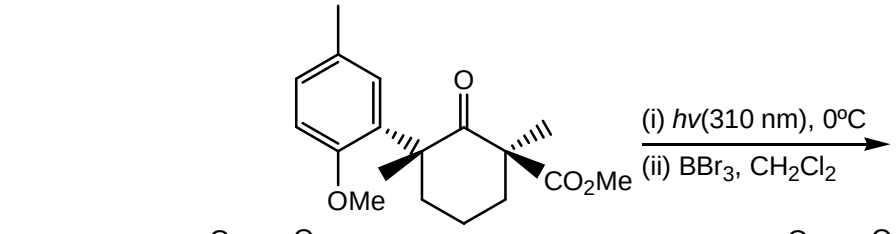
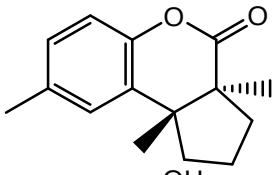
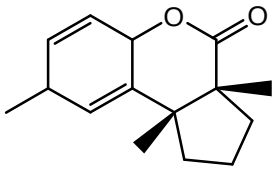
CHEMISTRY

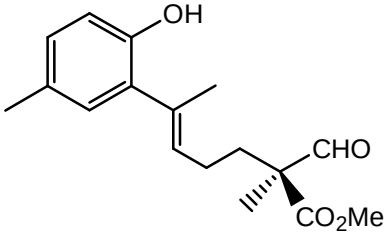
Q.01 – Q.25 : Carry ONE mark each.

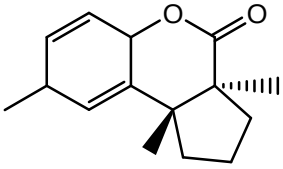
1. The major product in the following reaction sequence is



(a) 

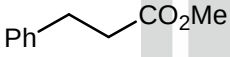
(b) 

(c) 

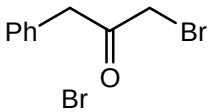
(d) 

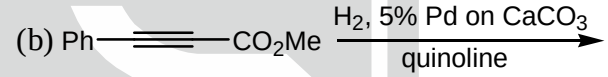
2. The correct statement(s) about $^4D_{5/2}$ state of an atom is (are)
(a) It can show spectral transition to $^4P_{3/2}$ state.
(b) It splits into five levels in the presence of magnetic field
(c) It can originate from s^1p^2 electronic configuration
(d) It corresponds to L = 2, S = 1/2 and J = 5/2

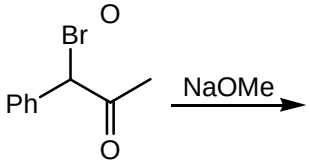
3. The reaction(s) that yield(s) X as the major product is (are)

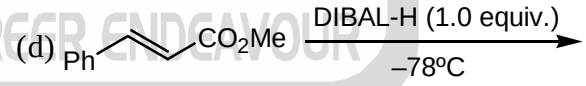


(X)

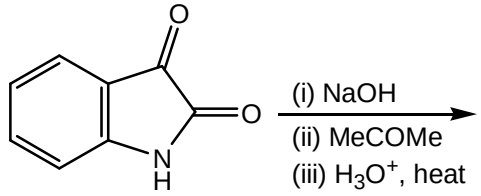
(a) 

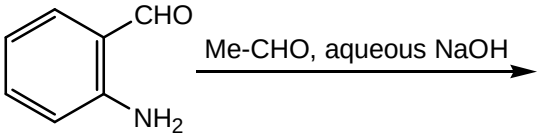
(b) 

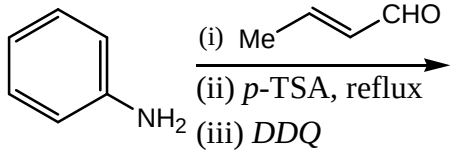
(c) 

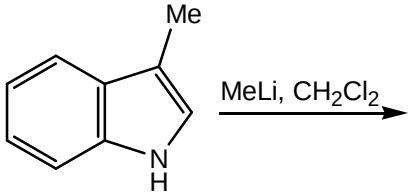
(d) 

4. The reaction(s) that yield(s) 2-methylquinoline as the major product is (are)

(a) 

(b) 

(c) 

(d) 

5. The order and the number of classes present in a group with the irreducible representation A_1, A_2, B_1, B_2, E_1 and E_2, are, respectively.
(a) 12 and 6 (b) 6 and 6 (c) 12 and 3 (d) 6 and 3

6. ^{1}H NMR spectrum of a mixture containing CH_3Br (x mol) and $(CH_3)_3CBr$ (y mol) shows two singlets at 2.7 ppm and 1.8 ppm, with the relative ratio of 3 : 1 (integration value), respectively. The value of x/y is _____(rounded off tothe nearest integer)

7. The partial vapor pressure of 0.1 molal solution of B in liquid A is 60 kPa at 300K. The partial vapor pressure (in kPa) of a solution containing B with mole fraction of 0.1 in liquid A at 300 K is _____
(Assume the solute B obey's Henry's law. The molar mass of A is 80 g mol^{-1})
(Rounded off to three decimal places)

8. Critical micellar concentration of a surfactant is 0.008 M in water at 25 °C. If the aggregation number of the micelles is 80, the concentration of the micelles (in M) present in 0.088 M aqueous solution of the surfactant at 25 °C is
(a) 0.010 (b) 0.001 (c) 0.088 (d) 0.008

9. The ground state of $\left[Cr(H_2O)_6\right]^{2+}$ is
(a) $^6A_{2g}$ (b) $^5T_{2g}$ (c) $^6A_{1g}$ (d) ^5E_g

10. The crystal field stabilization energy of $\left[Cr(NH_3)_6\right]^{3+}$ with Δ_0 value 21600 cm^{-1} is y cm^{-1}. The value of $|y|$ is _____
(rounded off to the nearest integer)

11. The value of $\frac{e^2}{2\pi\varepsilon_0 a_0}$ in atomic unit of energy is _____
(e : charge of electron; a_0: Bohr radius; $\in_0$: permittivity of vacuum)
(rounded off to the nearest integer)

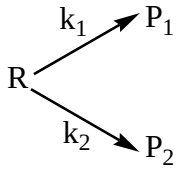
12. The molecule XY2 is microwave active and its vibration-rotation spectrum shows only P and R transitions. In the correct structure.
(a) X is the central atom in bent XY_2 (b) X is the central atom in linear XY_2
(c) Y is the central atom in bent XY_2 (d) Y is the central atom in linear XY_2

13. The complex (es) with distorted octahedral structure is (are)
(a) $\left[Fe(CN)_6\right]^{4-}$ (b) $\left[VF_6\right]^{3-}$ (c) $\left[FeF_6\right]^{3-}$ (d) $\left[MnF_6\right]^{3-}$

14. The correct statement(s) related to an ensemble is (are):
(a) an ensemble is a collection of an infinite number of imaginary replications of the system of interest.
(b) all members of an ensemble are macroscopically identical and also have identical microstates.
(c) all systems in a canonical ensemble need NOT have the same composition.
(d) an ensemble average of any macroscopic property of the system is equal to the value of the property averaged over a sufficiently long time.

15. The compound(s) which show(s) the perovskite structure in solid state is (are)
(a) $CaTiO_3$ (b) $CsPbI_3$ (c) $NiFe_2O_4$ (d) Fe_3O_4

16. Consider the following two parallel irreversible first-order reactions, where $k_1=2k_2$ at 300 K. After complete conversion of R at 300 K. the concentration of P1 in the reaction mixture was 15 mol L^{-1} . The initial concentration of R (in mol L^{-1}) was

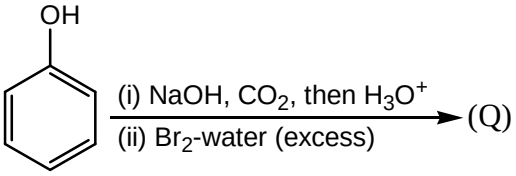


(k_1 and k_2 are the rate constants)
(rounded off to one decimal place)

17. The number of metal-metal bond(s) in the complex $\left[\left(^5\eta-Cp\right)Mo(CO)_2\right]_2$ is x and in $\left[\left(^5\eta-Cp\right)_2 Fe_2(CO)_3\right]$ is y. The value of x+y is _____
(Assume 18 electron rule is followed) (Answer in integer)

18. The non-dissociative adsorption of a gas on a given surface at a fixed temperature follows Langmuir isotherm. The plot(s) which give(s) a straight line is (are)
[Given: V = volume of the adsorbed gas, P = pressure of the gas]
(a) V versus 1/P (b) P/V versus P (c) V versus P (d) 1/V versus 1/P

19. The major product in the given reaction sequence is Q. The mass spectrum of Q shows
([M] = molecular ion peak)



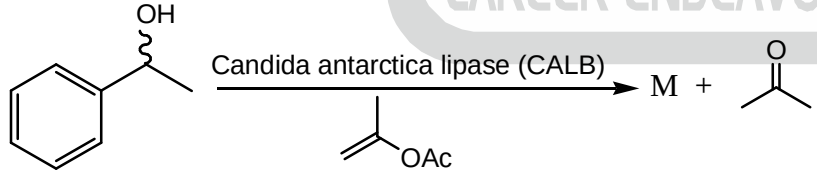
(a) [M], [M+2], [M+4]. and [M+6] peaks with relative intensity of 1:3:3:1
(b) [M], [M+2], and [M+4] peaks with relative intensity of 1:2:1
(c) [M], [M+2]. [M+4], and [M+6] peaks with relative intensity of 1:1:1:1
(d) [M] and [M+2] peaks with relative intensity of 1:1

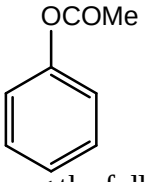
20. The correct statement(s) for decalin is (are)
(a) cis-Decalin is thermodynamically less stable than trans-decalin.
(b) cis-Decalin contains plane of symmetry.
(c) trans-Decalin undergoes ring inversion.
(d) trans-Decalin belongs to the point group of C_{2h}

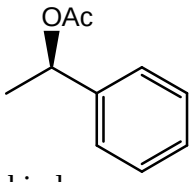
21. Among the following, the compound with the lowest CO stretching frequency is
(a) $[Mn(CO)_6]^+$ (b) $[Cr(dien)(CO)_3]$ (dien: diethylenetriamine)
(c) $[V(CO)_6]^-$ (d) $[Cr(CO)_5]$

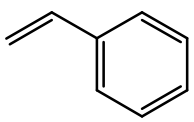
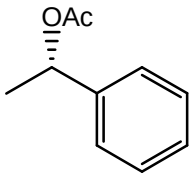
22. The reaction of XeF_2 with $HN(SO_2F)_2$ at 273 K in CF_2C1_2 solvent yields
(a) $FXeN(SO_2F)_2 + HF$ (b) $SOF_2 + XeO_2 + NH_3$
(c) $XeF_4 + SO_2 + NH_3$ (d) $Xe + SO_2 + N_2 + HF$

23. The product M in the following reaction is

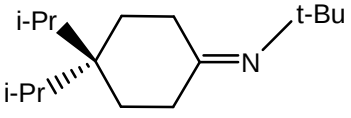


(a) 

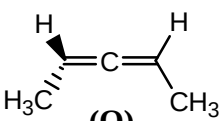
(b) 

(c) 
(d) 

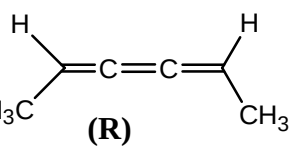
24. Among the following, the chiral compound is



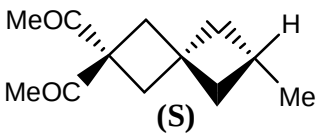
(P)



(Q)



(R)



(S)

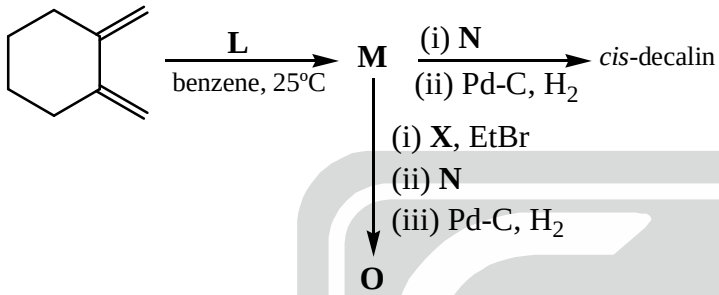
(a) Q (b) R (c) P (d) S

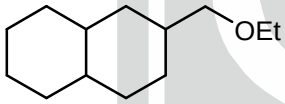
25. Among the following metalloproteins, the pair(s) of non-heme proteins is (are)
(a) Cytochrome P-450 and Hemocyanin
(b) Hemerythrin and Carbonic anhydrase
(c) Hemoglobin and Myoglobin
(d) Hemocyanin and Carboxypeptidase

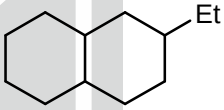
Q.26 – Q.55 : Carry TWO marks each.

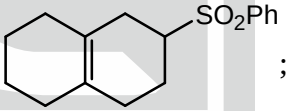
26. Among the following, the correct statement(s) is (are):
(a) the energy separation between any two adjacent states is same for a harmonic oscillator, while it is different for a rigid rotor.
(b) the normalization factor of a Slater determinant for a 3-electron atom is $\sqrt{1/3}$
(c) the magnitude of the total spin angular momentum of an a electron is the negative of that of a B electron.
(d) the number of nodes in the radial wave function of 3s orbital of a hydrogen atom. is the same as the number of nodes in the angular wave function of a 4d orbital of hydrogen atom.

27. Consider the following reaction sequence. The correct option(s) is (are)



(a) **L** = acrolein; **O** = 

(b) **X** = LDA; **O** = 

(c) **X** = $LiAlH_4$; **L** = (vinylsulfonyl) benzene (d) **M** = 

; **N** = Na-Hg/MeOH

28. In the given reaction sequence, the amount of R produced (in g) is

$$\underset{(7.8\,g)}{\text{Benzene}} \xrightarrow[80\%]{\text{oleum(excess), 200°C}} (P) \xrightarrow[75\%]{\text{NaOH, heat then } H_3O^+} (Q) \xrightarrow[50\%]{HNO_3(\text{excess})/H_2SO_4\,(\text{excess})} (R)$$

(Given: molar mass (in g mol^{-1}) of H = 1, C = 12, N = 14, O=16 and S = 32)
(rounded off to two decimal places)

29. The wave function of a particle in a cubic box (of side L) is given by

$$\psi(x,y,z) = \sqrt{32/L^3}\sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{\pi z}{L}$$

The ratio of the energy of the state corresponding to the above wave function to the ground state energy is _____(rounded off to the nearest integer)

30. If q_t and $Q_{t,m}$ are the molecular and molar translational partition functions x_2 respectively, then $\ln(Q_{t,m}) =$ (N is the Avogadro number)
(a) $N\ln q_t - N\ln N + N$
(b) $N\ln q_t - \ln N$
(c) $N\ln q_t - N\ln N$
(d) $N\ln q_t + N\ln N + N$

31. Consider the following six vibrational modes:
symmetric stretching of CO_2, O-H symmetric stretching of H_2O, stretching of HC1. stretching of H_2. N-H symmetric stretching of NH_3. and bending of CO_2.
Among these modes, if *k* number of modes are IR active but Raman inactive, *l* number of modes are IR inactive but Raman active, and m number of modes are both IR and Raman active.
k, *I*, and *m*, respectively, are
(a) 2, 1, and 3 (b) 1, 3, and 2 (c) 1. 2. and 3 (d) 3, 1, and 2

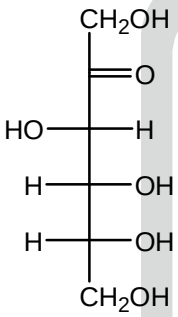
32. $\Delta S^0\left(in\ J\ mol^{-1}K^{-1}\right)$ for the given reaction at 298 K is _____

$$\left[Cu\left(H_2O\right)_6\right]^{2+} + en \rightleftharpoons \left[Cu\left(H_2O\right)_4\left(en\right)\right]^{2+} + 2H_2O$$

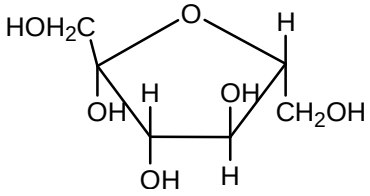
[Given: log K_1 = 10.6, where K_1 is the equilibrium constant, $\Delta H^0 = -54$ kJ mol^{-1} and R = 8.314 J mol^{-1} K^{-1}]
(rounded off to two decimal places)

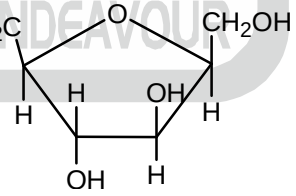
33. Among the following, the NMR active nucleus(nuclei) is (are)
(a) ^{16}O (b) ^{12}C (c) ^{2}H (d) ^{19}F

34. Fischer presentation of D-(-)-fructose is given below



The correct structure of α-L-(+)-fructofuranose is

(a)


(b)


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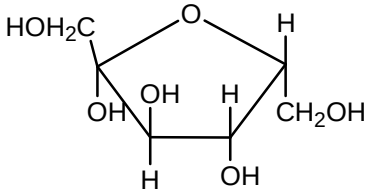
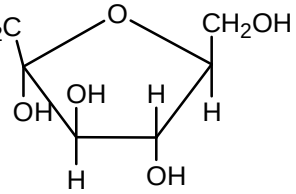


(d)


35. The complex(es) that exhibit(s) optical isomerism is (are)
(a) *trans*-$[Co(en)_2Cl_2]^+$ (b) $[Co(en)_3]^{3+}$
(c) $[Fe(acac)_3]$ (d) cis-$[Co(en)_2Cl_2]^+$

36. 2 mol of a monoatomic ideal gas with initial volume of 5 L and pressure 10 bar undergoes an irreversible adiabatic expansion against a constant final pressure of 1 bar The final volume (in L) is
(Given: R = 8.314×10^{-2} L bar mol^{-1} K^{-1})
(rounded off to one decimal place)

37. The turnover frequency (in h^{-1}) of a reaction where 5 mol% of a catalyst is required for 90% conversion in 3 h is _____ (rounded off to the nearest integer)

38. Among the following, the correct statement(s) is (are):

(a) σ_v symmetry element is present in NH_3 but NOT in BF_3.

(b) one σ_h and three σ_d symmetry elements are present in benzene.

(c) C_2 symmetry element is present in H_2O and H_2O_2 but NOT in $PC1_5$.

(d) both C_2 and C_3 symmetry elements are present in CCl_4 and SF_6.

39. Borax on treatment with NaOH and H_2O_2 forms X. The compound X on reaction. with PhCN at 60 °C in methanol-water mixture gives Y as the major product X and Y respectively, are

(a) $Na_2B_2(O_2)_2(OH)_4 \cdot nH_2O$ and PhCOOH

(b) $NaB(O)(OH)_2 \cdot nH_2O$ and PhCOOH

(c) $Na_2B_2(O_2)_2(OH)_4 \cdot nH_2O$ and $PhCONH_2$

(d) $NaB(O)(OH)_2 \cdot nH_2O$ and $PhCONH_2$

40. ψ_1, ψ_2, ψ_3 and ψ_4 are four Huckel molecular orbitals of benzene with orbital energies E_1, E_2, E_3 and E_4, respectively.

$$\psi_1 = \frac{1}{2}(\phi_B + \phi_C - \phi_E - \phi_F); \quad \psi_2 = 6^{-\frac{1}{2}}(\phi_A - \phi_B + \phi_C - \phi_D + \phi_E - \phi_F)$$

$$\psi_3 = 6^{-\frac{1}{2}}(\phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F); \quad \psi_4 = 12^{-\frac{1}{2}}(2\phi_A + \phi_B - \phi_C - 2\phi_D - \phi_E + \phi_F)$$

The correct order of the orbital energies is

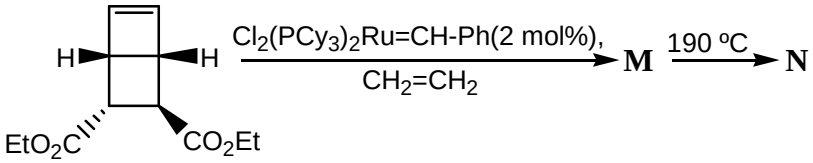
(The six carbon atoms of benzene are denoted by A to F and ϕ_j is the $2p_z$ orbital of J^{th} carbon of benzene)

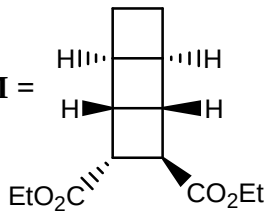
(a) $E_3 < E_2 < E_1 = E_4$ (b) $E_4 < E_1 = E_3 < E_2$

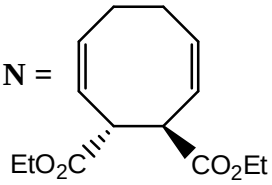
(c) $E_3 < E_1 = E_4 < E_2$ (d) $E_1 < E_2 = E_3 < E_4$

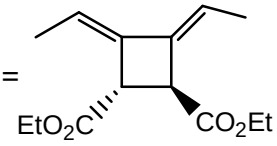
41. The correct statement for a thermally initiated radical polymerization in a solution is :
(Assume: Steady-state and equal reactivity of the propagating radicals, termination reactions are only by combination, and no chain transfer reaction.
Given: Rp rate of polymerization, DP degree of polymerization, [1] initiator concentration, and [M] monomer concentration.)
(a) with increase in [I]. both Rp and DP increase.
(b) Rp decreases with increase in [I] but DP increases with increase in [M].
(c) with increase in [M]. both Rp and DP increase.
(d) DP increases with increase in [I] and DP decreases with increase in [M].

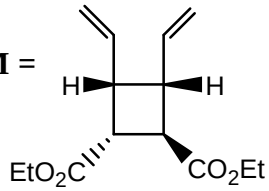
42. Consider the following reaction sequence where *M* and *N* are the major products.
The correct option(s) is (are)



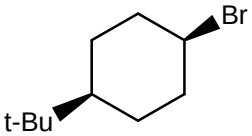
(a) **M** = 

(b) **N** = 

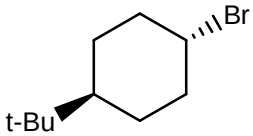
(c) **N** = 

(d) **M** = 

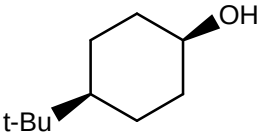
43. The correct statement(s) regarding P. Q. R. and S is (are):



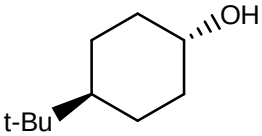
(P)



(Q)



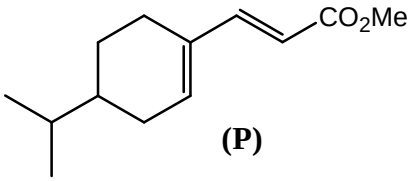
(R)



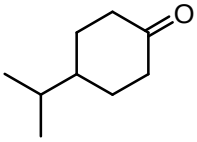
(S)

(a) R gets oxidized faster than S when reacted with CrO_3 in DCM as a solvent.
(b) Q reacts faster than P with NaN_3 in DMF as a solvent.
(c) P reacts faster than Q with PhSNa in DMF as a solvent.
(d) R reacts faster than S when treated with $TsCl/Et_3N$ in DCM as a solvent

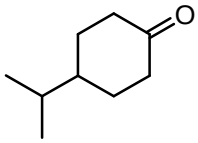
44. The correct option(s) that give(s) P as the major product is (are)



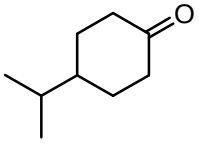
(P)

(a) 

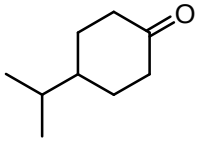
(i) L-Selectride, THF
(ii) MsCl, Et_3N; then NaCN
(iii) DIBAL-H (1 equiv.), THF, –78°C
(iv) $Ph_3P{=}CH\text{-}CO_2Me$

(b) 

(i) $TsNHNH_2$, MeLi (2 equiv.) THF, –78°C
(ii) DMF, 0°C
(iii) NaH, $(OMe)_2P(O)CH_2CO_2Me$, THF, 0°C to reflux

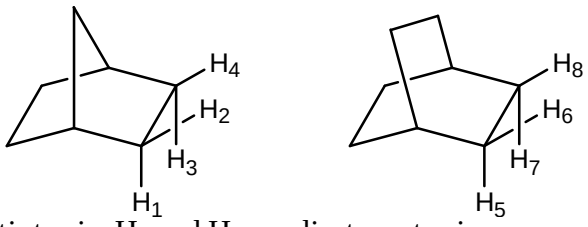
(c) 

(i) LDA, THF, –78°C, Tf_2O
(ii) Methyl acrylate, $Pd(Ph_3P)_2Cl_2$ (2 mol%),
Et_3N (3 equiv.), DMF

(d) 

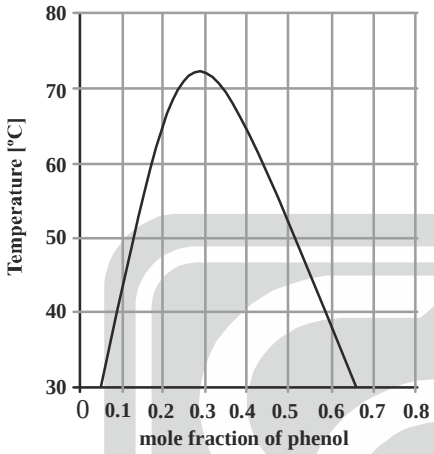
(i) $Me_3SiCH(Li)Cl$, THF, –78°C
(ii) $HClO_4$, THF
(iii) Zn, $BrCH_2CO_2Me$
(iv) p-TSA, reflux

45. The correct statement(s) about the relationship for the H-atoms in the following compounds is (are):



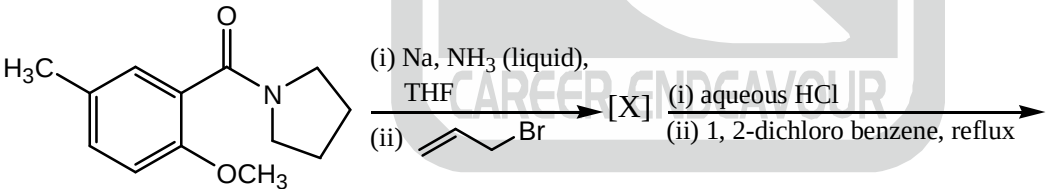
(a) H_1 and H_3 are enantiotopic; H_2 and H_3 are diastereotopic.
(b) H_5 and H_7 are enantiotopic; H_6 and H_7 are homotopic.
(c) H_1 and H_3 are diastereotopic; H_2 and H_3 are enantiotopic.
(d) H_5 and H_7 are homotopic; H_6 and H_7 are enantiotopic.

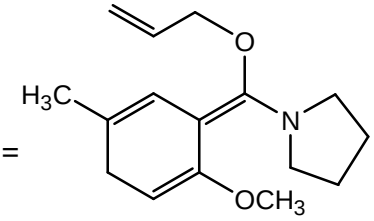
46. The following figure shows an experimental liquid-liquid phase diagram of phenol and water at the vapor pressure of the system. The total amount of phenol and water (in mol) present in the phenol-rich phase when 5 mol of water was shaken with 5 mol of phenol at 40 °C _____

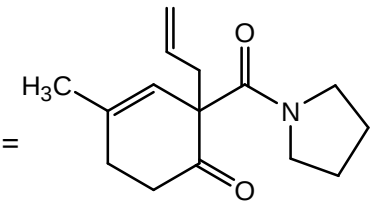


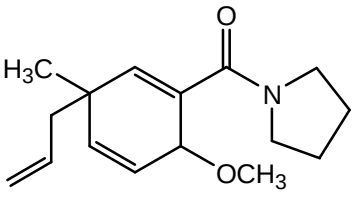
(round off to one decimal places)

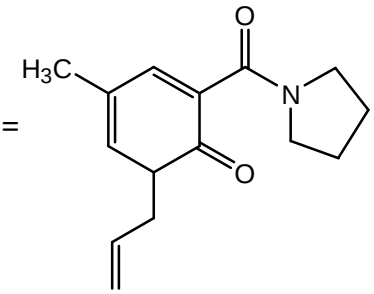
47. The major products X and Y in the following reaction sequence are

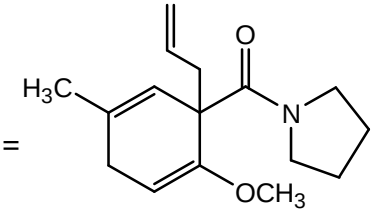
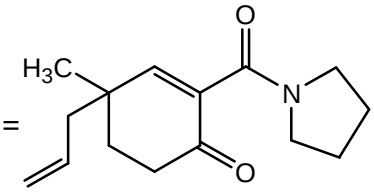


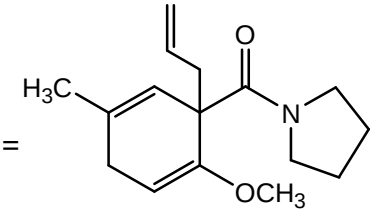
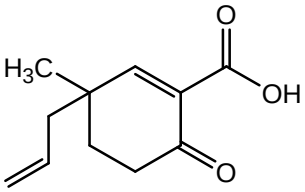
(a) **X** = 

Y = 

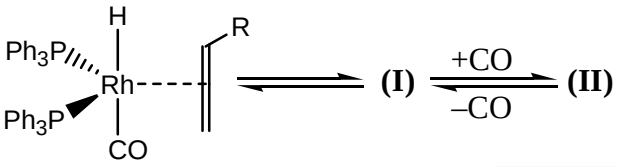
(b) **X** = 

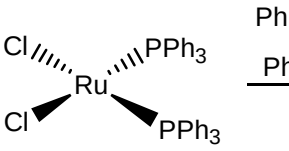
Y = 

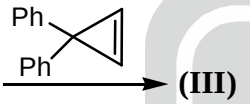
(c) **X** =  **Y** = 

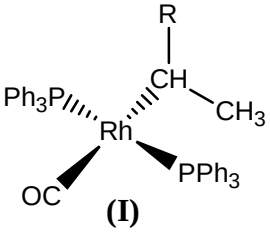
(d) **X** =  **Y** = 

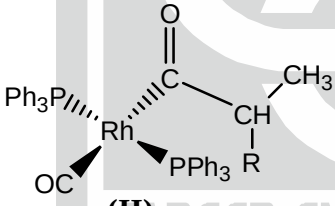
48. In the following reactions, the structures of I, II and III, respectively, are

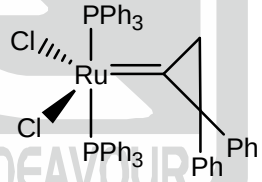


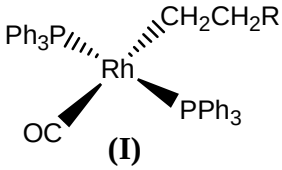


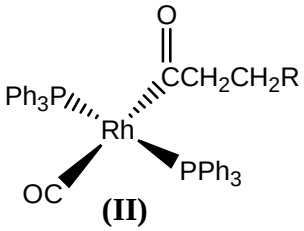


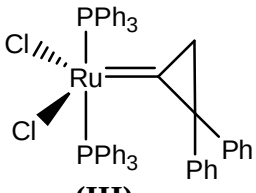
(a)  **(I)**

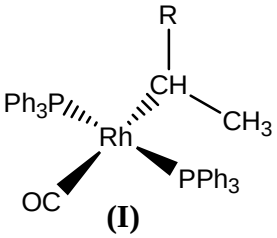
 **(II)**

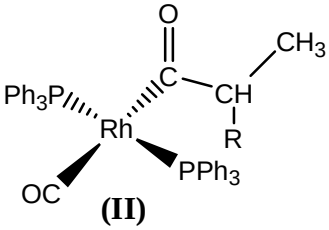
 **(III)**

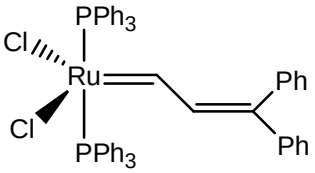
(b)  **(I)**

 **(II)**

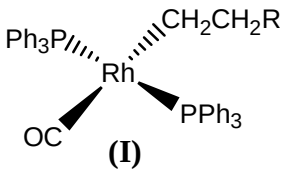
 **(III)**

(c)  **(I)**

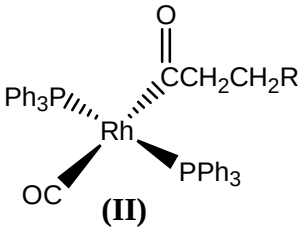
 **(II)**

 **(III)**

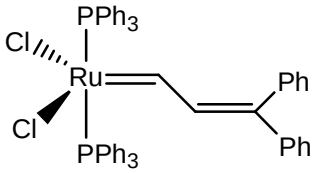
(d)



(I)



(II)



(III)

49. The heptacity of allyl and Cp and the ligation mode of NO in the thermodynamically stable complexes $[(\eta^x\text{-allyl})Ru(CO)_2(NO)]$ and $[(\eta^y\text{-Cp})Ru(CO)_2(NO)]$, respectively, are

(The heptacity of allyl and Cp are denoted by η^x and η^y, respectively.)

(a) (η^3, NO-bent) and (η^5, NO-linear) (b) (η^1, NO-bent) and (η^3, NO-bent)

(c) (η^3, NO-linear) and (η^5, NO-bent) (d) (η^1, NO-bent) and (η^5, NO-linear)

50. In thermogravimetric analysis, 12.45 mg of $CuSO_4.5H_2O$ was subjected to heating under N_2 atmosphere. At a particular temperature, there was a weight loss of 3.6 mg. The number of water molecule(s) lost per formula unit is

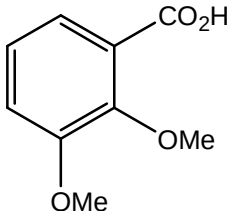
(Given: molar mass (in g mol^{-1} of H = 1.0, O = 16.0, S = 32.0 and Cu = 63.5) (rounded off to the nearest integer)

51. In aqueous solution of $K_4[Fe(CN)_6]$, the allowed transition(s) is (are)

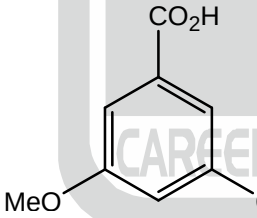
(a) $^5T_{2g}$ to ^5E_g (b) $^1A_{1g}$ to $^1T_{1g}$ (c) $^1A_{1g}$ to $^1T_{2g}$ (d) $^5T_{2g}$ to ^3E_g

52. Consider the following 'H-NMR (400 MHz. DMSO-d_6) data of a compound: δ in ppm: 3.85 (s. 6H), 6.73 (t. J=2.2 Hz. 1H). 7.1 (d. J=2.2 Hz. 2H), and 13.05 (brs. IH). The compound is

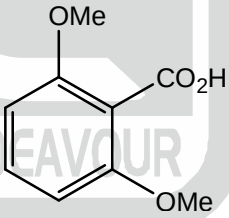
(a)



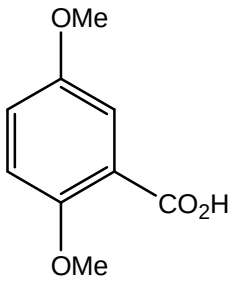
(b)



(c)



(d)



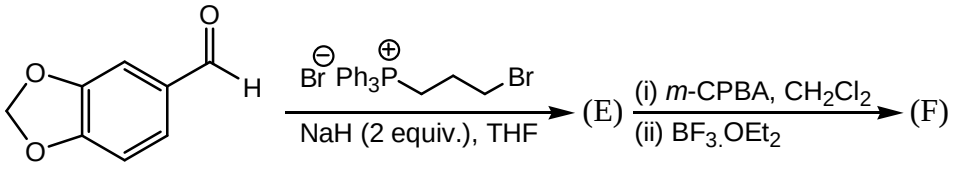
53. ϕ_1 and ϕ_2 are normalized eigenfunctions of a Hermitian operator.

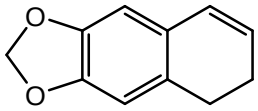
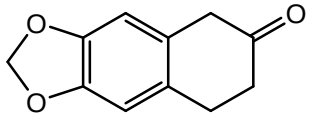
$|\psi\rangle = 3i|\phi_1\rangle + 2|\phi_2\rangle$ and $|\chi\rangle = -2i|\phi_1\rangle + 5|\phi_2\rangle$

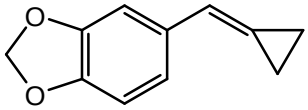
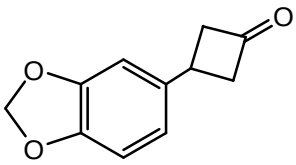
The value of $\langle\psi|\chi\rangle + \langle\chi|\psi\rangle$ is _____

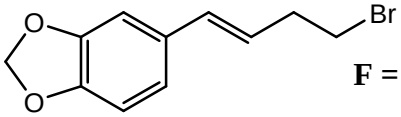
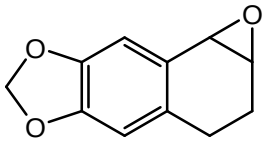
(Rounded off to the nearest integer)

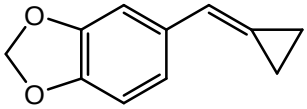
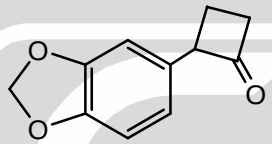
54. The major products E and F in the following reaction sequence are



(a) **E** =  **F** = 

(b) **E** =  **F** = 

(c) **E** =  **F** = 

(d) **E** =  **F** = 

55. In the EPR spectrum of an aqueous solution of $VOSO_4$ at room temperature, the total number of hyper-fine splitting signals is

(a) 5 (b) 7 (c) 8 (c) 3