(2) Carbon radicals do not typically rearrange, so that data is likely fairly accurate. Carbocations, however, readily rearrange and are much more complex structurally, so their heats of formation are probably not as accurate.


(3) Ref: Wontrup, "Reactive Molecules", Wiley, New York, 1984, pp 33-34. A resonance structure can be drawn for \( \text{S7} \) that has all \( \pi \)-electrons paired, hence it can exist as a singlet. No matter how you draw it, \( \text{S8} \) has resonance structures all being a diradical, so it is a triplet species.

![Resonance structures diagram]


A quick run using the SHMO on the benzyl radical shows that the HOMO (\( \psi_4 \)) has \( \pi \)-density at the benzyl carbon, as well as the ortho and para carbons, but none on the ipso or meta carbons. Simple resonance theory supports this as well, as you'll see radical
character of the benzylic, ortho, and para carbuns:

\[
\begin{align*}
\text{CH}_2 & \leftrightarrow \text{C} = \text{CH}_2 \\
\text{C} = \text{CH}_2 & \leftrightarrow \text{CH}_2
\end{align*}
\]


The products formed are shown below, with percentages shown:

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{Bu}_3\text{SnH}} \text{Br} \\
\text{Bu}_3\text{SnH} & \xrightarrow{\text{Bu}_3\text{SnH}} \text{Bu}_3\text{SnR} \\
\text{trace} & \xrightarrow{\text{Bu}_3\text{SnH}} \text{trace} \\
\end{align*}
\]

What should seem 'unusual' about the above results is the high % yield of the methylic cyclopentane compared to cyclohexane. The intermediate radical leading to the methylic cyclopentane is a 1° radical, which is less stable (thermodynamically) than the 2° radical intermediate that leads to the cyclohexane product. The cause for this is stereoelectronic in nature, which to have bond formation involves interaction of the p orbital with the LUMO (π*) of the alkane. The barrier for the process for exo cyclization (meaning forming a 5-membered ring) is lower than for endo cyclization (6-membered ring formation). Ref: Spellmeyer and Houk, J. Org. Chem. 1987, 52, p. 959.

6 Use eqn 1.16 (p. 111):

\[
\chi^2 = \frac{500}{1 + \chi^2}, \quad \text{so} \quad 169 = \frac{500}{1 + \chi^2}
\]

Thus \(1 + \chi^2 = 2.958\), then % s character = \(\frac{1}{1 + \chi^2} = \frac{1}{1 + 2.958\times100} = 33.8\% \)
Under superacid conditions, the carbonyl oxygen of formic acid can be protonated and the resulting cation is resonance stabilized (a bit analogous to the allyl carbocation)

\[
\begin{align*}
\text{H} & \text{C} & \text{O}^- \\
\text{H}^- & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\end{align*}
\]

This cation can exist in the following two isomeric (diastereomeric) forms:

\[
\begin{align*}
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\text{H} & \text{C} & \text{O} \\
\end{align*}
\]

A rapid proton shift from one end of the molecule to the other occurs faster than the NMR time-scale and all 4 methyl groups become magnetically equivalent:
The reason for the racemic product from the cyano substituted system is because this substituent allows resonance and delocalization of the negative charge into the N with the important point being the cyclopropyl carbon is 'flattened' due to the $sp^2$ character now. However, the isocyano group cannot delocalize the negative charge into the resulting resonance structure is not favorable (\(\text{C}=\text{N}^+\)).

\[\text{Ph} \quad \text{CN} \quad \xrightarrow{\text{LDA, -60°C, ether}} \quad \text{Ph} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad \xrightarrow{\text{CH}_3\text{I}} \quad \text{Ph} \quad \text{CN} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad + \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad \text{CH}_3 \quad \text{CN} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \]

\[\text{Ph} \quad \text{H} \quad \xrightarrow{\text{LDA, -75°C, THF}} \quad \text{Ph} \quad \text{NC} \quad \xrightarrow{\text{CH}_3\text{I}} \quad \text{Ph} \quad \text{NC} \quad \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \quad (S)-(+) \]

An intramolecular rxn initially occurs to convert the $\text{Z}$ allyllithium into an allyllithium, which subsequently reacts with CO$_2$ followed by $\text{NaOH}$ to give the benzoic acid derivative:

This dione has, in fact, many allylic hydrogens that could be deprotonated leading to various allyl carbanions. Using the general idea that carbanions with fewer allyl groups attacked are more stable (together w/ the fact that an allyl anion is resonance stabilized), leads to H" " being removed as it has only 2 R group directly bonded to the allyl unit:

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td># of alkyl groups in resulting allyl anion</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>


This carbanion rearrangement is simply amazing! As follows:

This is a free-radical chain reaction outlined as follows:

**Initiation:**

\[
\text{PhCOOCPh} \xrightarrow{\Delta} 2\text{PhCO}^+ \rightarrow 2\text{Ph}^+ + 2\text{CO}_2
\]
\[
\text{Ph}^+ + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{Ph-C}_6\text{H}_4^+ + \cdot\text{C}_6\text{H}_5\text{Cl}_3
\]

**Propagation:**

\[
\text{Ph}^+ + \cdot\text{C}_6\text{H}_5\text{Cl}_3 \rightarrow \text{Ph-C}_6\text{H}_4^+ + \cdot\text{C}_6\text{H}_5\text{Cl}_3
\]
\[
\text{Ph}^+ + \cdot\text{C}_6\text{H}_5\text{Cl}_3 \rightarrow \text{Ph-C}_6\text{H}_5^+ + \cdot\text{C}_6\text{H}_5\text{Cl}_3
\]

A resonance argument is made where electrons from the adjacent oxygens to the empty p orbital of the carbene make the carbene less electrophilic and hence less likely to react with nucleophiles:

\[ \text{[Diagram]} \]


The Brainford-Stearns vom converts the ketene into an aza compound and the resulting carbene can undergo both a 1,2-H shift and a 1,2-alkyl shift:

\[ \text{[Diagram]} \]
The first two saturated products are formed by stereoselective trans-annular C-N insertion runs. The two alken products are formed by hydrogen rearrangement.