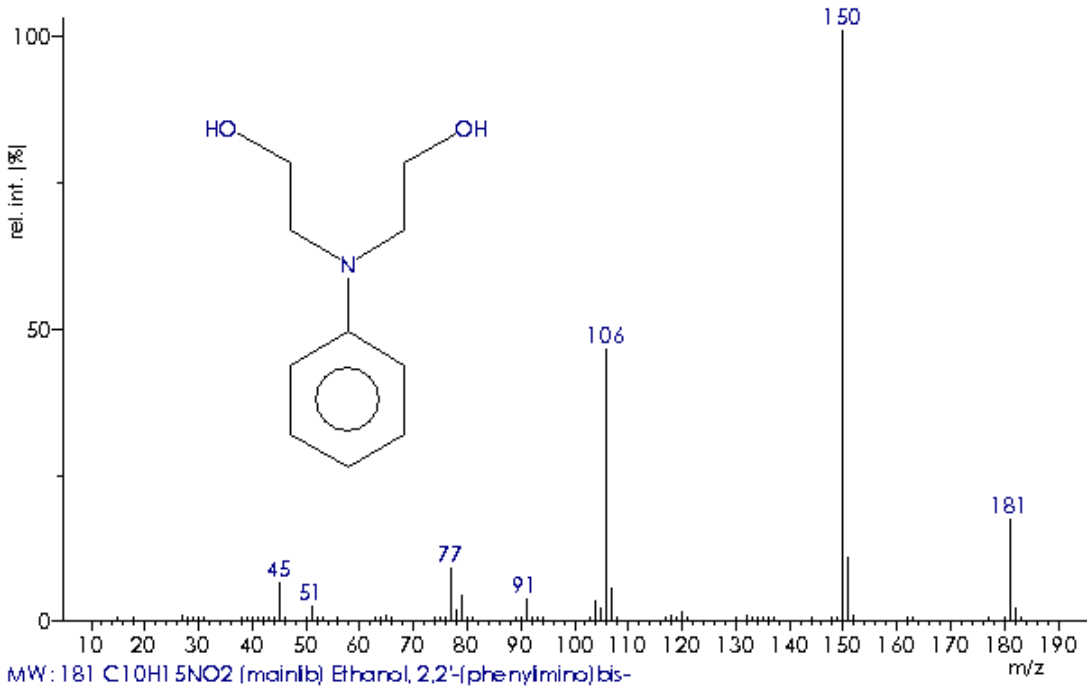
Answer 6.16

Identify the unknown from its 70 eV EI mass spectrum.
The ^{13}C-NMR spectrum shows 6 signals.
HR-MS: *m/z* 181.1086, *m/z* 150.0901, *m/z* 106.0644.



The presumed $M^{+\bullet}$ ion is observed at *m/z* 181.
Odd mass indicates 1, 3, 5, ... nitrogen atoms.
The isotopic pattern shows no Cl, Br, Si or S.
From 13 % (relative to $M^{+\bullet}$) for the contribution of ^{13}C we estimate 12 carbons.
The intensity distribution points towards an aromatic or heterocyclic compound.

HR-MS: Exploit the differences between accurate *m/z* values to identify neutral losses.
i) 181.1086 u – 150.0901 u = 31.0185 u which identifies $CH_3O^{\bullet}$ (calc. 31.0184 u) as can be expected for a neutral loss of 31 u and
ii) 150.0901 u – 106.0644 u = 44.02574 u correlating well with C_2H_4O (calc. 44.0262 u) whereas C_3H_8, $^{\bullet}N(CH_3)_2$ or CO_2 loss can be excluded.
→ Unknown contains ≥ 2 oxygen atoms and an alcohol or an ether group(s).
→ Nitrogen is still contained in the *m/z* 106.0644 ion. Assuming *m/z* 77 as phenyl, the remaining 29 u have to consist of C, H, and N. Thus, we try $[C_7H_8N]^+$
(calc. *m/z* 106.0651) that nicely fits the experimental value.

Molecular formula: $C_{10}H_{15}NO_2$; calc. 181.1097
r+d = 10 – 7.5 + 0.5 + 1 = 4

The occurrence of only 6 peaks in the ^{13}C-NMR spectrum requires symmetry to comply with 10 carbons. A singly substituted phenyl yields 4 signals for 6 carbon atoms, and thus, the remaining 4 carbon atoms yield only 2 signals, i.e., there are pairs of equal carbon atoms.

Fragmentation scheme: