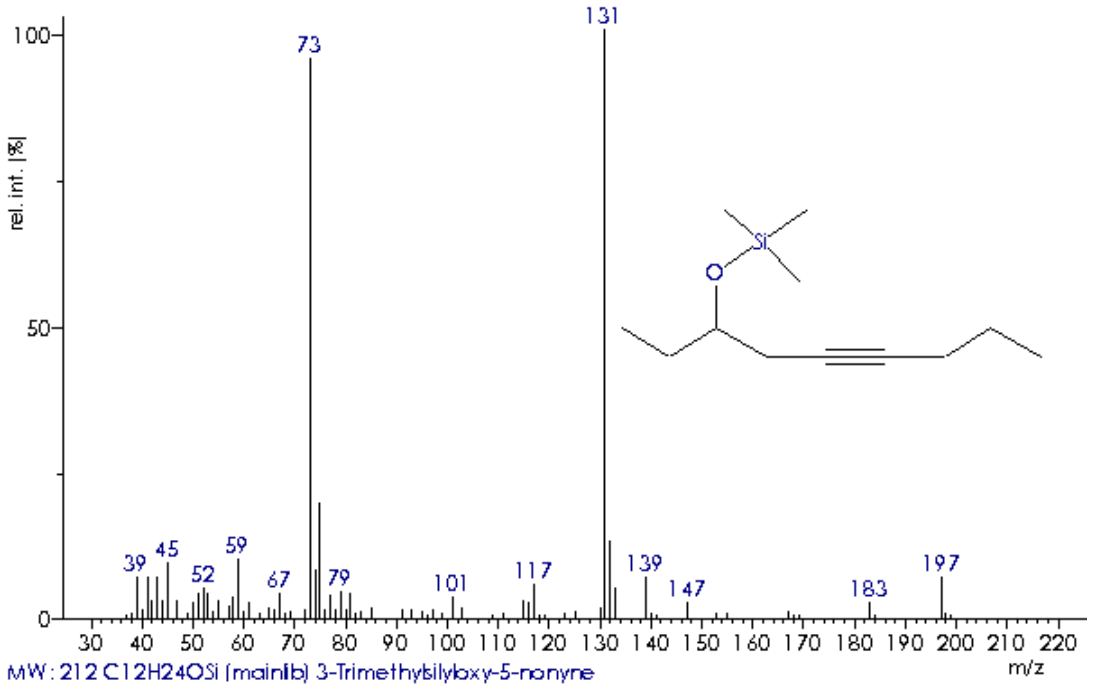
Answer 6.15

Identify the unknown from its 70 eV EI mass spectrum.
HR-MS: *m/z* 197.1366, *m/z* 131.0870.
The positive-ion CI mass spectrum, isobutane reagent gas, gave
m/z 213 (100 %), 214 (18.9 %), 215 (5.0 %).



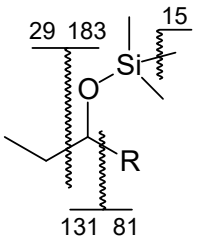
CI: Given the above conditions, the CI mass spectrum exhibits a $[M+H]^+$ ion at *m/z* 213. Thus, we have *M* = 212 u; even mass indicates 0, 2, 4, ... nitrogen atoms.
The isotopic pattern is worth a closer look: according to Table 3.2, a [M+1] peak of 18.9 % is accompanied by a [M+2] peak of less than 2 % if carbon alone contributes to it. The observed difference of about 3 % is best explained by the presence of ^{30}Si, whereas ^{34}S would add 4.5 %. Consequently, one has to subtract 5.1 % from [M+1] leaving 13.8 % for the contribution of ^{13}C, i.e., we estimate 12–14 carbon atoms.
The isotopic pattern shows no Cl or Br.

HR-MS: The difference between both accurate *m/z* values is 66.0496 u. Knowing that *m/z* 197.1366 represents the $[M–CH_3]^+$ ion, *m/z* 131 is a [M–81] ion, the exact difference being 81.0730 u.

No $M^{+\bullet}$ but $[M–CH_3]^+$ in the EI mass spectrum plus a Si isotopic pattern is typical for silylated compounds. Furthermore, the *m/z* 73 ion can be assigned $[SiMe_3]^+$.

m/z 197	[M–15], $[M–CH_3]^+$, Si pattern
m/z 183	[M–29], $[M–C_2H_5]^+$, Si pattern
m/z 139	[M–73], $[M–SiMe_3]^+$
m/z 131	[M–81], [M–alkyl]$^+$, Si pattern
m/z 73	$[SiMe_3]^+$, Si pattern

Loss of $CH_3^{\bullet}$ chiefly comes from the silyl group making an α-cleavage for $C_2H_5^{\bullet}$ loss probable. Si doesn't much induce α-cleavages, while O (here presumably protected by the silyl) does well. This lets us assume a structure like

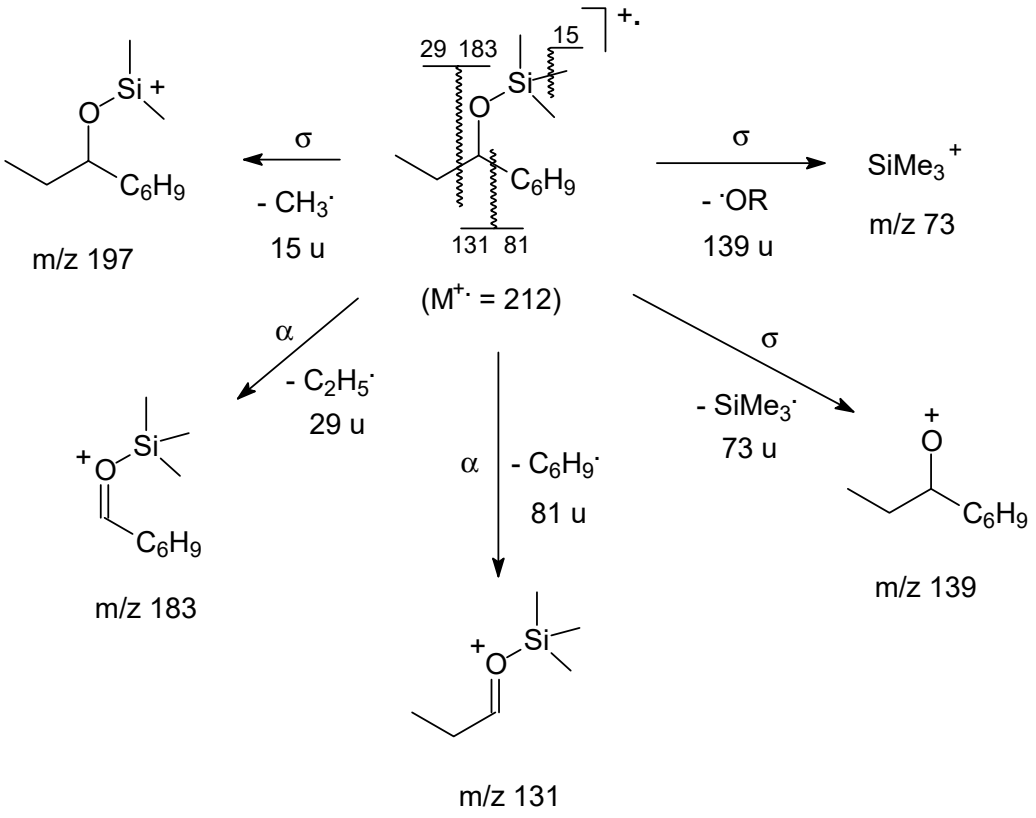


Now, we can check *m/z* 131 using HR-MS data. We calculate *m/z* 131.0887 for $[C_6H_{15}OSi]^+$ which agrees well with the experimental value. Trying a C_xH_y composition for R gives C_6H_9; calc. 81.0704 u, exp. difference 81.0730 u

Molecular formula: $C_{12}H_{24}OSi$; r+d = 13 – 12 + 1 = 2 (check *m/z* 197 HR-MS now!)

The structure of R cannot really be assigned from the spectrum.

Fragmentation scheme (next page):


29 183
15
+.
Si
O
C6H9
131 81
σ
- CH3·
15 u
m/z 197
σ
- ·OR
139 u
SiMe3 +
m/z 73
(M+· = 212)
α
- C2H5·
29 u
α
- C6H9·
81 u
σ
- SiMe3·
73 u
m/z 183
m/z 131
m/z 139