1 (a)

	Deductions
B is soluble in water	Not MgO, Al_2O_3, SiO_2
Aq. solution of **B** reacts with Na_2CO_3 in 2:3 ratio to form $CO_2(g)$	Aq. solution of **B is acidic** (✓) Since the reacting ratio is 2:3, the acid formed must be tribasic ∴ **B is P_4O_{10}/P_4O_6** [1]
C is soluble in water	Not MgO and Al_2O_3, SiO_2
Aq. solution of **C** reacts with NH_4^+ to give $NH_3(g)$	Aq. solution of **C is basic** (✓) ∴ **C is Na_2O** [1]
A reacts with both **B** and **C**	**A is amphoteric** (✓) ∴ **A is Al_2O_3** [1]

2-3✓: 1m

Equations for reaction with water:

B: $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ **[1]**

C: $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ **[1]**

(b) **(i)** $3Mg(NH_2)_2(s) \rightarrow Mg_3N_2(s) + 4NH_3(g)$

(ii) **$Mg(NH_2)_2$** is **less thermally stable** than $Ba(NH_2)_2$. (✓)

Mg^{2+} has the same charge but a **smaller** ionic **radius** hence a **higher charge density** than Ba^{2+}. Thus Mg^{2+} **polarises** the large **NH_2^- anion more**. (✓) This **weakens the N-H bond** in the $Mg(NH_2)_2$ **more** (✓) and thus a lower temperature is needed to decompose magnesium amide.

4✓: 2m; 2-3✓: 1m

(iii) Rxn 1: $Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(aq)$

Rxn 2: $NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Amount of acid $= \frac{12.0}{1000} \times 0.50 = 0.00600$ mol

From rxn 2: 1 H^+ ≡ 1 NH_3
Amount of NH_3 produced from reaction with air = 0.00600 mol
From rxn 1: 1 Mg_3N_2 ≡ 2 NH_3

Amount of Mg_3N_2 formed $= \frac{0.00600}{2} = 0.00300$ mol [1]

Mass of Mg_3N_2 in 1.00 g sample $= 0.00300 \times 100.9 = 0.303$ g

∴ percentage of Mg_3N_2 in 1.00 g sample $= \frac{0.303}{1.00} \times 100$

$= 30.3$ % [1]

1 **(c)** **(i)** Precipitate formed is AgCl.

$\left[Ag^+\right]$ at point of mixing $= \dfrac{0.0100 \times 5}{30+5}$ **[1]**

$= 1.428 \times 10^{-3}$ mol dm^{-3}

$\left[Cl^-\right]$ at point of mixing $= \dfrac{\left[Cl^-\right]_{initial} \times 30}{30+5}$

For precipitation to take place: ionic product (AgCl) ≥ K_{sp}(AgCl)

ionic product $= \left(1.428 \times 10^{-3}\right)\left(\dfrac{\left[Cl^-\right]_{initial} \times 30}{30+5}\right) \geq 1.8 \times 10^{-10}$

$\therefore \left[Cl^-\right]_{initial} \geq \underline{1.47 \times 10^{-7}\ \text{mol dm}^{-3}}$ **[1]**

(ii) Cream ppt is **AgBr**, halide present is **Br^-**.

(iii) $\Delta G = \underline{(8.31)(298)\ln\left(1.8 \times 10^{-10}\right)}$

$= -5.56 \times 10^4$ J mol^{-1}

$= \underline{-55.6\ \text{kJ mol}^{-1}}$ **[1]**

Using $\Delta G^{\varnothing}_{ppt} = \Delta H^{\varnothing}_{ppt} - T\Delta S^{\varnothing}_{ppt}$

$-5.56 \times 10^4 = \Delta H^{\varnothing}_{ppt} - (298)(-410)$

$\therefore \Delta H^{\varnothing}_{ppt} = \underline{-178000\ \text{J mol}^{-1} / -178\ \text{kJ mol}^{-1}}$ **[1]**

(iv) Since $\Delta H^{\varnothing}_{ppt} = -178$ kJ mol^{-1}, hence $\Delta H^{\varnothing}_{soln} = \underline{+178\ \text{kJ mol}^{-1}}$ **[1]**

Since $\Delta H_{soln} = -LE + \sum \Delta H_{hyd}\left(\text{ions}\right)$

$+178 = -LE + (-473) + (-378)$

$\therefore LE = \underline{-1030\ \text{kJ mol}^{-1}}$ **[1]**

(v) This difference indicates that **AgCl is not purely ionic** / there **exists covalent character in the ionic bond in AgCl**. **[1]**

The **electronegative difference between Ag and Cl is so small** that complete transfer of an electron from the silver to the chlorine is not possible. **[1]**

OR

Cl^- has a **large anion radius** allowing it to be **readily polarised** by Ag^+ ions. **[1]**

[Total: 20]

2 (a) (i) Indicator for first end point: cresol red

Indicator for second end point: methyl yellow **[1] – for both indicators**

pK_a of indicator matches the pH change at equivalence point **[1]**

OR

Equivalence point pH lies within working range of the indicator **[1]**

(ii) Since CO_3^{2-} the stronger base, it will react with acid first.

Rxn at first end point: $CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$

$$\text{amount of } H^+ = \underline{\frac{8.40}{1000} \times 0.200} = \mathbf{0.00168 \text{ mol}}$$

Since $1\ CO_3^{2-} \equiv 1\ H^+$

amount of CO_3^{2-} in 20.0 cm^3 solution $= \underline{0.00168 \text{ mol}}$ **[1]**

$$[Na_2CO_3] = \underline{0.00168 \times \frac{1000}{20.0}} \times 106 = \underline{8.90 \text{ g dm}^{-3}}$$ **[1]**

Rxn at second end point: $HCO_3^-(aq) + H^+(aq) \rightarrow CO_2 + H_2O$

Vol. of acid reacting with HCO_3^- formed from CO_3^{2-}

$= 8.40 \text{ cm}^3$

Vol. of acid reacting with HCO_3^- originally in solution

$= \underline{(18.80 - 8.40) - 8.40} = \underline{2.00 \text{ cm}^3}$

amount of acid reacting $= \underline{\dfrac{2.00}{1000} \times 0.200}$

$= \underline{4.00 \times 10^{-4} \text{ mol}}$ **[1]**

$=$ amount of HCO_3^- originally in solution

$\therefore [HCO_3^-]$ originally in solution $= \underline{4.00 \times 10^{-4} \times \dfrac{1000}{20.0} \times 84.0}$

$= \underline{1.68 \text{ g dm}^{-3}}$ **[1]**

OR

Vol. of acid used to react with total amount of HCO_3^-

$= \underline{18.80 - 8.40} = 10.40 \text{ cm}^3$

Total amount of acid used $=$ Total amount of HCO_3^- present

$= \underline{\dfrac{10.40}{1000} \times 0.200}$

$= \underline{0.00208 \text{ mol}}$

At first end point, $1\ CO_3^{2-} \equiv 1\ HCO_3^-$

Amount of HCO_3^- formed from $CO_3^{2-} = 0.00168$ mol

original amount of HCO_3^- $= \underline{0.00208 - 0.00168}$

$= \underline{4.00 \times 10^{-4} \text{ mol}}$ **[1]**

$[HCO_3^-]$ originally in solution $= \underline{4.00 \times 10^{-4} \times \dfrac{1000}{20.0} \times 84.0}$

$= \underline{1.68 \text{ g dm}^{-3}}$ **[1]**

2 (b) (i) It is more difficult/energy required to remove a positively charged H^+ ion from anion than a neutral molecule due to greater electrostatic attraction. **[1]**

OR

Doubly charged anion is more unstable than a singly charged anion. **[1]**

(ii) A higher pK_{a1} value for succinic acid implies it is the weaker acid than malonic acid, indicating the anion of succinic acid is less stable/anion of tartaric acid is more stable (✓)$_1$.

Any one of the following reasons:

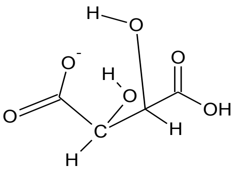
1. Two electron-withdrawing -OH groups that helps to disperse the negative charge on O^- in the monoanion of tartaric acid (✓)$_2$, making it more stable.

   There is electron-donating alkyl group that intensifies the negative charge on O– in the monoanion of succinic acid, (✓)$_3$ making it less stable.

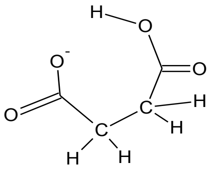
2. Monoanion of tartaric acid can form (more extensive) intramolecular hydrogen bonding forming 5- or 6-membered rings. (✓)$_2$

   Monoanion of succinic acid cannot form (have less extensive) intramolecular hydrogen bond as it forms an unstable 7-membered ring. (✓)$_3$

structural formulae of mono-anions



Monoanion formed from tartaric acid



Monoanion formed from succinic acid

3✓: 2m; 2✓: 1m

(iii) $HO_2CCH(OH)CH(OH)CO_2^- + H^+ \rightarrow HO_2CCH(OH)CH(OH)CO_2H$ **[1]**

$HO_2CCH(OH)CH(OH)CO_2^- + OH^- \rightarrow {}^-O_2CCH(OH)CH(OH)CO_2^- + H_2O$ **[1]**

Accept also :

$HO_2CCH(OH)CH(OH)CO_2^- + H_2O \ll {}^-O_2CCH(OH)CH(OH)CO_2^- + H_3O^+$

$HO_2CCH(OH)CH(OH)CO_2^- + H_2O \ll HO_2CCH(OH)CH(OH)CO_2H + OH^-$

2 **(b)** **(vi)** At point **X**: initial pH of tartaric acid (weak acid)

$$[H^+] = \sqrt{K_a \times [\text{acid}]}$$

$$= \sqrt{(10^{-2.95})(0.20)}$$

$$= 0.0150 \text{ mol dm}^{-3}$$

$$\text{pH} = \underline{-\lg 0.0150} = \underline{1.82}$$ [1]

At point **Y**: pH of amphiprotic species $^-O_2C(CH(OH))_2(CO_2H)$

$$\text{pH} = \frac{1}{2}(pK_{a1} + pK_{a2})$$

$$= \frac{1}{2}(2.95 + 4.25) = \underline{3.60}$$ [1]

At point **Z**: solution is at maximum buffering capacity when $[^-O_2C(CH(OH))_2(CO_2H)] = [^-O_2C(CH(OH))_2(CO_2^-)]$

$$\text{pH} = pK_{a2} = \underline{4.25}$$ [1]

(c) **(i)** D: $CH_2{=}CHCO_2H$ [1]

E: $CH_2BrCH(OH)CO_2H$ [1]

(ii) Step II: $\underline{Br_2(aq)}$ [1]

Step IV: $\underline{H_2SO_4(aq)/HCl(aq)\text{, heat}}$ [1]

(iii) Use **aqueous bromine** to test the reaction mixture. [1]

If aqueous bromine **remains orange**, reaction is **complete**. / If **orange aqueous bromine decolourises**, reaction is **incomplete**. [1]

[Total: 20]

3 **(a)** **(i)** NaOH is required to **generate the nucleophile CN^-**. [1]

HCN is a weak acid/ionises only partially. Thus **$[CN^-]$ is low** and reaction is slow. [1]

(ii) **Comparing experiments 1 and 2**:

When **$[CH_3CHO]$ increases by 2x**, **rate increases by 2x**
➔ rate ∝ $[CH_3CHO]$

∴ **order of reaction wrt CH_3CHO is 1**. [1]

Comparing experiments 1 and 3:

Let rate = $k[CH_3CHO][NaOH]^a$

$$\frac{1.15 \times 10^{-14}}{6.90 \times 10^{-14}} = \frac{k(1.25 \times 10^{-2})(1.25 \times 10^{-4})^a}{k(3.75 \times 10^{-2})(2.50 \times 10^{-4})^a}$$

$$\therefore a = \text{order of reaction wrt NaOH} = \underline{1}$$ [1]

3 **(b)** **(i)** The rate equation defines the slow step and shows that there is only 1 molecule of carbonyl compound and one CN^- involved.

Hence, the rate-determining step is Step **1**.

(ii) The **bigger K_c value** indicates **position of equilibrium** to form the cyanohydrin compound **lies more to the right**, compound is more susceptible to nucleophilic substitution. [1]

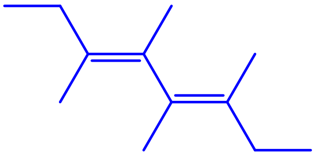
Comparing reactions I and II:

The **electron donating $-CH_3$** group make the **carbonyl C less electron deficient**, thus **less susceptible to nucleophilic attack**. [1]

Comparing reactions I and III:

The **electron withdrawing/electronegative –Cl group** makes the **carbonyl C more electron deficient**, thus **more susceptible to nucleophilic attack**. [1]

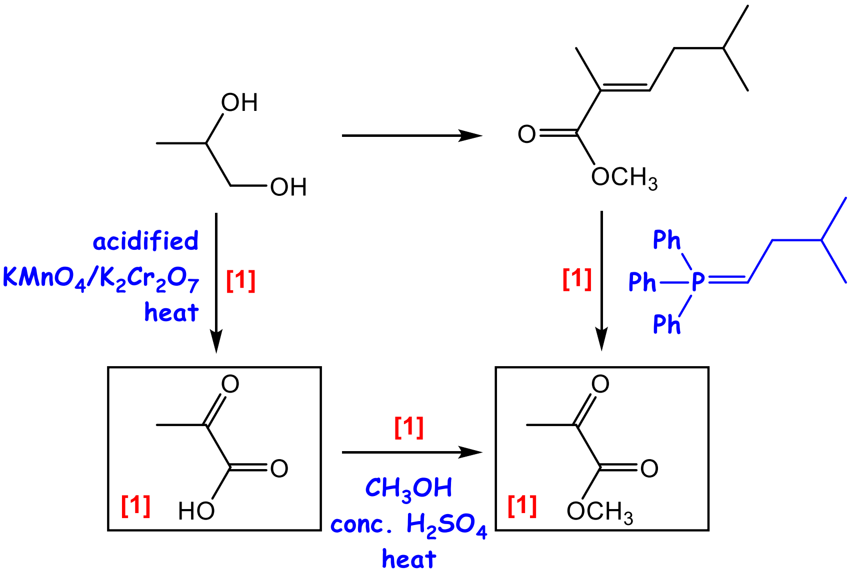
(c) **(i)** The product formed:



[1]

Since the product has two C=C double bonds, total number of isomers formed 2^2 = **4**. [1]

(ii)



(iii) There is **less steric hindrance** from the primary alkyl halide compared to a secondary alkyl halide. [1]

OR

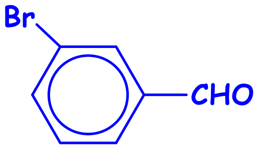
There is one **less electron-donating alkyl group** in the primary alkyl halide hence the C is less δ+ and is more susceptible to nucleophilic attack. [1]

3 (c) (iv) N cannot expand octet/have more than 8 valence electrons because N does not have energetically accessible/low-lying vacant (3)d orbitals to accept the electrons. **[1]**

(d) (i) The tertiary carbocation formed/one more electron-donating CH_3 group attached to the C+ (✓) when the Br^+ electrophile is substituted at the 2- and 4-positions is more stable (✓) as the the positive charge on C+ is more dispersed (✓), stabilising the carbocation.

3✓: 2m; 2✓: 1m

(ii)



[1]

[Total: 20]

For Examiner's Use

4 (a) (i)

or

[1]

(ii) CO_2 has lower boiling point. (✓)

Both have simple covalent structure. However, more energy (✓) is required to overcome the stronger permanent dipole-permanent dipole attractions between N_2O molecules (✓) compared to the weaker instantaneous dipole-induced dipole attractions between CO_2 molecules. (✓)

4✓: 2m; 2-3✓: 1m

(b) (i) Considering the spontaneity of the two reactions using the relationship $\Delta G = \Delta H - T\Delta S$

For reaction 2: $\Delta G = \underbrace{\Delta H}_{-ve} \underbrace{- \underbrace{T\Delta S}_{0}}_{0}$

ΔS for reaction 2 is negligible/approximately zero since there is (no change in the number of moles of gas). As such, the reaction is enthalpy driven. Since ΔH is negative, ΔG is always negative. Thus, lowering temperature will have no impact on ΔG for reaction 2. **[1]**

For reaction 1: $\Delta G = \underbrace{\Delta H}_{+ve} \underbrace{- \underbrace{T\Delta S}_{+ve}}_{-ve}$

ΔS for reaction 1 is positive since there is (an increase in the number of moles of gas). However, since ΔH is positive, the reaction is only spontaneous at high temperatures. **[1]**

As such, at lower temperatures, reaction 2 is favoured. **[1]**

(ii)

$$\begin{tikzcd}
\frac{3}{2}C(s) + \frac{3}{2}CO_2(g) \arrow[rr, "\frac{3}{2}\Delta H_r"] \arrow[dr, "\begin{array}{c}+ Fe_2O_3(s)\\ +234\end{array}"'] & & 3CO(g) \arrow[dl, "\begin{array}{c}+ Fe_2O_3(s)\\ -24.8\end{array}"] \\
& 2Fe(s) + \frac{3}{2}CO_2(g) + \frac{3}{2}CO_2(g) &
\end{tikzcd}$$

$$\therefore \Delta H_r = \frac{2}{3} \times \left[(+234) - (-24.8)\right]$$ **[1] - or from balanced cycle**

$$= \underline{+173 \text{ kJ mol}^{-1}}$$ **[1]**

(c) **(i)**

$$\text{amount of } H_2 = \frac{38.0}{2} = 19.0 \text{ mol}$$

$$\text{amount of } CO = \frac{462}{28} = 16.5 \text{ mol}$$

$$\text{amount of } CH_3OH = \frac{7200}{32} = 225 \text{ mol}$$

$$\therefore \text{ Total amount of gas} = 19.0 + 16.5 + 225 = \underline{260.5 \text{ mol}}$$ **[1]**

$$\text{mole fraction of } H_2 = \frac{19.0}{260.5} = \underline{0.0729}$$

$$\text{mole fraction of } CO = \frac{16.5}{260.5} = \underline{0.0633}$$

$$\text{mole fraction of } CH_3OH = \frac{225}{260.5} = \underline{0.864}$$

[1]

(ii)

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2}$$ **[1]**

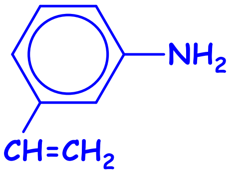
$$= \frac{0.864 \times 7500}{(0.0633 \times 7500)(0.0729 \times 7500)^2}$$

$$= \underline{4.57 \times 10^{-11} \text{ kPa}^{-2}}$$ **[1] - units**

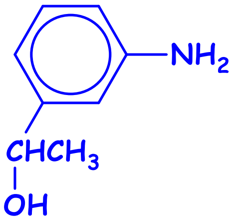
4 (d)

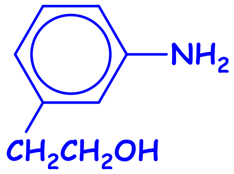
	Type of reaction	Deductions
J has MF C_8H_9N		C:H ≈ 1:1, benzene ring present in **J** (✓) – mark under phenylamine.
J is soluble in dilute HCl	Acid-base (✓)	**J** is an amine (✓).
J reacted with steam in the presence of catalyst at high temp. and pressure	Electrophilic addition (✓a)	**J** contains an alkene (✓b). **L** and **M** are alcohols (✓).
J reacts with 4 mol of $Br_2(aq)$	Electrophilic addition (✓a) Electrophilic substitution (✓)	**J** contains an alkene (✓b). **J** is phenylamine (✓). 2,4,6-position relative to amine group is unsubstituted
L is optically active		**L** contains a chiral C (✓).
L reacts with alkaline $I_2(aq)$	Triiodomethane /Iodoform test / oxidation (✓)	**L** contains —$CH(OH)CH_3$ (✓)
J, **L** and **M** reacts with acidified $KMnO_4$ to form **Q** $C_7H_8O_2N$	oxidation (✓)	**Q** contains —CO_2H group / benzoic acid (✓)
Q $C_7H_8O_2N$ (crystalline solid)	Intra-molecular acid-base (✓)	**Q** is a ionic salt (✓)

15-12 ✓: 5m; 10-11 ✓: 4m; 7-9 ✓; 3m; 4-6 ✓: 2m; 2-3 ✓: 1m



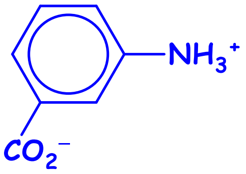
compound J [1]





compound L **compound M**

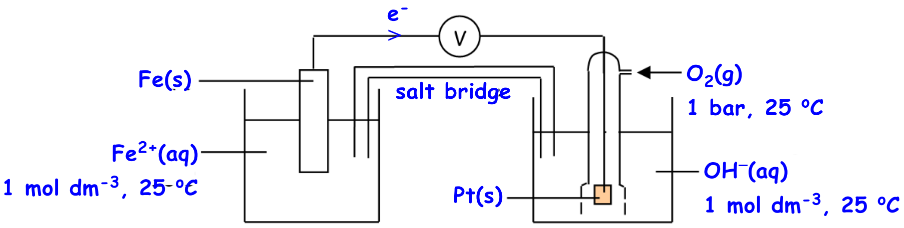
[1]



compound Q [1]

[Total: 20]

5 **(a)** **(i)**



[1] for each correctly drawn half-cell *mark for temp only once
[1] for salt bridge and voltmeter
[1] for electron flow

Minus 1m if "1 mol dm^{-3} H_2O" is stated

(ii) $E^{\ominus}_{cell} = +0.40 - (-0.44) = +0.84\ V$

(iii) $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$

Do not accept if "$Fe(OH)_2$" is used to balance eqn

(iv) $\Delta G = -nFE = -(4)(96500)(+0.84) = -324000\ J\ mol^{-1}$

$= -324\ kJ\ mol^{-1}$ **[1]**

Since $\Delta G < 0$, reaction is energetically feasible. **[1]**

(v) NaOH reacts with Fe^{2+} to form $Fe(OH)_2$ that reduces $[Fe^{2+}]$. (✓)

This causes the position of equilibrium for $Fe^{2+} + 2e \rightleftharpoons Fe$ to shift left (✓), $E(Fe^{2+}/Fe)$ to be less positive and thus E_{cell} to be more positive. (✓)

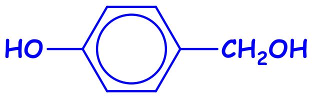
This will result in a more negative ΔG value, thus reaction becomes more feasible. (✓)

4✓: 2m; 2-3✓: 1m

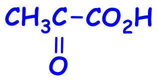
(b)

	Type of reaction	Deductions
G boiled with NaOH gives **H** and **J**	Alkaline hydrolysis (✓) Nucleophilic substitution (✓)	G is an ester (✓) G is an alkyl halide (✓)
H $C_7H_8O_2$ forms violet colouration with neutral ferric chloride		C:H ≈ 1:1, benzene ring present in H (✓) – mark under phenol. H is a phenol (✓)
1 mole of **H** reacts with 2 moles of Br_2 to form a symmetrical product.	Electrophilic substitution (✓)	H is 1,4-disubstituted (✓)
J + $NaHCO_3$ forms gas	Acid-carbonate reaction (✓)	J is a carboxylic acid (✓)
J + aq. alkaline I_2 gives yellow ppt and **K**	Iodoform test (✓)	J contains $-CH(OH)CH_3$ or $-COCH_3$ group (✓)
J heated with $H_2(g)$ and Ni forms **L**	Reduction (✓)	J is a ketone (✓) L is an alcohol (✓)
Heat **L** in acid catalyst forms **M**	condensation (✓)	M is an ester (✓)

14-17 ✓: 5m; 10- 13 ✓: 4m; 7-9 ✓; 3m; 4-6 ✓: 2m; 2-3 ✓: 1m

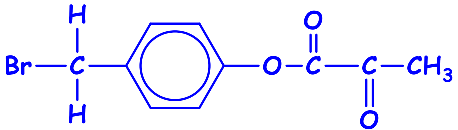


Compound **H** [1]

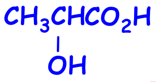


$CH_3\underset{\underset{O}{\|}}{C}-CO_2H$

Compound **J** [1]

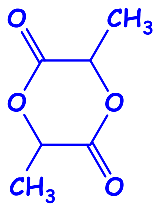


Compound **G** [1]



$CH_3\underset{\underset{OH}{|}}{C}HCO_2H$

Compound **L** [1]



Compound **M** [1]

[Total: 20]