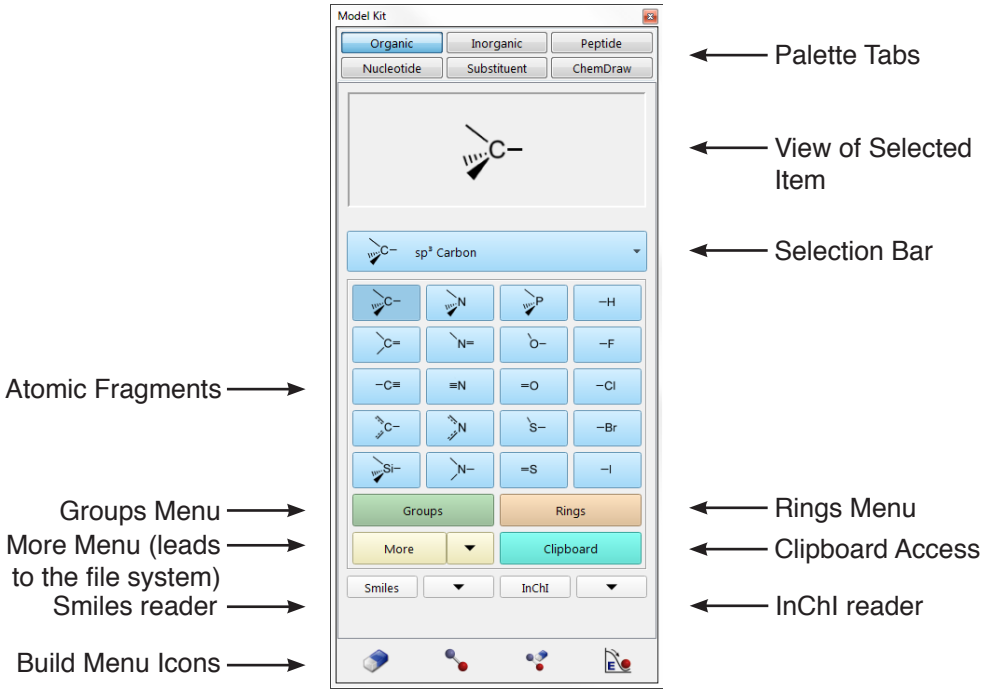
Chapter 3
Building Organic Molecules in 3D

The tutorials in this chapter introduce and illustrate tools to build 3D molecular structures. These include atomic fragments, functional groups and rings contained in the organic model kit together with tools for making and breaking bonds, deleting atoms and refining structure.

Organic Model Kit

Click on  to bring up the 3D model kit. The organic model kit contains a selection of atomic fragments corresponding to elements commonly found in organic molecules. The kit may be scrolled if your display is too small to display it.*



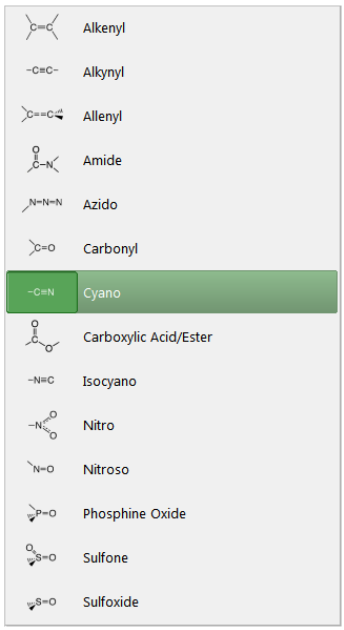
* Additionally, you can save space by removing the icons at the bottom of the model kit. *Uncheck* **Show Toolbar** from the **Miscellaneous** tab of the **Preferences** dialog (**Options** menu; **Chapter 25**).

Different hybridization states are provided for some elements (from left to right and then top to bottom):

$C(sp^3)$	$N(sp^3)$	$P(sp^3)$	H
$C(sp^2)$	$N(sp^2)$	$O(sp^3)$	F
C(sp)	N(sp)	$O(sp^2)$	Cl
C(aromatic)	N(aromatic)	$S(sp^3)$	Br
$Si(sp^3)$	N(planar)	$S(sp^2)$	I

A fragment is chosen by *clicking* on its icon, which is then displayed in a box at the top of the model kit. The name of the fragment is displayed in the selection bar underneath, for example, 

. Once selected, the fragment may be used to initiate building, to add alongside of an existing structure or bond onto an existing structure. To initiate building, *double click* anywhere on screen.* To add alongside of an existing structure, *double click* in a blank area on screen. To bond to an existing structure, *click* on a free valence (***not an atom***). (Free valences are colored yellow on the selected molecule.) Bond type in the case of atomic fragments with multiple bond types, for example, sp^2 carbon, depends on the nature of the free valence selected.



Clicking on the **Groups** button near the bottom of the model kit changes the focus from fragments to groups, one of which will be shown in the box at the top of the model kit and named in the selection bar directly underneath. *Clicking* on the selection bar brings up a menu of available groups.

Once selected from the menu, a group may be used to initiate building, to add alongside of an existing structure on screen, or to add to an existing structure.

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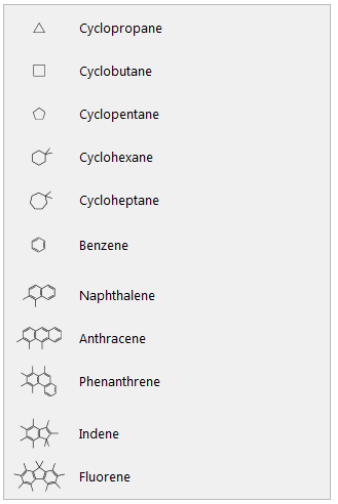
* For users of much earlier versions of ***Spartan*** that have grown accustomed to (or new users who prefer) a *single-click* motion to initiate building, this preference can be set from the **Options** menu > **Preferences** dialog > **Settings** tab, by deselecting the **Double-Click Start** check box and *clicking* the **OK** button. The choice to move to a *double-click* start for 3D building was made to maintain consistency with the behavior of the 2D sketch builder.



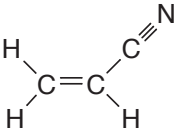
Clicking on the **Rings** button near the bottom of the model kit changes the focus to rings, one of which will be shown in the box at the top of the model kit and named in the selection bar underneath. *Clicking* on the selection bar brings up a menu of available rings.

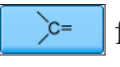
Once selected from the menu, a ring may be used to initiate building, to add alongside of an existing structure on screen, or to add to an existing structure.

Note that only hydrocarbon rings are available. Heteroatoms may be substituted for carbons, for example, substituting an oxygen for one of the carbons in cyclohexane leading to tetrahydropyran. With cyclohexane on screen, *click* on sp^3 oxygen () in the model kit and then *double click* on one of the cyclohexane carbons.

The amide and carboxylic acid/ester groups and the cyclohexane, cycloheptane, naphthalene, phenanthrene, indene and fluorene rings have more than one unique free valence. The free valence that is to be used is marked with a gold • (in the icon shown in the box at the top of the model kit). The marked position circulates among the possible positions with repeated *clicking* on the icon. Selection of an *axial* or *equatorial* free valence in cyclohexane and cycloheptane is indicated by the label **ax** or **eq** appearing alongside the icon.

Acrylonitrile



1. To bring up the organic model kit, *click* (left button) on the **File** menu and select (*click* on) **New Build**. Alternatively, *click* on  if it appears at the top of the screen.* *Click* on trigonal planar sp^2 hybridized carbon  from the fragment library.

* Icons are fully customizable from the **Options** menu > **Preferences** dialog > **Icons** tab. So whether or not a particular icon is displayed is at the discretion of the user.

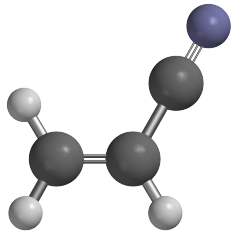
A model of the fragment appears at the top of the model kit. Bring the cursor anywhere on screen and *double click* (left button). Rotate the carbon fragment (*drag* the mouse while holding down the left button) so that you can clearly see both the double free valence (=) and the two single free valences (–).

2. sp^2 carbon is still selected. *Click* on the double free valence. The two fragments are connected by a double bond, leaving you with ethylene, meaning that ethylene is in the Spartan Spectra and Properties Database (SSPD). The name ***ethylene*** will appear at the bottom right of the screen. If you make a mistake and *click* instead on the single free valence, select **Undo** from the **Edit** menu (or *click* on  if it appears at the top of the screen). You can also start over by selecting **Clear** from the **Edit** menu (or *click* on  if it appears at the top of the screen).

3. *Click* on the **Groups** button at the bottom of the model kit, *click* on the selection bar at the top of the model kit, and select **Cyano** from the groups available from the menu. *Click* on any of the four single free valences on ethylene (they are equivalent). This bonds the cyano group to ethylene, leaving you with acrylonitrile. Its name will appear at the bottom right of the screen.

4. *Click* on  at the bottom of the model kit. (You can also select **Minimize** from the **Build** menu or *click* on  if the icon appears in the toolbar at the top of the screen.) The molecular mechanics energy (36.2 kJ/mol) and symmetry point group (C_s) are provided at the bottom right of the screen.

5. Select **View** from the **Build** menu (or *click* on the  icon in the toolbar). The model kit disappears, leaving only a ball-and-spoke model of acrylonitrile on screen. The name appears at the bottom of the screen as acrylonitrile is also in the SSPD.



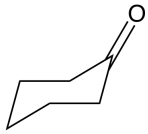
ball-and-spoke model

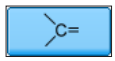
This model can be rotated, translated and zoomed by using the mouse in conjunction with keyboard functions. To rotate the model, *drag* the mouse while holding down the left button; to rotate in the plane of the screen also hold down the **Shift** key. To translate the model, *drag* the mouse with the right button depressed. To zoom the model, use the center mouse wheel (scroll wheel) if available, or hold down the **Shift** key in addition to the right button while *dragging* the mouse up (zoom in) or down (zoom out).

Rotate the molecule by moving one finger over the screen. Rotate the molecule in the plane of the screen by twisting two fingers. Translate by moving two fingers. Zoom by pinching two fingers.

6. Close ***acrylonitrile*** (**Close** from the **File** menu or *click* on the icon in the toolbar).

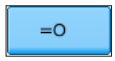
Cyclohexanone



1. *Click* on the **File** menu and select **New Build** from the palette or *click* on  at the top of the screen. *Click* on the **Rings** button near the bottom of the model kit, *click* on the selection bar and choose **Cyclohexane** from the menu of rings. *Double click* anywhere on screen.
2. Select sp^2 carbon  from the model kit. *Double click* on

any carbon atom (***not a free valence***). The sp^3 hybridized center will be replaced by an sp^2 hybridized carbon.

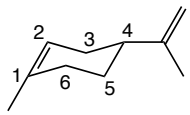
> Fragment replacement is subject both to the usual valence rules and to the availability of free valences. For example, replacement of an sp^3 carbon by an sp^2 carbon requires that at least two free valences are available.

3. Select sp^2 oxygen 

from the model kit. *Click* on the double free valence on the sp^2 carbon. You have made cyclohexanone. *Click* on  at the bottom of the model kit to produce a structure with C_s symmetry. *Click* on  . The name ***cyclohexanone*** appears at the bottom of the screen as the molecule is in SSPD.

4. Close ***cyclohexanone***.

Limonene



1. Select **New Build** from the **File** menu (or *click* on the  icon in the toolbar) to bring up the model kit. *Click* on the **Rings** button near the bottom of the model kit, *click* on the selection bar and choose **Cyclohexane** from the menu of rings. *Double click* anywhere on screen.

2. *Click* on the **Groups** button near the bottom of the model kit, *click* on the selection bar and choose the **Alkenyl** group. *Click* on the *equatorial* free valence on C_4 (see figure above for numbering). You have made vinylcyclohexane.

3. *Click* on the **Make Bond** icon () at the bottom of the model kit. One after another *click* on the *axial* free valence on C_1 and then the *axial* free valence on C_2. You have made 4-ethenylcyclohex-1-ene.

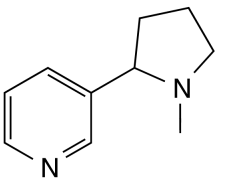
4. Select sp^3 carbon 

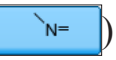
from the model kit and one after another *click* on the free valence on C_1 and on the free valence of the

vinylic carbon attached to the ring. You have made limonene. The name will appear at the bottom of the screen as limonene is in SSPD. *Click* on  at the bottom of the model kit to give a refined geometry and finally *click* on ().

5. Close ***limonene***.

Nicotine

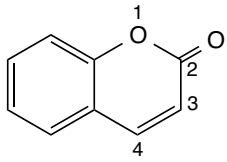


1. Select **New Build** from the **File** menu (). *Click* on the **Rings** button in the model kit. *Click* on selection bar at the top of the model kit and choose **Benzene**. *Double click* anywhere on screen.
2. *Click* on the selection bar and choose **Cyclopentane**. *Click* on one of the free valences on benzene. You have made phenylcyclopentane.
3. *Click* on the sp^2 nitrogen in the model kit () and *double click* on the appropriate (*meta*) carbon (not a free valence) in the benzene ring. You have made 3-cyclopentylpyridine.
4. *Click* on sp^3 nitrogen in the model kit () and *double click* on the appropriate carbon in the cyclopentyl ring. You have made nornicotine.
5. *Click* on sp^3 carbon in the model kit () and *click* on the free valence on the nitrogen in the pyrrolidine ring. You have made nicotine. *Click* on  at the bottom of the model kit to clean up your structure. The name ***nicotine*** will appear at the bottom of the screen as the molecule is in SSPD.
6. Select **R/S Chirality** from the **Model** menu (). The R/S chirality will be displayed. The S isomer is the naturally occurring isomer of nicotine. If you have built the R isomer and wish to invert the chiral center, hold down the **Ctrl** key on

your keyboard and *double-click* on the chiral center.

7. Close ***nicotine***.

Coumarin

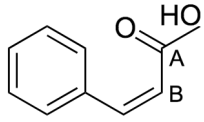


1. Select **New Build** from the **File** menu ( ). *Click* on the **Rings** button in the model kit. *Click* on the selection bar at the top of the model kit and choose **Benzene**. *Double click* anywhere on screen.

2. *Click* on the **Groups** button, *click* on the selection bar and choose **Alkenyl**. *Click* on one of the free valences of benzene to make styrene.

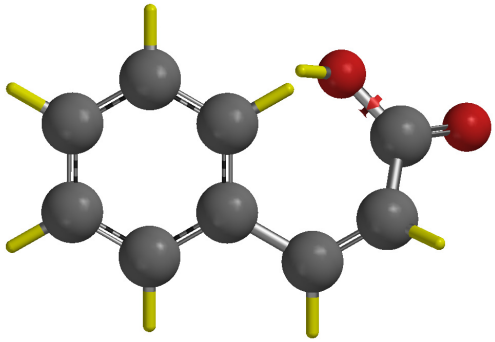
3. *Click* on the selection bar and choose **Carboxylic Acid/Ester**. A yellow dot should mark the free valence ***on carbon*** in the group shown in the window at the top of the model kit. If instead it marks the free valence on oxygen, *click* inside the window to move it. *Click* on the free valence on the methylene end of the vinyl group that is *cis* to benzene to make *cis*-cinnamic acid.

4. It may be necessary to rotate around the bond marked A and B marked below to properly position the molecule for bonding.



In turn, *click* on bonds A and B. A red arrow will curl around the bond and an icon will appear at the top of a narrow shaded area at the far left of the screen. *Click* inside this area and move the mouse up and down. Position the bond such that the OH bond is near the phenyl ring as shown below.

Move one finger up and down inside the area at the far left of the screen to rotate about the selected bond.



When you can clearly see the two free valences, *click* on  at the bottom of the model kit and, one after another, *click* on the two free valences. You have made coumarin, its name will appear at the bottom of the screen.

5. Close ***coumarin***.

Spartan is able to fuse rings in 3D. This makes building molecules like coumarin much easier. To build coumarin using the fused-ring approach, select **Benzene** from the **Rings** menu *double-click* to insert benzene on screen. Select **Cyclohexane** from the **Rings** menu, *double-click* on one of the CC bonds in benzene to form benzocyclohexane. Choose sp^3 oxygen and *double-click* to replace C_1 by oxygen (see numbering on previous page). Choose sp^2 carbon and *double-click* on C_2. Choose sp^2 oxygen and add this to the double-bond on the sp^2 carbon. *Click* on **Make Bond** () and *click* on the open *axial* valences the sp^3 ring carbons C_3 and C_4 to complete coumarin.

Note, however, that fusing two rings with both bonds involving sp^3-sp^3 hybridized centers, for example, two cyclohexane rings, can lead to one of two different results, in the case of two cyclohexane rings, either *cis* or *trans*-decalin. In this case, it may be necessary to invert the chirality of one of the resulting ring-fused carbons. This is accomplished by holding down on the **Control** (**Ctrl**) key (**Command** on Mac), positioning the cursor over the carbon and *double clicking*.