



UNIVERSITY OF
MICHIGAN

DEPARTMENT OF CHEMISTRY

HNMR explanations for molecule 5 and molecule 12 in the synthesis of bryostatin 16.

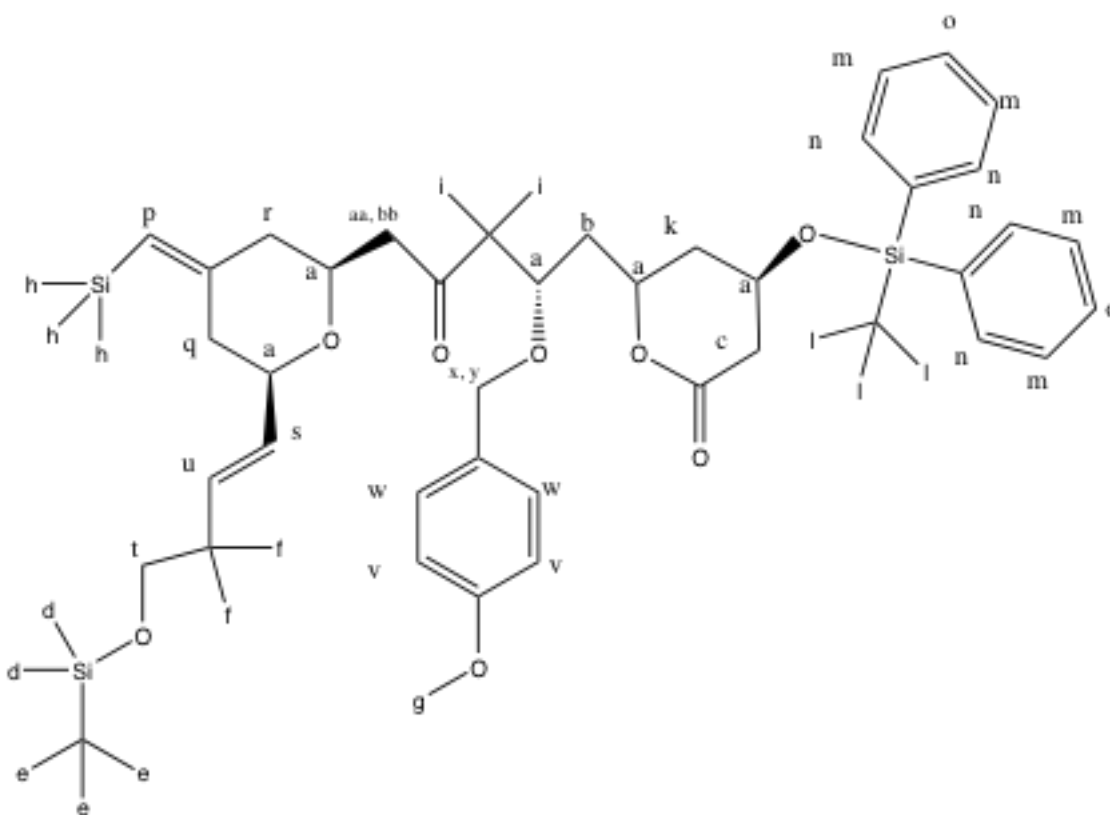
Trost, B. M.; Dong, G. *J. Am. Chem. Soc.* **2010**, *132*, 16403-16416.

Organic Chemistry 215HH Winter 2011

Joe Lee
Anila Kumar
Shanna Cheng
Marshall Westfall

¹HNMR Correlation: Molecule 5

Assignment	Shift (ppm)	Integration	Splitting Pattern	J-Value
<i>a</i>	4.03-3.89, 3.88, 3.73	5H	Multiple	
<i>b</i>	1.58-1.55, 1.48	3H	Multiple	
<i>c</i>	2.47-2.38	2H	Multiple	
<i>d</i>	0	6H	Singlet	
<i>e</i>	0.88	9H	Singlet	
<i>f</i>	0.93	6H	Singlet	
<i>g</i>	3.73	3H	Singlet	
<i>h</i>	0.09	9H	Singlet	
<i>i</i>	1.08-1.18	4H	Singlet?	
<i>k</i>	1.9	2H	Doublet of Doublet of Doublet	2.5, 5.5, 14
<i>l</i>	1.03	9H	Singlet	
<i>m</i>	7.37 – 7.43	4H	Multiple	
<i>n</i>	7.59 – 7.63	2H	Multiple	
<i>o</i>	4.43	1H	Doublet	11
<i>p</i>	5.26	1H	Singlet	
<i>q</i>	1.97	1H	Broad Doublet of Doublet	12,24
<i>r</i>	2.53	1H	Doublet of Doublet	7, 18
<i>s</i>	5.63	1H	Doublet of Doublet	0.5, 16
<i>t</i>	3.25	2H	Singlet	
<i>u</i>	5.40	1H	Doublet of Doublet	7, 16
<i>v</i>	6.76	2H	Doublet	8.5
<i>w</i>	7.13	2H	Doublet	8.5
<i>x</i>	4.55	1H	Doublet	11
<i>y</i>	4.34	1H	Doublet	11
<i>aa</i>	3.0	1H	Doublet of Doublet	5.5, 17
<i>bb</i>	2.23	1H	Broad Doublet	13



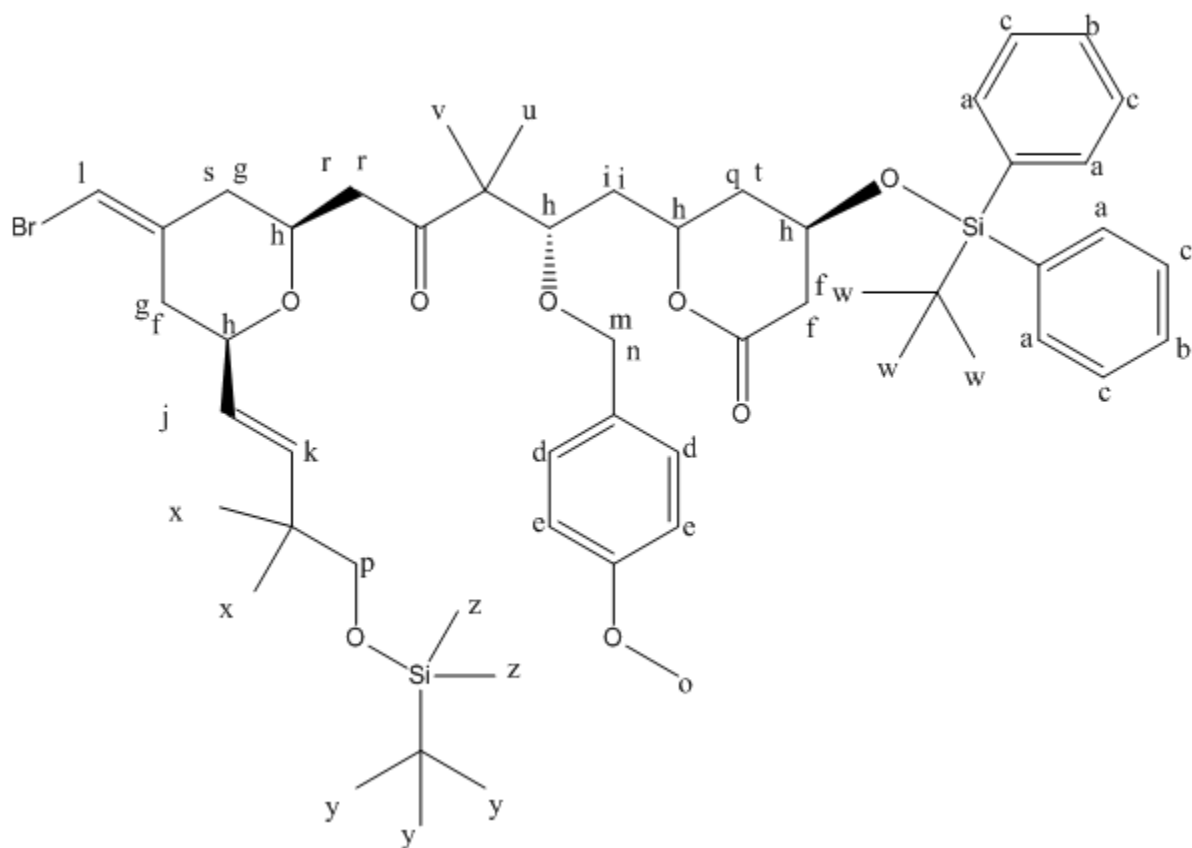
- The peak at 4.03-3.89 corresponds to the two H's that are next to b. This is because they are more deshielded due to the presence of the Oxygens. The peaks at 3.88 and 3.73 correspond to the 3 H's—one is next to c, and the other two are near r and q. This is because they are more shielded than the other two H's in this grouping. They show up as a multiplet because they are on a ring.
- There are two peaks for these two H's because they are diastereotopic. They are upfield because they are not in close proximity to an electronegative atom. They show up as a multiplet because they are on a ring.
- The peak at 2.47-2.38 corresponds to the 2 H's labeled "c." They show up as a multiplet because they are on a ring and have multiple neighbors.
- The peak at 0 corresponds to the 6 H's labeled "d" because it is very shielded. This makes sense because TBS and TMS, usually used as the reference point of 0 in NMR, are very similar in structure. They show up as a singlet because there is no difference between these hydrogens and have no neighbors.
- The peak at 0.88 corresponds to the 9 H's labeled "e." These H's are very upfield because of the Si atom. This makes the H's very shielded and thus, more upfield. They show up as a singlet because all of these H's are similar and have no neighbors.

- f. The peak at 0.93 corresponds to the 6 H's labeled "f." They all show up as a singlet because they have no neighbors and are the same.
- g. The peak at 3.73 corresponds to the 3 H's labeled "g." It is relatively upfield because it is next to Oxygen, a relatively electronegative atom. They show up as a singlet because all 3 H's are similar and have no vicinal neighbors to couple with.
- h. The peak at 0.09 corresponds to the 9 H's labeled "h." These are very upfield because of the Si. This is consistent with what was said with the H's labeled "d." They show up as singlets because all the H's are the same. Furthermore, they have no neighbors.
- i. The peak at 1.08-1.18 corresponds to the 6 H's labeled "i." This is because they are around other carbons. They show up as a singlet because they have no neighbors and the H's are the same.
- k. The peak at 1.9 corresponds to the 2H's labeled "k." This is because carbons surround them. They show up as a doublet of a doublet of a doublet because of the neighboring hydrogens around them. The corresponding J-values are 2.5, 5.5, and 14 Hz.
- l. The peak at 1.03 corresponds to the 9 H's labeled "l." This is because it is near the Si atom. They show up as a singlet because all of the H's are the same. Furthermore, they have no neighbors.
- m. The peak at 7.37-7.43 ppm represents the hydrogens on a benzene ring. It is a multiplet because it is on a benzene ring. It is also highly deshielded because of the benzene ring and the peaks are downfield.
- n. The peak at 7.59-7.63 ppm represents the hydrogens on a benzene ring. It is a multiplet because it is on a benzene ring. It is also highly deshielded because of the benzene ring and the peaks are downfield.
- o. The peak at 4.43 ppm represents a hydrogen off a benzene ring. It is a doublet because it is neighbors with one group of hydrogens.
- p. The peak at 5.26 ppm represents a hydrogen off a double bond. It is a singlet because it has no vicinal neighbors.
- q. The peak at 1.97 ppm represents the two hydrogens on a benzene ring. The peaks are not exactly 1.97 and each hydrogen at r is a distinct/unique hydrogen. The two hydrogens are diastereotopic thus the peak is a doublet of a doublet. In addition, the J value is 12 and 24.
- r. The peak at 2.53 ppm represents the two hydrogens on a benzene ring. The peaks are not exactly 2.53 and each hydrogen at r is a distinct/unique hydrogen. The two hydrogens are diastereotopic thus the peak is a doublet of a doublet. In addition, the J value is 7 and 18.
- s. The peak at 5.63 ppm represents a hydrogen off a carbon-carbon double bond. It is a doublet of doublet and has a J value of 0.5 and 16 due to the carbon on the other side of the double bond.

- t. The peak at 3.25 ppm represents two hydrogens with no vicinal neighbors. Thus, the peak is a singlet.
- u. The peak at 5.40 ppm represents a hydrogen off a carbon-carbon double bond. It is a doublet of doublet and has a J value of 7 and 16 due to the carbon on the other side of the double bond.
- v. The peak at 6.72 ppm represents two hydrogens on the benzene ring. They are highly deshielded due to the benzene ring, thus their peak is highly upfield. Each hydrogen has one neighbor thus the peak is a doublet. Its J value is 8.5Hz.
- w. The peak at 7.13 ppm represents two hydrogens on the benzene ring. They are highly deshielded due to the benzene ring, thus their peak is highly upfield. Each hydrogen has one neighbor thus the peak is a doublet. Its J value is 8.5Hz.
- x. The peak at 4.55 ppm represents the hydrogen at y. It is very deshielded due to the presence of the electronegative oxygen. In addition, it has one neighbor (hydrogen y), thus it is a doublet. Its j-value is 11Hz because it is diastereotopic with the other hydrogen coming off the carbon it is on.
- y. The peak at 4.34 ppm represents the hydrogen at y. It is very deshielded due to the presence of the electronegative oxygen. In addition, it has one neighbor (hydrogen x), thus it is a doublet. Its j-value is 11Hz because it is diastereotopic with the other hydrogen coming off the carbon it is on.
- aa.bb. The peaks at 3.0 ppm and 2.23 ppm each represent hydrogens that are -diastereotopic. The J value for one is 5.5 and 17 and the other J value is 13.

¹HNMR Correlation: Molecule 12

Assignment	Shift (ppm)	Integration	Splitting Pattern	J-Value (Hz)
<i>a</i>	7.63-7.59	4H	Multiple	
<i>b</i>	7.47-7.43	2H	Multiple	
<i>c</i>	7.41-7.37	4H	Multiple	
<i>d</i>	7.13	2H	Doublet	8.5
<i>e</i>	6.76	2H	Doublet	8.5
<i>f</i>	2.47-2.36	3H	Multiple	
<i>g</i>	1.88 - 1.78	2H	Multiple	
<i>h</i>	4.02 - 3.97, 3.84-3.74	5H	Multiple	
<i>i</i>	1.60 - 1.54, 1.47	3H	Multiple	
<i>j</i>	5.67	1H	Doublet of Doublet	1.0, 16
<i>k</i>	5.41	1H	Doublet of Doublet	6.5, 16
<i>l</i>	5.98	1H	Singlet	
<i>m</i>	4.56	1H	Doublet	11.5
<i>n</i>	4.35	1H	Doublet	11.5
<i>o</i>	3.73	3H	Singlet	
<i>p</i>	3.26	2H	Singlet	
<i>q</i>	3.03	1H	Doublet of Doublet	5.5, 18
<i>r</i>	2.80	2H	Broad Doublet	13.5
<i>s</i>	2.55	1H	Doublet of Doublet	7.0, 18
<i>t</i>	1.91	1H	Doublet of Doublet of Doublet	3.5, 5.5, 14
<i>u</i>	1.18	3H	Singlet	
<i>v</i>	1.09	3H	Singlet	
<i>w</i>	1.03	9H	Singlet	
<i>x</i>	0.95	6H	Singlet	
<i>y</i>	0.89	9H	Singlet	
<i>z</i>	0.01	6H	Singlet	



- These peaks correspond to benzene ring hydrogen.
- These peaks correspond to benzene ring hydrogens.
- These peaks correspond to benzene ring hydrogen.
- These peaks correspond to benzene ring hydrogens. They are higher field than E hydrogens because they are in the meta position relative to the attached O causing them to be more electron rich.
- These peaks correspond to benzene ring hydrogens. They are in the ortho position relative to the attached O causing the H's to be more electron deficient.
- These peaks are group together only because they have similar ppm and have a messy splitting pattern making it impossible to differentiate individual chemical shifts.
- These peaks are group together because they have similar ppm and have a messy splitting pattern making it impossible to differentiate individual chemical shifts.
- These peaks are group together because they have similar ppm and have a messy splitting pattern making it impossible to differentiate individual chemical shifts.
- These peaks are group together because they have similar ppm and have a messy splitting pattern making it impossible to differentiate individual chemical shifts.

- J. This hydrogen is coming off of a double bonded carbon, giving it a chemical shift at around 5.5 ppm. It is coupling with the hydrogen across the double bond as well as a hydrogen from group H.
- K. This hydrogen is coming off of a double bonded carbon, it a chemical shift at around 5.5 ppm. The coupling constant matches with J indicating that it is trans across the double bond.
- L. This hydrogen is coming off of a double bonded carbon, giving it a chemical shift at around 6 ppm. It is a single peak indicating that it has no vicinal neighbors
- M. This hydrogen has a very similar ppm to hydrogen N along with the same coupling constant. Since they are both doublets, they must be diastereotopic hydrogens on the same carbon.
- N. This hydrogen has a very similar ppm to hydrogen N along with the same coupling constant. Since they are both doublets, they must be diastereotopic hydrogens on the same carbon.
- O. These peaks are a singlet indicating an isolated methyl group. Since it is relatively downfield indicating that it must be a methyl group attached to an oxygen atom.
- P. These peaks showed up as a singlet, however in theory they should be diastereotopic and show up as a doublet.
- Q. This hydrogen is diastereotopic to hydrogen t. It's coupling constant matches that of hydrogen T. IT shows up as a doublet of a doublet as it also couples with group H hydrogen
- R. The peak at 2.80 corresponds to the 2 H's labeled "r." This is because they are near carbons attached to oxygens. They show up as a broad doublet due to the coupling with each other. The J-value is 13.5 Hz.
- S. The peak at 2.55 corresponds to the H labeled "s." This is because it is near a double bond. It shows up as a doublet of a doublet because it couples with the H labeled "g" and the H labeled "h." These H's (g and h) are different. The J-values are 7.0 Hz and 18.0 Hz.
- T. The peak at 1.91 corresponds to the single H labeled "t." It shows up as a doublet of a doublet of a doublet because it couples with 3 other H's that are not similar to eachother. The J-values are 3.5 Hz, 5.5 Hz, and 14 Hz.
- U. The ppm values are 1.18 ppm and 1.09 ppm respectively. U has three hydrogens that are diasterotopic with the three hydrogens on v. The hydrogens are singlets because they do not have any vicinal neighbors.
- V. The ppm values are 1.18 ppm and 1.09 ppm respectively. U has three hydrogens that are diasterotopic with the three hydrogens on v. The hydrogens are singlets because they do not have any vicinal neighbors.
- W. The peak at 1.03 ppm represent nine hydrogens. They are all singlets because they do not have any vicinal neighbors.

- X. The peak at 1.03 ppm represents two methyl groups. The hydrogens are singlets because they do not have any vicinal neighbors.
- Y. The peak at 0.89 ppm represents three methyl groups. The hydrogens are singlets because they do not have any vicinal neighbors. They are also very upfield and shielded due to their attachment to Si.
- Z. The peak at 0.01 ppm represents two methyl groups. The hydrogens are singlets because they do not have any vicinal neighbors. They are also very upfield and shielded due to their attachment to Si.