

CEM 351, Fall 2012
Final Exam
Dec. 12th, 2012

The answers for short answer questions must be written in pen for any potential regrading requests.

Name: _____ PID: _____

Section #: _____ TA name: _____

NAME	SEC.#	DAY/TIME	ROOM
Aaron Baker	1	Tuesday, 9:10-10:00	085
Qian Qin	2	Monday, 10:20-11:10	281
Aaron Baker	3	Tuesday, 10:20-11:10	085
Peng Wang	4	Thursday, 10:20-11:10	287
Qian Qin	5	Tuesday, 10:20-11:10	283
Aaron Baker	6	Tuesday, 11:30-12:20	283
Peng Wang	7	Thursday, 11:30-12:20	085
Qian Qin	8	Monday, 4:10-5:00	110
Peng Wang	9	Thursday, 4:10-5:00	183

Questions 1-30 (90 pts) _____

Question 35 (10 pts) _____

Question 31 (9 pts) _____

Question 36 (6 pts) _____

Question 32 (12 pts) _____

Question 33 (12 pts) _____

Question 37 (8 pts) _____

Question 34 (33 pts) _____

Question 38 (20 pts) _____

Total (200 pts) _____

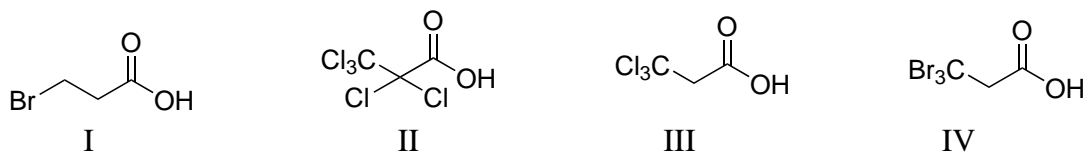
This exam packet should have total 12 pages including the cover.

For questions 1-30, select the best answer and put it in the bubble sheet. You will not receive any credits if you select more than one answer. (3 pts each, 90 pts total)

1) Which one of the following is the most stable?



2) Rank the following compounds in INCREASING order of acidity.



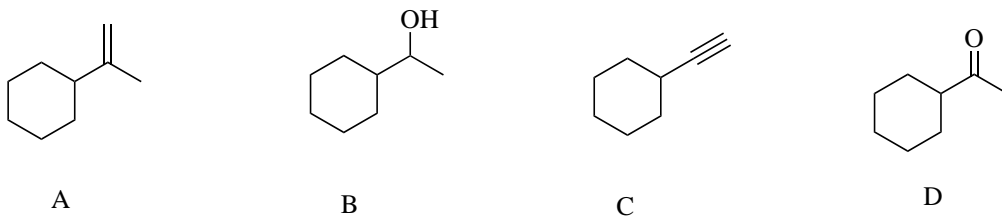
a) I, III, IV, II b) II, III, IV, I c) I, IV, III, II d) I, II, III, IV e) None of the above choices

3) What is the relationship of the following pairs of compounds?



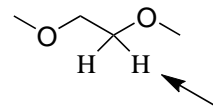
a) enantiomer, diastereomer b) diastereomer, enantiomer
c) diastereomer, diastereomer d) enantiomer, enantiomer e) None of the choices given

4) Which of the following compound will give an IR spectrum with strong absorbance around 3400 cm^{-1} ?



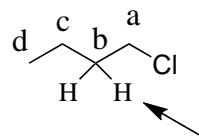
5) What is the multiplicity of the proton marked with an arrow in $^1\text{H-NMR}$?

A B C D E
1 2 3 5 10



6) What is the multiplicity of the proton marked with an arrow in $^1\text{H-NMR}$ ($J_{\text{HaHb}} \neq J_{\text{HbHc}}$)?

A B C D E
2 5 6 9 18



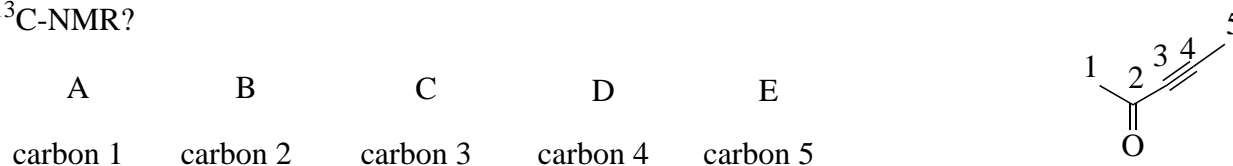
7) Which of the following molecules has an IR absorption between 3000 - 3100 cm^{-1} ?



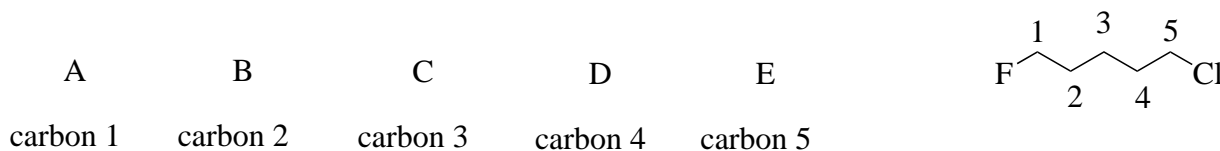
8) Which of the following molecules does NOT have an IR absorption around 2250 cm^{-1} ?



9) Which of the carbon atoms in the following molecule appears most downfield (highest chemical shift) in its ^{13}C -NMR?



10) The proton on which of the carbon atoms in the following molecule appears most downfield in its ^1H -NMR?



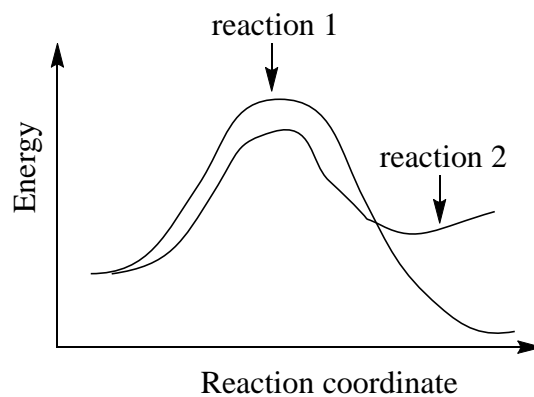
11) Based on the reaction energy diagram for the two reactions, answer the following questions:

1) Which reaction will be faster?

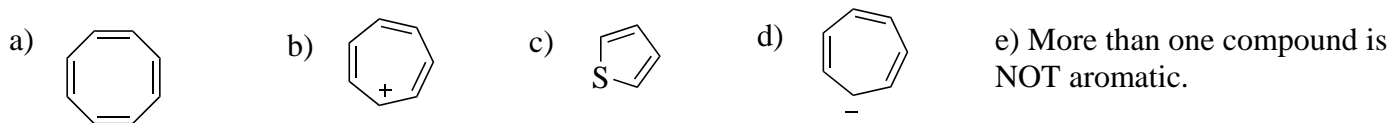
2) Which reaction is endothermic?

a) reaction 1; reaction 1; b) reaction 1; reaction 2;

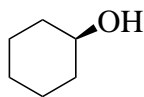
c) reaction 2; reaction 1; d) reaction 2; reaction 2;



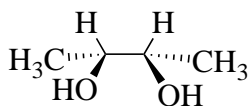
12) Which one of the following compound is NOT aromatic?



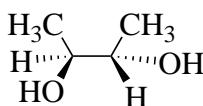
13) Which of the following compound(s) is meso?



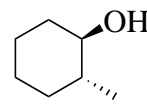
I



II



III



IV

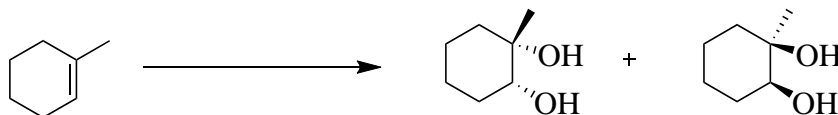
- a) I b) II c) III d) IV e) More than one compound is meso

14) How many monochlorination products will you obtain for the following reaction (you should consider stereochemistry)?



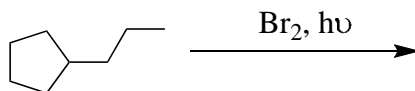
- a) 6; b) 5; c) 4; d) 3; e) 2.

15) Which of the reagent can be used to carry out the transformation as drawn?



- a) H_2O_2 ; b) H_3O^+ ; c) O_3 ; then Zn dust d) mCPBA; then H_3O^+ e) OsO_4 .

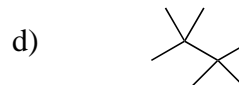
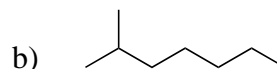
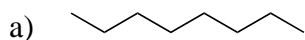
16) Which one of the following compound will be the major product of the follow reaction:



- a) b) c) d) e)

17) The heat of combustion of the following four compounds was measured and four values were obtained. However, the researcher forgot to label the compounds. Which one of the four compounds you think gives heat of combustion of -1304.6 kcal/mol?



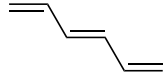
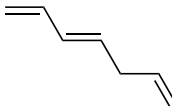
- 1303.0 kcal/mol
- 1304.6 kcal/mol
- 1306.3 kcal/mol
- 1307.5 kcal/mol



18) If the chemical shift of a hydrogen is 1 ppm, on a 300MHz NMR instrument, what is the frequency difference between this hydrogen and hydrogens of tetramethylsilane (TMS)?

- a) 300 MHz; b) 300 Hz; c) 1 Hz; d) 0 Hz; e) None of the above.

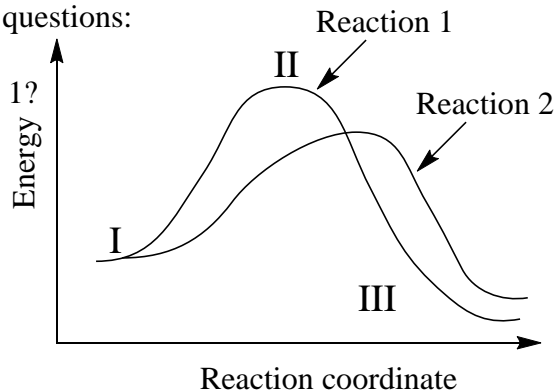
19) Which of the following compound will have the longest wavelength at its maximum absorbance peak in the UV-vis spectrum?

- a)  b)  c)  d)  e) not enough info to determine that

20) Based on the reaction energy diagram, answer the following questions:

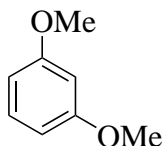
- 1) Which point on the diagram is the transition state for reaction 1?
 2) Which reaction gives a more stable product?

- a) I; Reaction 1; b) I; Reaction 2; c) II; Reaction 1;
 d) II; Reaction 2; e) III; Reaction 1; f) III; Reaction 2;



21) How many peaks will be in the ^{13}C -NMR spectrum of the following compound?

- a) 8; b) 7; c) 6; d) 5; e) 4; f) 2



22) How of the following electromagnetic radiations (wavelength given) has the highest energy?

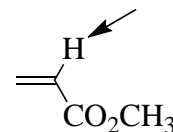
- a) 200 nm; b) 500 nm; c) 1 m; d) 1 μm

23) Which one of the following compound is meso?

- a) (1R, 3R) 1,3-dichlorocyclohexane b) (1R, 3S) 1,3-dichlorocyclohexane
 c) (1R, 2R) 1,2-dichlorocyclohexane d) (1R, 2S) 1,2-dichlorocyclohexane
 e) More than one compound is meso

24) What is the multiplicity of the hydrogen marked with an arrow in ^1H -NMR?

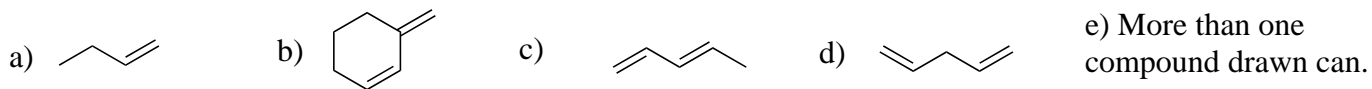
- a) 1; b) 2; c) 3; d) 4; e) 6; f) none of the above.



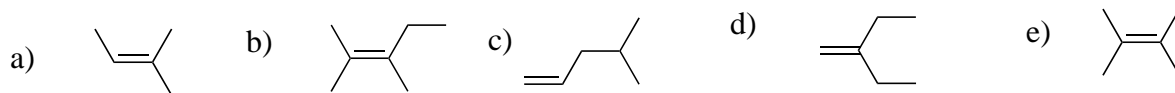
25) Which of the following reaction would yield 1-butyne?

- a) $\text{—}\equiv\text{—}^- \text{Na}^+ + \text{CH}_3\text{Br} \longrightarrow$ b) $\text{CH}_3\text{CH}_2\text{Br} + \text{H—}\equiv\text{—}^- \text{Na}^+ \longrightarrow$
 c) $\text{—}\equiv\text{—H} + \text{NaCH}_3 \longrightarrow$ d) $\text{—}\equiv\text{—} + \text{NaCH}_3 \longrightarrow$
 e) More than one reaction will give the desired product f) None of the above

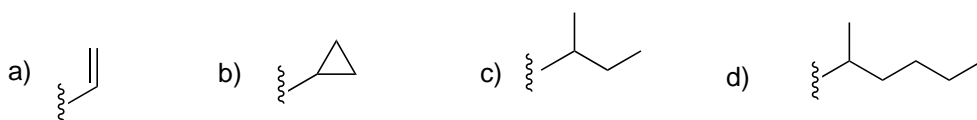
26) Which of the following compound can function as a diene in Diels-Alder reaction?



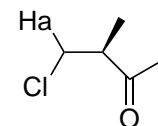
27) Which one of the following is the most stable isomer of C_6H_{12} among the group?



28) According to the Cahn-Ingold-Prelog rule, which one of the following substituents has the HIGHEST priority for alkene E/Z assignment? ?

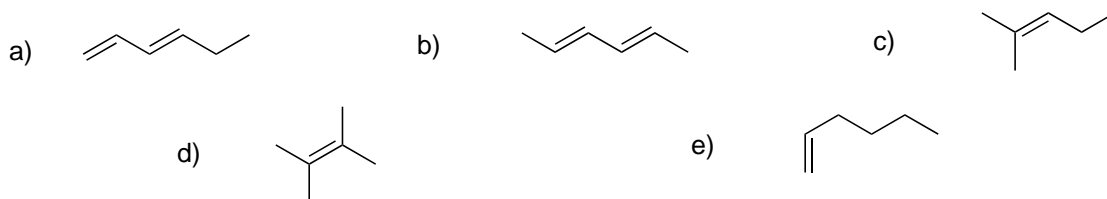


29) What is multiplicity of Ha in the following compound in its 1H -NMR spectrum?

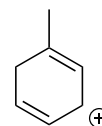
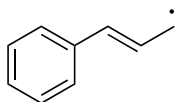
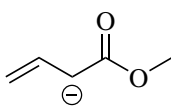


- a) 1 b) 2 c) 3 d) 4 e) none of the above

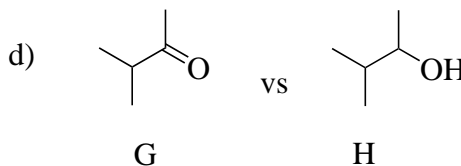
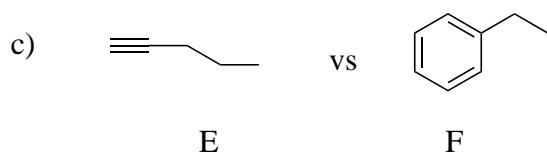
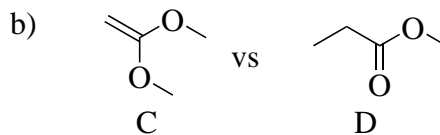
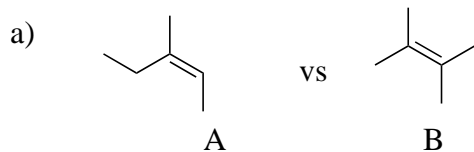
30) Each of the following alkenes is subjected to catalytic hydrogenation adding only ONE mol of hydrogen. Which would give the MOST heat for the reaction?



31. Provide two resonance structures of each of the following compounds (9 pts total).



32. List **two** differences in IR absorptions between the two compounds in each pair that will allow you to differentiate the two compounds by IR (3 pts each, 12 pts total).



33. Provide answers to the following questions. Make sure you write the answers in the boxes provided. Answers outside the boxes will not be graded. (2 pts each, 12 pts total)

1) The number of signals in $^1\text{H-NMR}$ spectrum of compound 1:

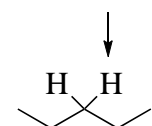
2) The ratio of integrations of those signals:

3) The multiplicity of the proton marked with an arrow in the $^1\text{H-NMR}$ spectrum of compound 1:

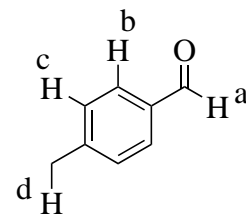
4) The hydrogen in compound 2 most downfield in its $^1\text{H-NMR}$ spectrum:

5) The number of signals in $^1\text{H-NMR}$ spectrum of para-dichlorobenzene.

6) The number of signals in $^{13}\text{C-NMR}$ spectrum of para-dichlorobenzene.



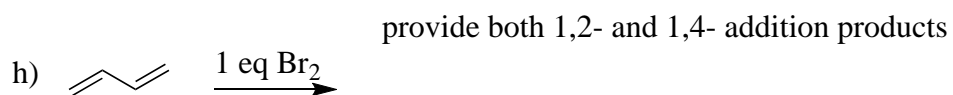
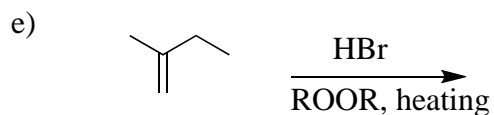
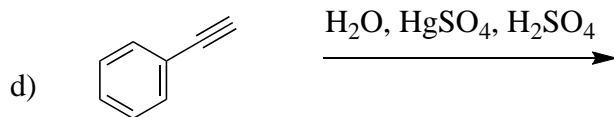
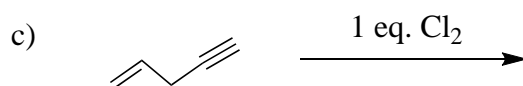
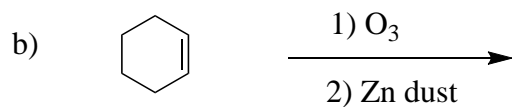
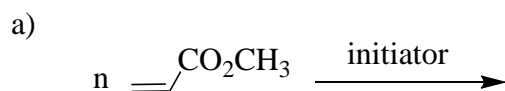
compound 1

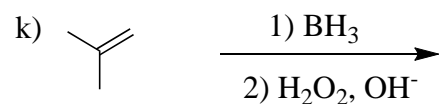
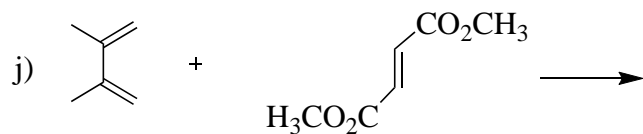
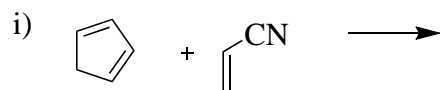


compound 2

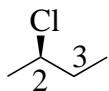
34. Provide the missing info for the following reactions. Clearly draw out stereochemistry if applicable. If there are multiple stereoisomers formed, draw out the structures of all stereoisomers. (3 pts each, 33 pts total).

polymer structure

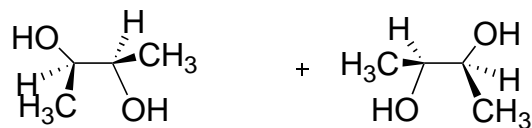




35. Draw five Newman projections (two elipsed forms and three staggered forms) of the following molecule along C2-C3 bond. Of the three staggered forms, two of them must have two methyl groups gauche to each other and the third one has two methyl groups anti (2 pts each, 10 pts total).



36. Provide a synthesis of the following two compounds starting from propyne. You can use any other reagents or reactants. (6 pts)



37. Write out the structure of the major organic product of the following reaction and provide a DETAILED mechanism for this transformation. Use curved arrows to clearly indicate movement of electrons (8 pts):



38. Propose structures for compounds that are most consistent with the following data. The following questions will guide you to the structure. Provide your answers in the boxes provided.

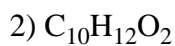
	¹ H-NMR	¹³ C-NMR
1) C ₄ H ₆ Cl ₂	peak a: 2.18 ppm (3H, singlet) peak b: 4.16 ppm (2H, doublet, <i>J</i> = 7 Hz) peak c: 5.71 ppm (1H, triplet, <i>J</i> = 7 Hz)	25.9, 39.2, 122.4, 134.6 ppm

Degree of unsaturation (2 pts)

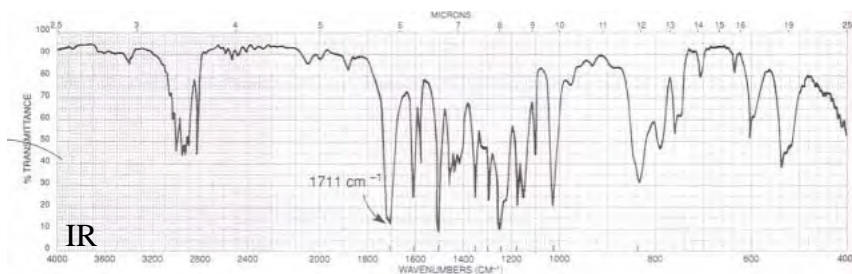
How many hydrogens are there on the carbons neighboring the hydrogens corresponding to peaks a and b? (2 pts)

Based on the degree of unsaturation, NMR chemical shifts of this compound, what functional group must it have (2 pts)?

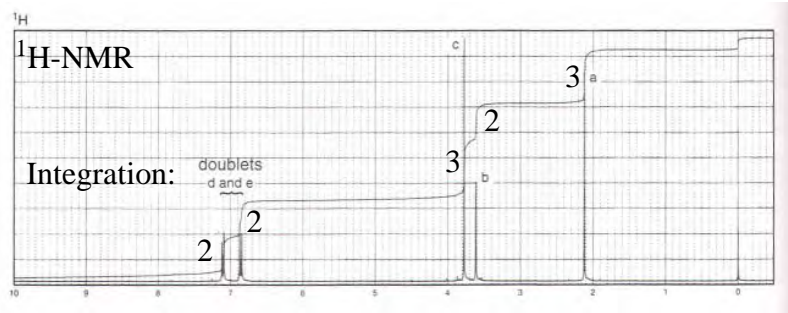
Your proposed structure structure is (4 pts):



Degree of unsaturation (2 pts)



Number of non-equivalent carbon (2 pts)




Does this molecular contain H linked to sp^2 C?
Provide a yes or no answer in the box. (2 pts)

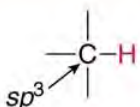
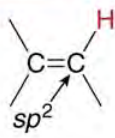
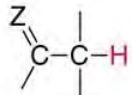
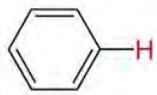
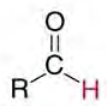
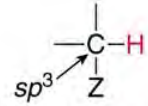
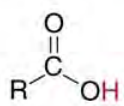
^{13}C -NMR of this compound contains the following peaks:
29, 50, 55, 114, 126, 130, 159, 207 ppm.

Which functional group is most likely responsible
for the IR band at 1711 cm^{-1} ? (2 pts)

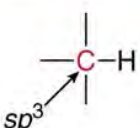

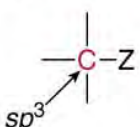
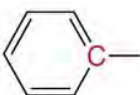

Your proposed structure structure is (2 pts)

Bond type	Approximate $\tilde{\nu}$ (cm^{-1})	Intensity
O-H	3600-3200	strong, broad
N-H	3500-3200	medium
C-H	~3000	
• C_{sp^3} -H	3000-2850	strong
• C_{sp^2} -H	3150-3000	medium
• C_{sp} -H	3300	medium
$C\equiv C$	2250	medium
$C\equiv N$	2250	medium
C=O	1800-1650 (often ~1700)	strong
C=C	1650	medium
	1600, 1500	medium

Common $^1\text{H-NMR}$ chemical shift values.

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
 <ul style="list-style-type: none"> • RCH_3 ~0.9 • R_2CH_2 ~1.3 • R_3CH ~1.7 	0.9–2		4.5–6
 $\text{Z} = \text{C}, \text{O}, \text{N}$	1.5–2.5		6.5–8
$-\text{C}\equiv\text{C}-\text{H}$	~2.5		9–10
 $\text{Z} = \text{N}, \text{O}, \text{X}$	2.5–4		10–12
		$\text{RO}-\text{H}$ or $\text{R}-\text{N}-\text{H}$	1–5

Common $^{13}\text{C-NMR}$ chemical shift values.

Type of carbon	Chemical shift (ppm)	Type of carbon	Chemical shift (ppm)
	5–45		100–140
 $\text{Z} = \text{N}, \text{O}, \text{X}$	30–80		120–150
$-\text{C}\equiv\text{C}-$	65–100		160–210