M1.(a) (nucleophilic) addition-elimination

M4 for 3 arrows and lp

Allow wrong amine in M1 but penalise in M3

Allow C₃H₇ in M3

Minus sign on NH₃ loses M1 (but not M4 if NH₃ also shown here)

- Allow attack by: NH₂CH₂CH₂CH₃
- M2 not allowed independent of M1, but allow M1 for correct attack on C⁺
- + rather than δ+ on C=O loses M2
- If CI lost with C=O breaking, max 1 for M1
- M3 for correct structure <u>with charges</u> but lone pair on O is part of M4
- 3 arrows in M4 can be shown in two separate steps.
- If M3 drawn twice, mark first answer eg ignore missing + if missed off second structure
- Only allow M4 after correct / very close M3
- For M4, ignore RNH₂ removing H⁺ but lose M4 for Cl-removing H⁺ in mechanism,
- but ignore HCl shown as a product.

N-propylethanamide must be this name even if wrong amine used NOT N-propylethaneamide

(b) (i)

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4

1

Not allow ambiguous C₃H₇NH₂

BEWARE No mark for the original amine CH₃CH₂CH₂NH₂

Label and structure must both be correct for each type to score the mark.

1

Allow C₂H₅

Penalize wrong number of carbons but otherwise correct, first time only.

1

1

(ii) Absorption at 3300-3500 (cm⁻¹) in spectrum

Allow trough, peak, spike.

Ignore absorption at 750 – 1100 for C–C bond in secondary - this is within fingerprint region.

Allow any number in this range.

If range missing, no further marks.

If range linked to tertiary, no further marks.

1

N–H (bond) (only) present in secondary amine or not present in tertiary amine

OR

This peak or N–H absorption (only) present in spectrum of secondary amine or not present in spectrum of tertiary amine

1

(c) (i) M1 Route A: stage 1 KCN

Apply list principle for extra reagents or catalysts NOT HCN NOT KCN / acid Not KCN / HCN

1

M2 Aqueous or ethanolic

M2 only scores after correct M1

1

1

1

1

1

M3 Route **A** Intermediate CH₃CH₂CN or propanenitrile

If M3 intermediate wrong, max 2 for M1 & M2 ie no mark for stage 2

Name alone must be exactly correct to gain M1 but mark on if name close

But if M3 intermediate close, eg "nitrile" or wrong nitrile, can award marks in stage 2

correct formula gains M1 (ignore name if close)

If stage 1 correct and intermediate is missing, can award marks in stage 2

contradiction of name and formula loses mark

stage 1 wrong & intermediate missing, no marks.

M4 Route **A**: stage 2 H₂

H loses M4 but mark on

LiAIH₄

Apply list principle for extra reagents or catalysts. M5 only scores after correct M4

Not NaBH, not Sn or Fe / HCl

Allow (dil) acid after but not with LiAIH,

Penalise conc acid.

M5 Ni or Pt or Pd

ether

M6 Route **B** NH₃

With acid loses M6 & M7

Apply list principle for extra reagents or catalysts.

Excess NH₃
Ignore conc, ignore high P, ignore solvent.

1

M7

(ii) Route **A** disadv HCN

Toxic / poisonous KCN or cyanide or CN⁻ or

Expensive LiAIH₄ ignore acidified

OR lower yield because 2 steps

Allow H₂ flammable / explosive etc. Not just dangerous. Ignore time reasons.

1

Route **B** disadv Further reaction / substitution likely *Allow impure product.*

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M2.(a) Sn / HCl **OR** Fe / HCl not conc H₂SO₄ nor any HNO₃

Ignore subsequent use of NaOH

Ignore reference to Sn as a catalyst with the acid Allow H₂ (Ni / Pt) but penalise wrong metal But NOT NaBH₄ LiAlH₄ Na / C₂H₅OH

1

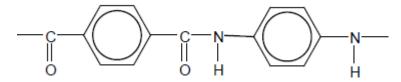
Equation must use molecular formulae

 $C_6H_4N_2O_4 + 12[H]$

12[H] and 4H₂O without correct molecular formula scores 1 out of 2

1

 \rightarrow C₆H₈N₂ + 4H₂O Allow + 6H₂ if H₂ / Ni used Allow -CONH- or -COHN- or -C₆H₄-



Mark two halves separately: lose 1 each for

- · error in diamine part
- error in diacid part
- error in peptide link
- missing trailing bonds at one or both ends
- either or both of H or OH on ends Ignore n

2

(b) H_2 (Ni / Pt) but penalise wrong metal NOT Sn / HCl, NaBH₄ etc.

1

 CH_2

1

In benzene 120°

1

In cyclohexane 109° 28' or 109½° *Allow 108*° - *110*°

If only one angle stated without correct qualification, no mark awarded

1

(c) (i) Nucleophilic addition

M4 for lp, arrow and H+

$$M2$$
 CH_3CH_2
 CH_3
 CH_3CH_2
 CH_3
 C

- M2 not allowed independent of M1, but allow M1 for correct attack on C+
- + rather than δ+ on C=O loses M2
- M3 is for correct structure including minus sign but lone pair is part of M4
- Allow C₂H₅
- M1 and M4 include Ip and curly arrow
- Allow M4 arrow to <u>H</u> in H₂O (ignore further arrows)
- (ii) M1 Planar C=O (bond / group)

 Not just planar molecule
 - M2 Attack (equally likely) from either side

 Not just planar bond without reference to carbonyl
 - M3 (about product): Racemic mixture formed **OR** 50:50 mixture or each enantiomer equally likely

M3. (a) (i)

[17]

4

1

Allow -CONH- or - COHN -

Mark two halves separately

lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends

Not allow –(C₀H₁₂)– Ignore n

1

1

(ii) M1 in polyamides - H bonding

1

M2 in polyalkenes - van der Waals forces

Penalise forces between atoms or van der Waals bonds

1

M3 Stronger forces (of attraction) in polyamides
Or H bonding is stronger
(must be a comparison of correct forces to score M3)

Do not award if refer to stronger bonds

1

(b) (i) (nucleophilic) addition elimination

Not allow N-H₂

1

M2 not allowed independent of **M1**, but allow **M1** for correct attack on C+

+ rather than δ + on C=O loses **M2**If CI lost with C=O breaking, max 1 for **M1 M3** for correct structure with charges but Ip on O is part of **M4**only allow **M4** after correct/ very close M3

For M4, ignore NH3 removing H5 but lose **M4** for CI removing H5 in mechanism, but ignore HCI as a product

4

(ii) N-methylpropanamide

Not N-methylpropaneamide

1

(c)

Allow -CONH- or -COHN-

1

(d) (i) <u>2-amino-3-hydroxypropanoic acid</u>

1

(ii)

Must be salts of aspartic acid

allow -CO2-

allow NH₂-

1

(iii) Penalise use of aspartic acid once in d(iii) and d(iv)

1

(iv) Penalise use of aspartic acid once in d(iii) and d(iv)

allow –CO₂must show C-N bond don't penalize position of + on N(CH₃)₃

[16]