.** proposed mechanisms for the DMF-DMA derivatization of secondary amines, (1)
66 methylation, (2) dimethoxymethylation and (3) formylation.

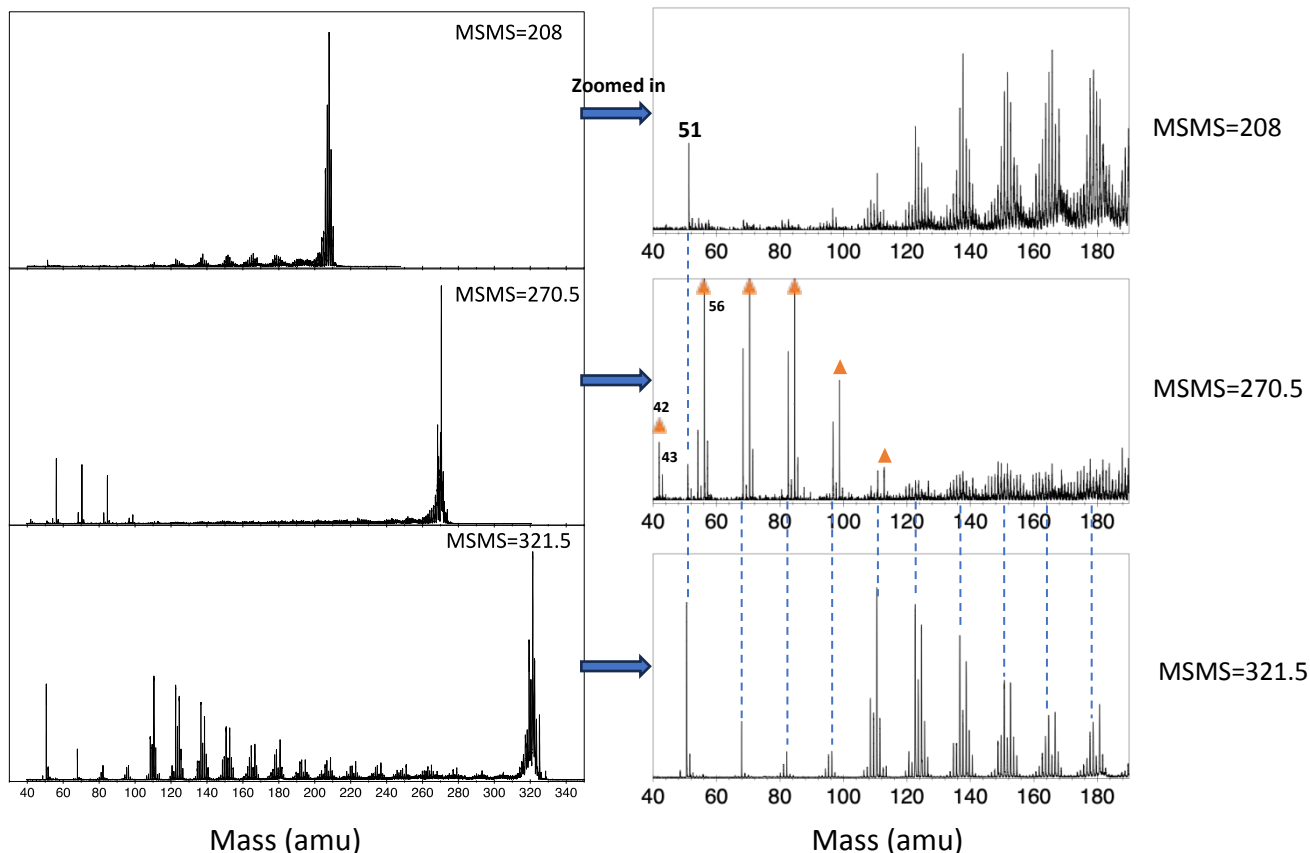
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68
 69 **Figure S3.** Merged chromatograms of free pentylamine (blue) and derivatized pentylamine with
 70 DMF-DMA (orange). The tailing of the free pentylamine is due to the polarity of the amine
 71 functional group. The tailing is suppressed when the amine functional group is derivatized.
 72 Relative MS response is not to the same scale for the two peaks.

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 74

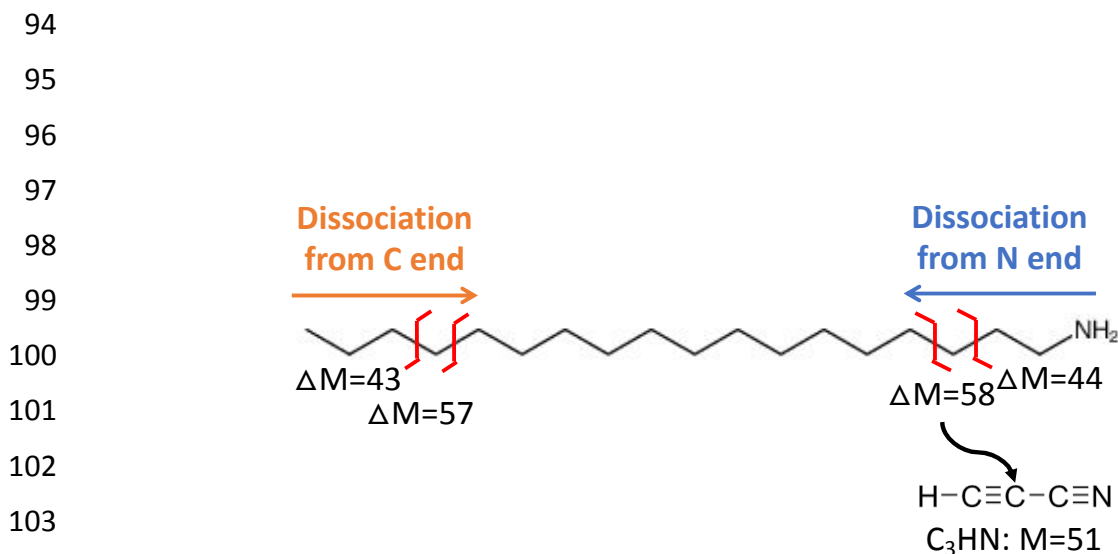
75 MS/MS analysis of peaks in the mass spectrum of octadecylamine



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77
78
79 **Figure S4.** The MS/MS spectra of main peaks ($M = 208, 270.5$ and 321.5) observed in the positive
80 mode mass spectrum of Octadecylamine (parent mass = 269.5). The full spectra are on the left side
81 while the zoomed in spectra (mass from 40 to 190).

82
83 Across all linear amines, the MS/MS analysis and peak assignments exhibit similarities, differing
84 only in accordance with the varying chain lengths of the molecular structures. Figure S1 provides
85 representative results showing the MS/MS analysis of octadecylamine samples. A comparative
86 examination was conducted between the MS/MS spectra of the protonated parent peak ($M = 270.5$)
87 and the two more pronounced peaks, namely the spectra corresponding to the mass 208 and the
88 $[M+H+51]^+$ adduct. Notably, despite relative intensity discrepancies, the spectra of 208 and the
89 $[M+H+51]^+$ adduct exhibit a general similarity. In both spectra, the peak at 51 was consistently
90 observed as a prominent fragment. While certain segments of the MS/MS spectra of the parent
91 270.5 peak align with the other two spectra, as indicated by the dotted lines in Figure S1, an
92 additional series of peaks (labeled by triangles) was observed, presenting a different structural
93 characteristic of the parent ion.



108 **Figure S5.** The possible fragmentation pathways for MS/MS spectrum of octadecylamine. The
109 peak of mass 51 could be assigned as C_3HN , probably converted from a fragment of
110 octadecylamine. The cases for the other amines are similar.

111
112
113 One plausible explanation for the observed spectra is rooted in the linear structure of the parent ion
114 octadecylamine, as shown in Figure S2, wherein one end has a CH_3 group and the other end has
115 an NH_2 group. The fragmentation therefore may occur via two pathways, originating from either
116 terminal of the chain, with the residual fragments forming positive ions in the spectra. Given that
117 fragments of differing masses would arise from the two opposing ends, the series labeled by dotted
118 lines showed a 2 mass units lower compared to the series labeled with triangles in Figure S1. Thus,
119 we speculate that the series marked by dotted lines correspond to fragmentation initially occurring
120 from the NH_2 end, yielding lower mass fragments, while the series labeled with triangles
121 originating from the CH_3 end.

122
123 Despite its relatively weak intensity, the presence of the mass 51 peak in the parent ion MS/MS
124 spectrum suggests the potential generation of the species of mass 51 as a stable fragment derived
125 from the parent amine. Subsequently, this fragment might reattach to the parent ion, forming a
126 larger adduct in the mass spectrum. A possible formula for the mass 51 fragment could be C_3HN ,
127 as shown in Figure S2, potentially stemming from the dehydration of a fragment originating from
128 the NH_2 side. For the adduct peak ($M = 321.5$), the incorporation of the mass 51 group appears to
129 obstruct the fragmentation pathway from the CH_3 side, possibly through interaction with the CH_3
130 moiety, thereby resulting in an MS/MS spectrum displaying only one series of fragmentation. The
131 resemblance in MS/MS spectra between the mass 208 peak and the 321.5 adduct peak implies a
132 structural similarity between the two entities.

133
134 The cases for other linear amines studied in this work are similar. The mass of 208 peak seems to
135 be a stable fragment from the adduct peak. Although the mass of the adduct peaks in different
136 amines are different, they only varied by the length of the chain, and always formed the same stable
137 fragment of the mass 208 peak.