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**CHM 2120
MIDTERM 2
November 9, 2011
8:30-9:50 am**

Approximate total number of marks: 70
(subject to slight changes)

Notes:

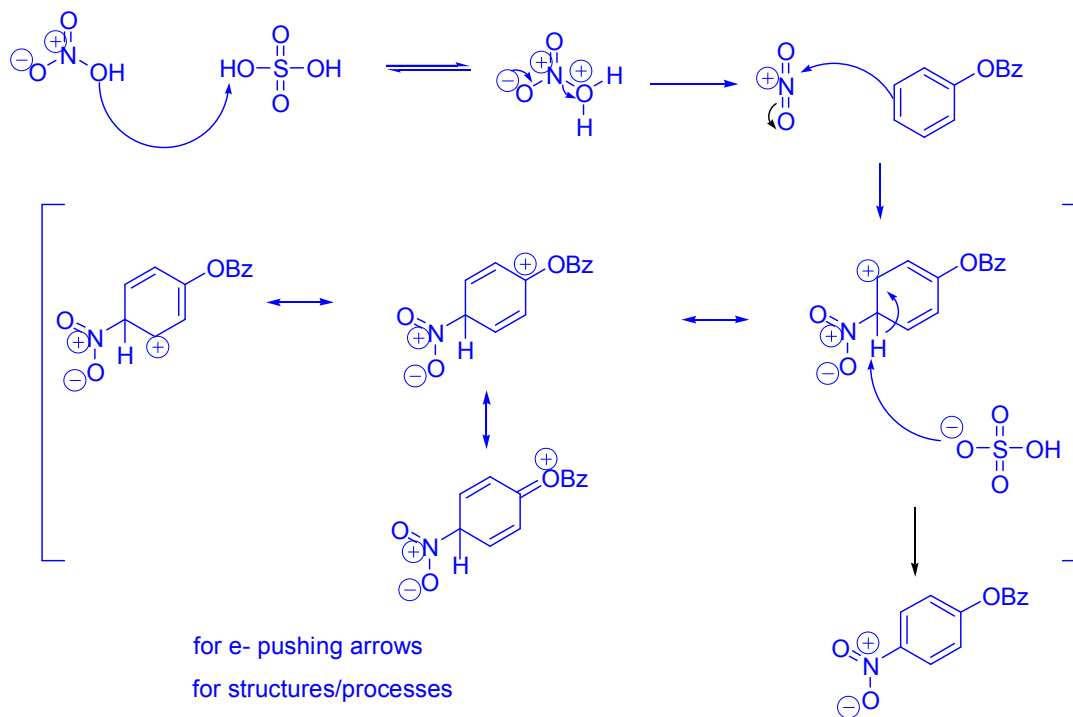
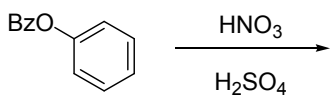
- For questions in which mechanisms are not required, part marks might be given for incorrect answers with plausible mechanisms.
- Re-marks requests might not be granted for midterms written in pencil (all questions will be re-graded if a re-mark is requested).
- There is a pK_a table on the last page.

1a	2a	3b	4b	5b	6b	7b		8		1b	2b	3a	4a	5a	6a	7a	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

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1.

- a. Give the full detailed mechanism for the formation of the major product in the reaction below, including the key resonance structures involved. (10 pts)



ortho is OK.

- b. Name the reactive electrophile formed in this reaction. (1 point)

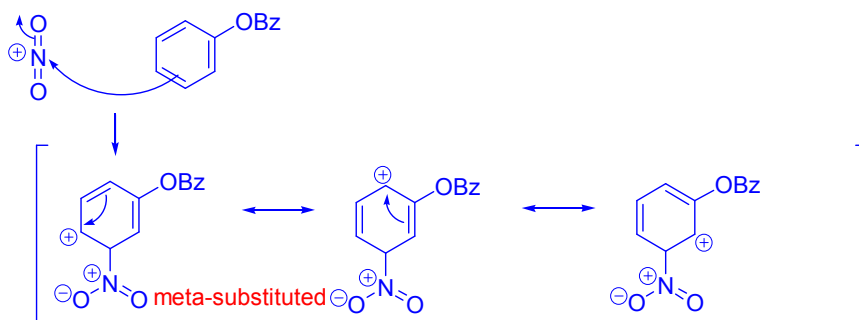
Nitronium

- c. Which aromatic ring is more reactive and why? (2 points)

The ring not bonded to the carbonyl group. It is more electron rich than the carbonyl containing ring (which is electron poor) because the oxygen can donate its lone pair of electrons into the aromatic ring. Because it is e- rich it is thus a better nucleophile. Also OK for an answer is that the oxygen can donate a lone pair into the aromatic ring to stabilize the transition state (or intermediate).

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- d. Clearly explain, *using structures primarily*, the reason for the formation of the favoured regio-isomer as compared to the unfavoured regio-isomer on the most reactive ring. (4 points)

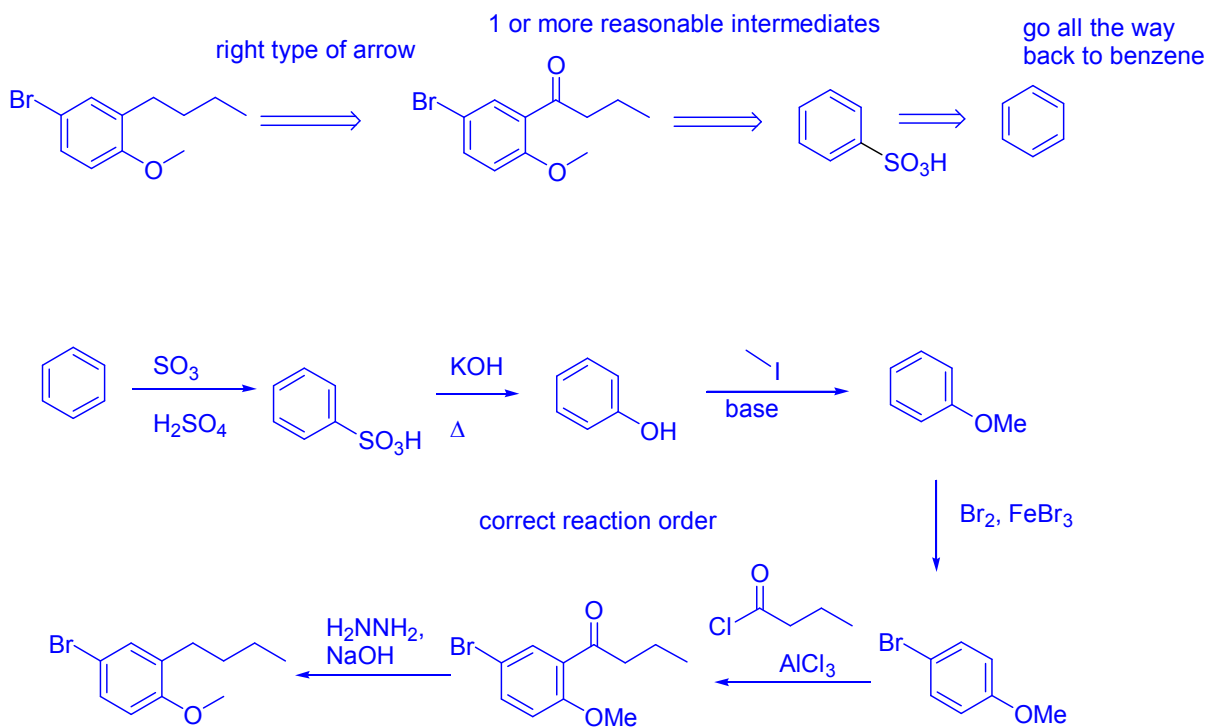
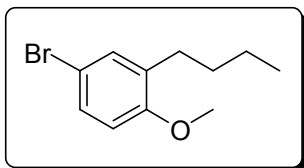


The meta intermediate is stabilized by resonance with the π electrons ONLY, not by resonance with the O's lone pair. Only the ortho and para-substituted intermediates benefit from this additional resonance stabilization with the O's lone pair (see structure above)

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2. Propose a synthesis of the following compound from benzene. Show all required reagents and intermediates. *A retrosynthesis is required.* (10 points)

Note: your synthesis must give the compound shown as the major product of the sequence.

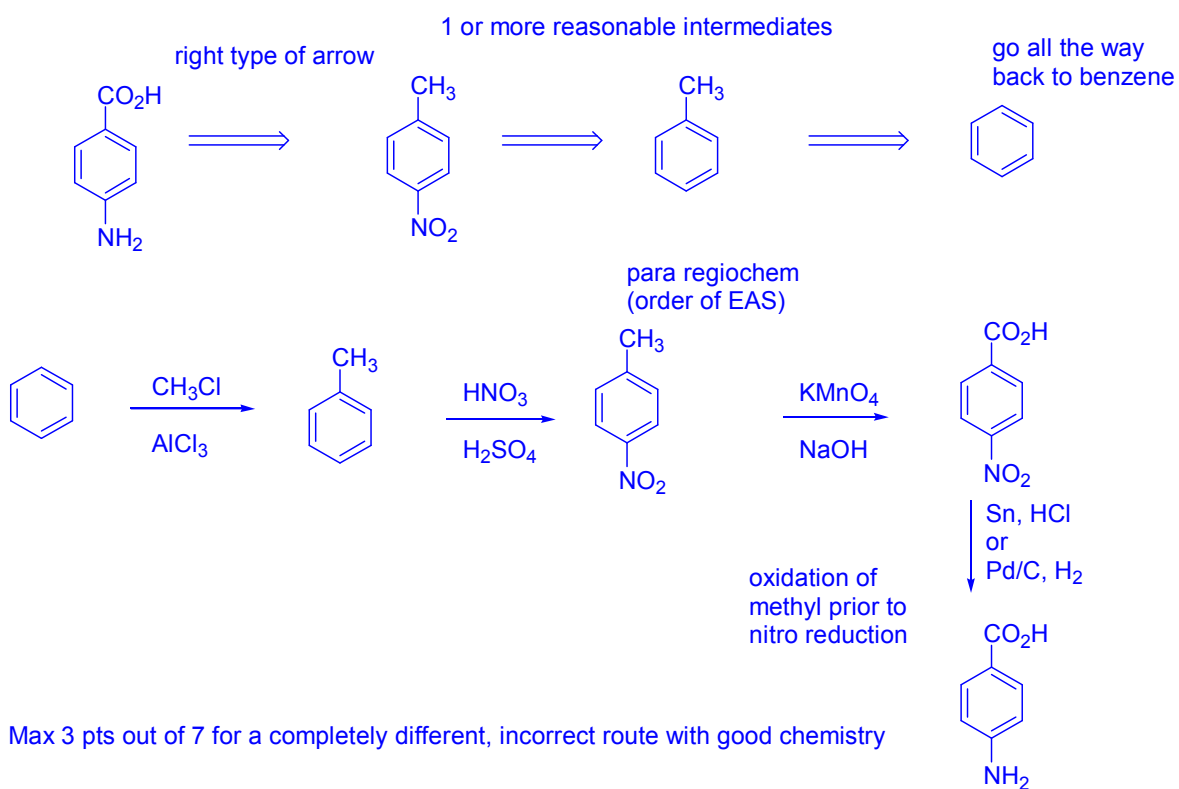
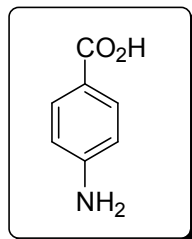


Max 3 pts out of 7 for a completely different, incorrect route with good chemistry

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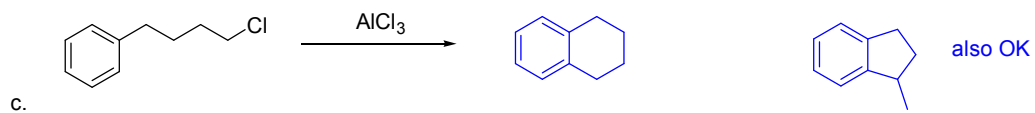
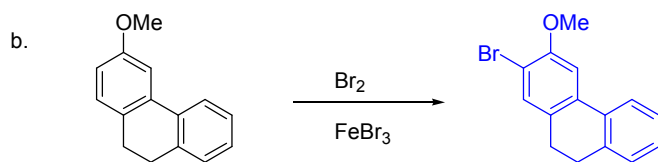
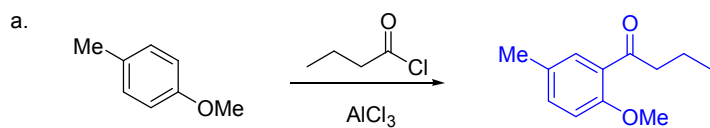
3. Propose a synthesis of the following compound from the aromatic starting material given. Show all required reagents and intermediates. *A retrosynthesis is required.* (10 points)

Note: your synthesis must give the compound shown as the major product of the sequence.



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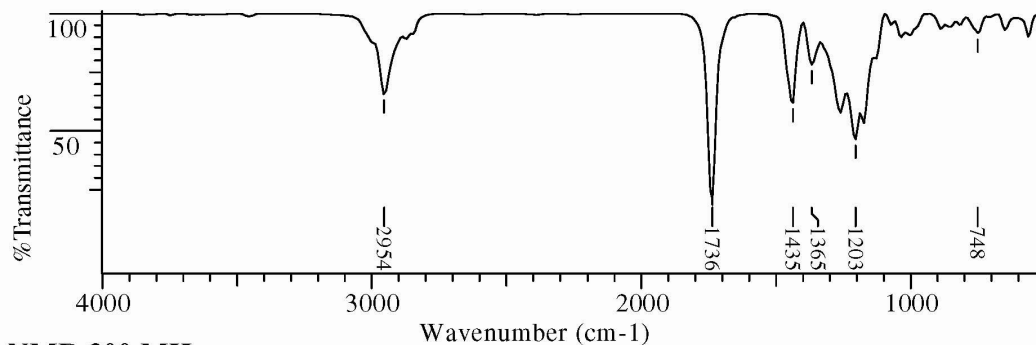
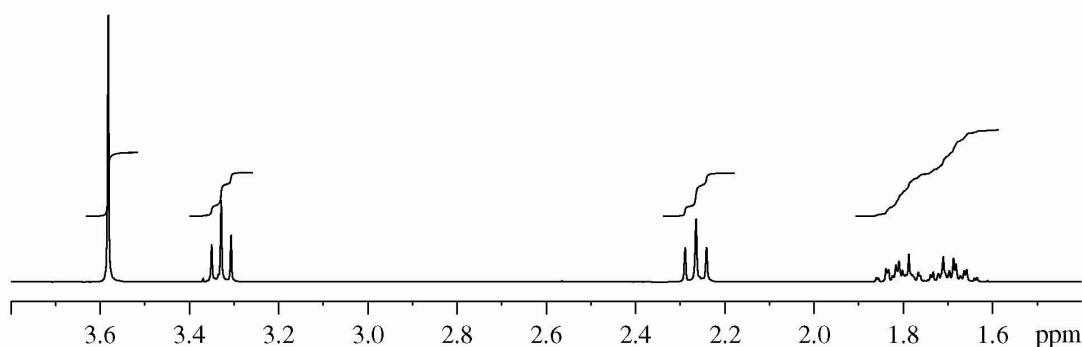
4. Give the major product of each of the following reactions. (9 points)



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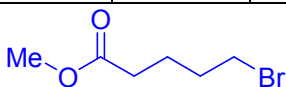
5. Identify the structure of the compound with the molecular formula $C_6H_{11}O_2Br$ and the IR and NMR spectra shown. (2 points) Justify your answer by accounting for all the information provided (10 points).

IR

¹H NMR 300 MHz

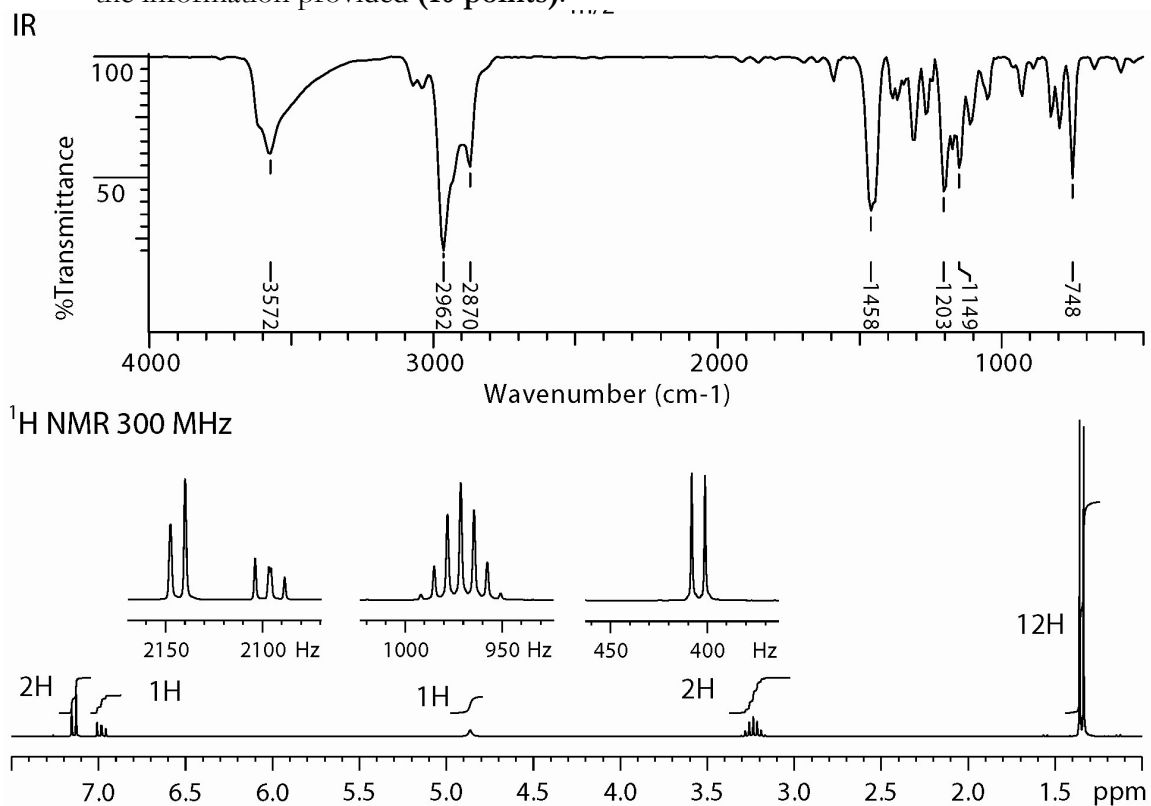
Filling in table with correct data from spectra and proposing a fragment

Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A	3.6	3	s	CH ₃ - Attached to EWG likely O since it is more EW than Br No Hs on adjacent atoms
B	3.3	2	t	-CH ₂ - Attached to EWG likely Br since it is less EW than O 2 Hs on adjacent atoms
C	2.25	2	t	-CH ₂ - Attached to mild EWG likely C=O (IDed from IR at 1736 cm ⁻¹) 2 Hs on adjacent atoms
D	1.8	2	m	-CH ₂ - no EWG lots of Hs on adjacent atoms Note: could have D and E as one peak for 4H
E	1.7	2	m	-CH ₂ - no EWG lots of Hs on adjacent atoms



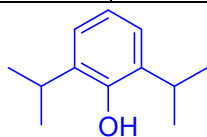
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6. Identify the structure of the compound with the molecular formula $C_{12}H_{18}O$ and the IR and NMR spectra shown. (2 points) Justify your answer by accounting for all the information provided (10 points).



Filling in table with correct data from spectra and proposing a fragment. DU = 4.

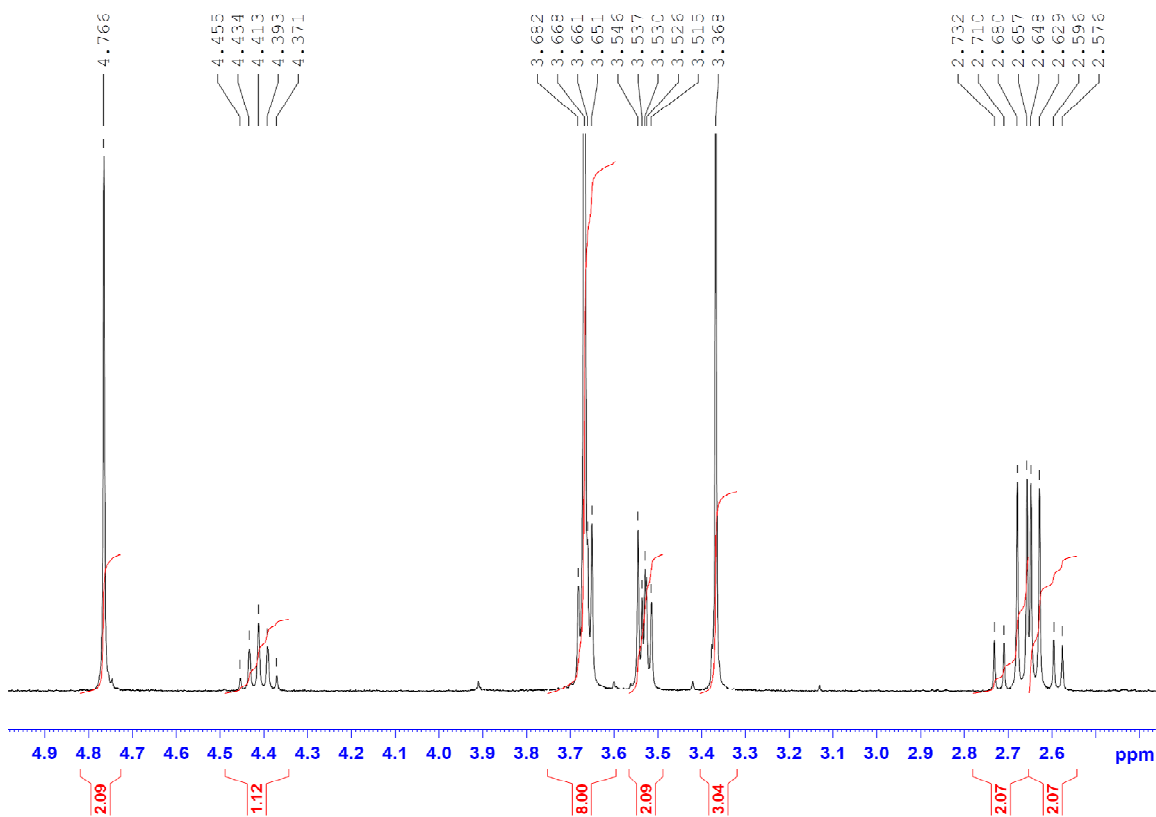
Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A	7.1	2H	d	2 x CH Aromatic hydrogen symmetry to make equivalent 1 H on adjacent carbon
B	7.0	1H	t	CH Aromatic hydrogen 2 H on adjacent carbon
C	4.8	1H	br	-OH Strong EWG likely OH from IR at 3572 cm ⁻¹ broad signal – in NMR suggest OH also
D	3.2	2H	septet	2 x -CH- mild EWG – possibly bonded to aromatic 6 Hs on adjacent atoms Likely 2 CH ₃ attached
E	1.4	12H	d	4 x -CH ₃ no EWG 1 Hs on adjacent atoms



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BONUS: (6 points)

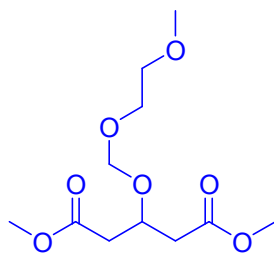
Provide the structure of the compound with molecular formula $C_{11}H_{20}O_7$ and the NMR spectra below.



Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A	4.8	2H	s	-CH ₂ - Very strong EWG or 2 strong EWGs no Hs on adjacent carbon
B	3.4	1H	p	CH Strong EWG 4 Hs on adjacent atoms Likely bonded to oxygen
C	3.7	6H	s	2 x -CH ₃ Strong EWG no Hs on adjacent atoms Likely bonded to oxygen / symmetry element
D	3.6	2H	m	-CH ₂ - strong EWG Hs on adjacent atoms Likely bonded to O
E	3.5	2H	m	-CH ₂ - strong EWG Hs on adjacent atoms Likely bonded to O

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F	3.4	3H	s	-CH ₃	Strong EWG no Hs on adjacent atoms Likely bonded to oxygen
G	2.7	4H	m	2 x -CH ₂	mild EWG symmetry element



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pK_a table

Acid	pK _a
HCl	-8
ROH ₂ ⁺	-2
H ₃ O ⁺	-1.75
RCOOH	5
R ₃ NH ⁺	10-11
H ₂ O	15.75
ROH	16-18
H ₂	36
RNH ₂	35-40
RCH ₃	55

