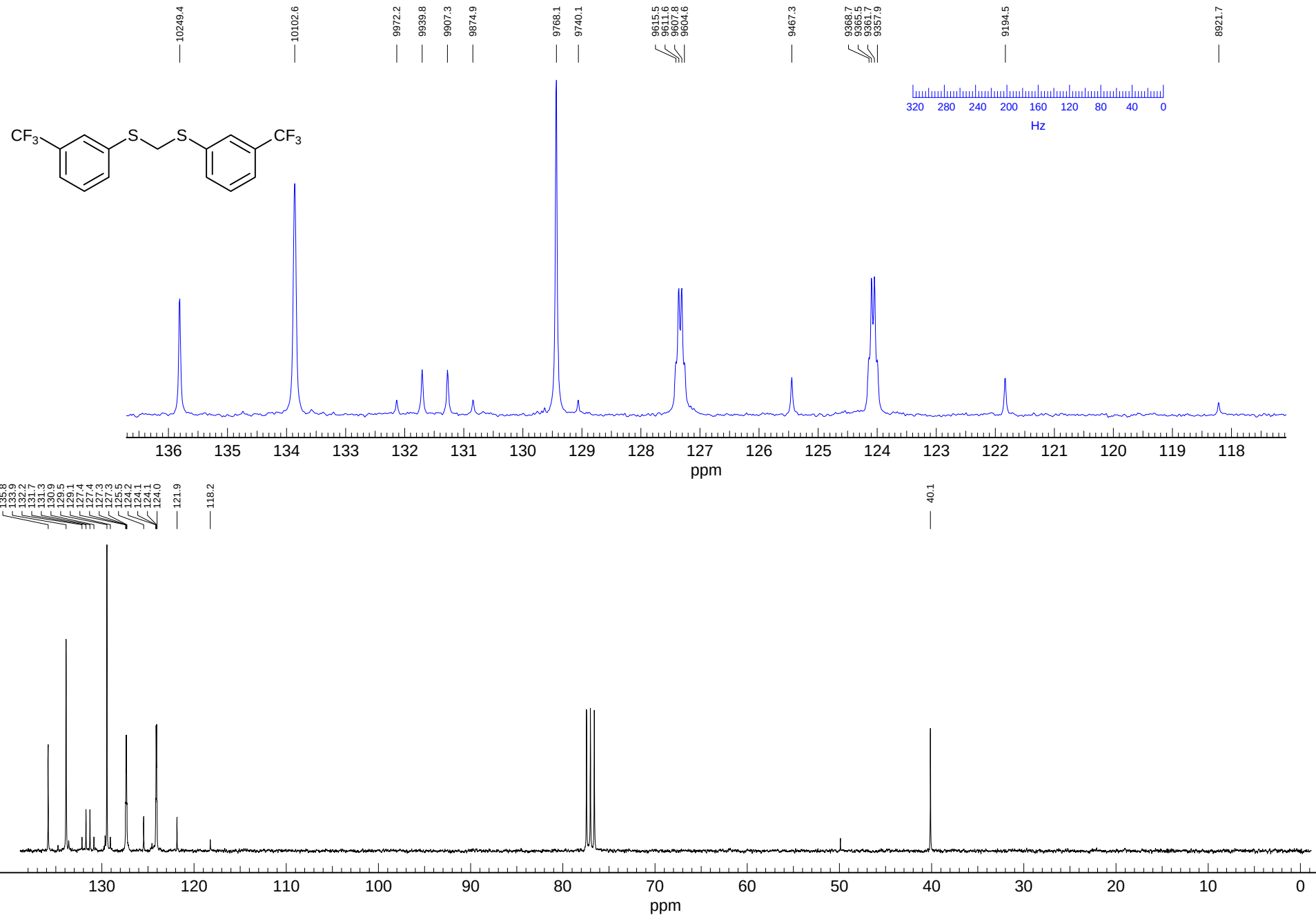
Problem R-03R ($C_{15}H_{10}F_6S_2$)

75.5 MHz ^{13}C {^1H} NMR spectrum in $CDCl_3$.

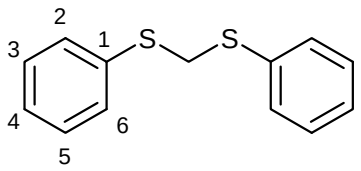
Source: Bill Sikorski / Reich 12/33 g



PLT ex-3-2003-g.plt

Problem R-03R ($C_{15}H_{10}F_6S_2$). This problem requires you to determine the substitution pattern and assign the signals in the ^{13}C NMR spectrum of a bis-trifluoromethyl substituted bis(phenylthio)methane.

(a) Determine the position of the CF_3 groups on the two rings, and put them on the structure below (please us the lowest available carbon number for placing the substituents). Explain your reasoning.



(b) Determine the ^{13}C chemical shifts, and report any couplings you have identified (use the standard format: δ 0.00, $^{n}J_{XY}$ = 0 Hz). Use the numbering system indicated on the structure above

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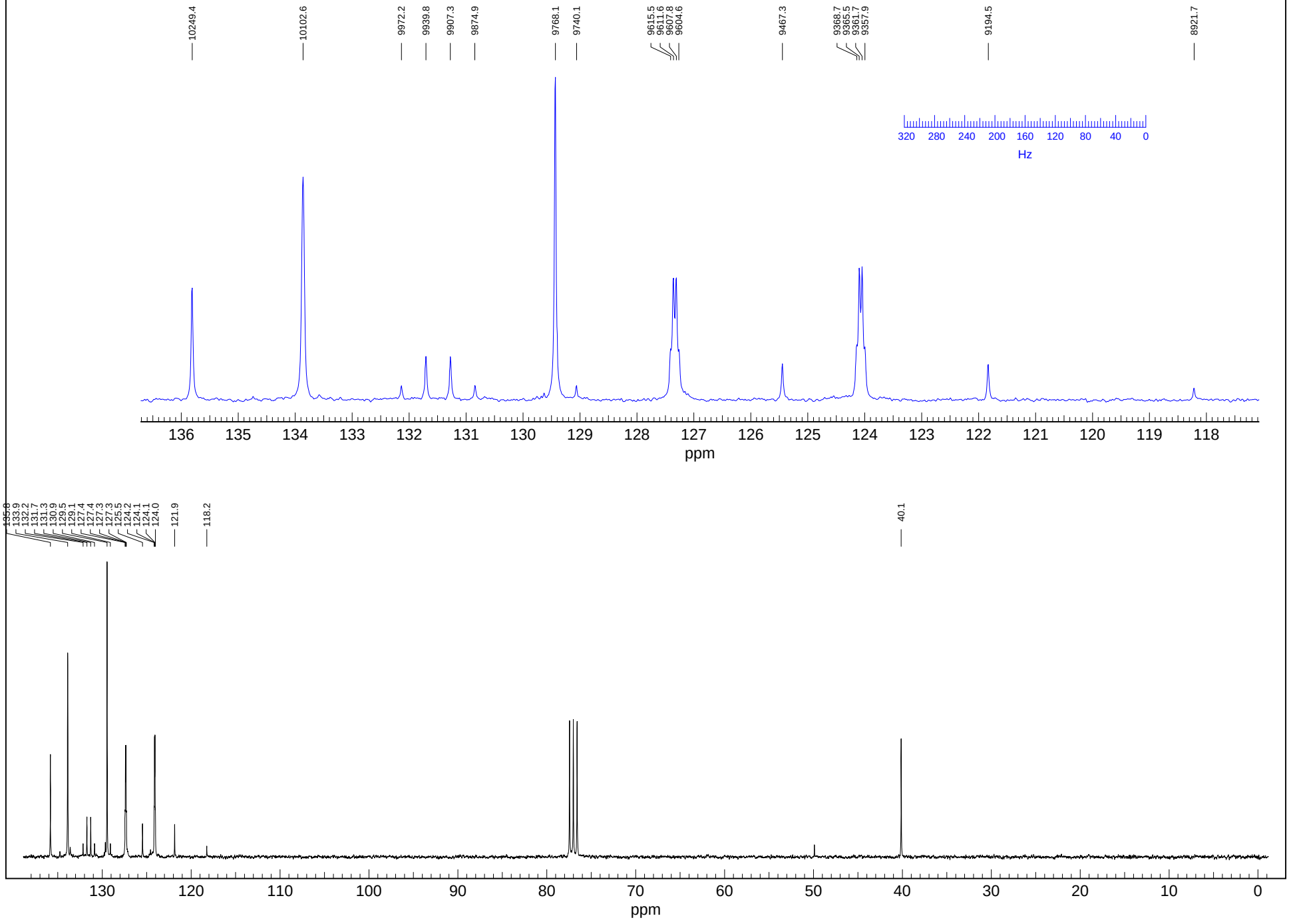

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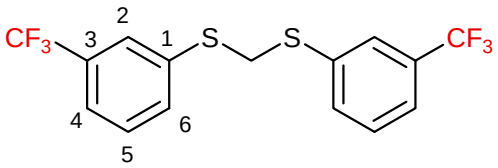

- In addition to the CF_3 quartet (centered at δ 123.8) there are 6 aromatic peaks

- The structure must be symmetrical (same sunstitution on each ring) oterwise there would be more aryl C, more than one **C**F_3 and more than one **C**-CF_3.

- The substituents can't be *para*, since there are too many C (only 4 C)

- The substituents can't be ortho, since the **C**-S aromatic carbon C^1 at δ 135.8 is not coupled to F. Would expect a $^3J_{C\text{-}F}$ to be detectable, and in fact two of the other carbons at δ 127.3 and δ 124.1 do have a small coupling to fluorine, these must be the two carbons ortho to the CF_3 groups

- Thus the CF_3 substituents must be meta (on C^3), and this carbon must be the quartet at δ 131.5 ($^2J_{C\text{-}F}$ = 32 Hz).

- The chemical shift calculations below support this assignment

(b) Determine the ^{13}C chemical shifts, and report any couplings you have identified (use the standard format: δ 0.00, $^nJ_{XY}$ = 0 Hz). Use the numbering system indicated on the structure above

		i-RS m-CF_3		Using Me-S	Using Allyl-S
CH_2	δ 40.1, s				
CF_3	δ 123.6, q, $^1J_{C\text{-}F}$ = 272.8 Hz				
C^1	δ 135.8, s	128.5 + 4.4 + 0.4 = 133.3	$\Delta\delta$ = 2.5	δ (calc) = 138.8	δ (calc) = 136.5
C^2	δ 127.3, q, $^3J_{C\text{-}F}$ = 3.8 Hz	128.5 + 2.3 - 3.1 = 127.3	$\Delta\delta$ = 0.0	δ (calc) = 123.4	δ (calc) = 126.4
C^3	δ 131.5, q, $^2J_{C\text{-}F}$ =32.4 Hz	128.5 + 0.5 + 2.6 = 131.6	$\Delta\delta$ = 0.1	δ (calc) = 131.2	δ (calc) = 131.4
C^4	δ 124.1, q, $^3J_{C\text{-}F}$ =3.6 Hz	128.5 - 1.0 - 3.1 = 124.4	$\Delta\delta$ = 0.3	δ (calc) = 121.7	δ (calc) = 123.1
C5	δ 129.4, s	128.5 + 0.5 +0.4 = 129.4	$\Delta\delta$ = 0.4	δ (calc) = 129.0	δ (calc) = 129.2
C^6	δ 133.9, s	128.5 +2.3 + 3.4 = 134.3	$\Delta\delta$ = 0.4	δ (calc) = 129.9	δ (calc) = 133.4

The chemical shift calculations are very close to the experimental ones, supporting the assignment of the carbons and the structure

For the chemical shift calculations, use the following parameters for i, o, m, p substituent chemical shifts (SCS):

	CF_3	$(PhS)_2CH_2$	Me-S	Allyl-S
i	2.6	4.4	9.9	7.6
o	-3.1	2.3	-2.0	1.4
m	0.4	0.5	0.1	0.3
p	3.4	-1.0	-3.7	-2.3

Can also use the SCS values for Me-S or Allyl-S, which are not as accurate, but still allow correct assignment

The SCS values were obtained from data in https://www.chem.wisc.edu/areas/reich/nmr/c13-data/cdata.htm under "Benzene - Substituent Effects," "Sulfide," and "Thioacetals"

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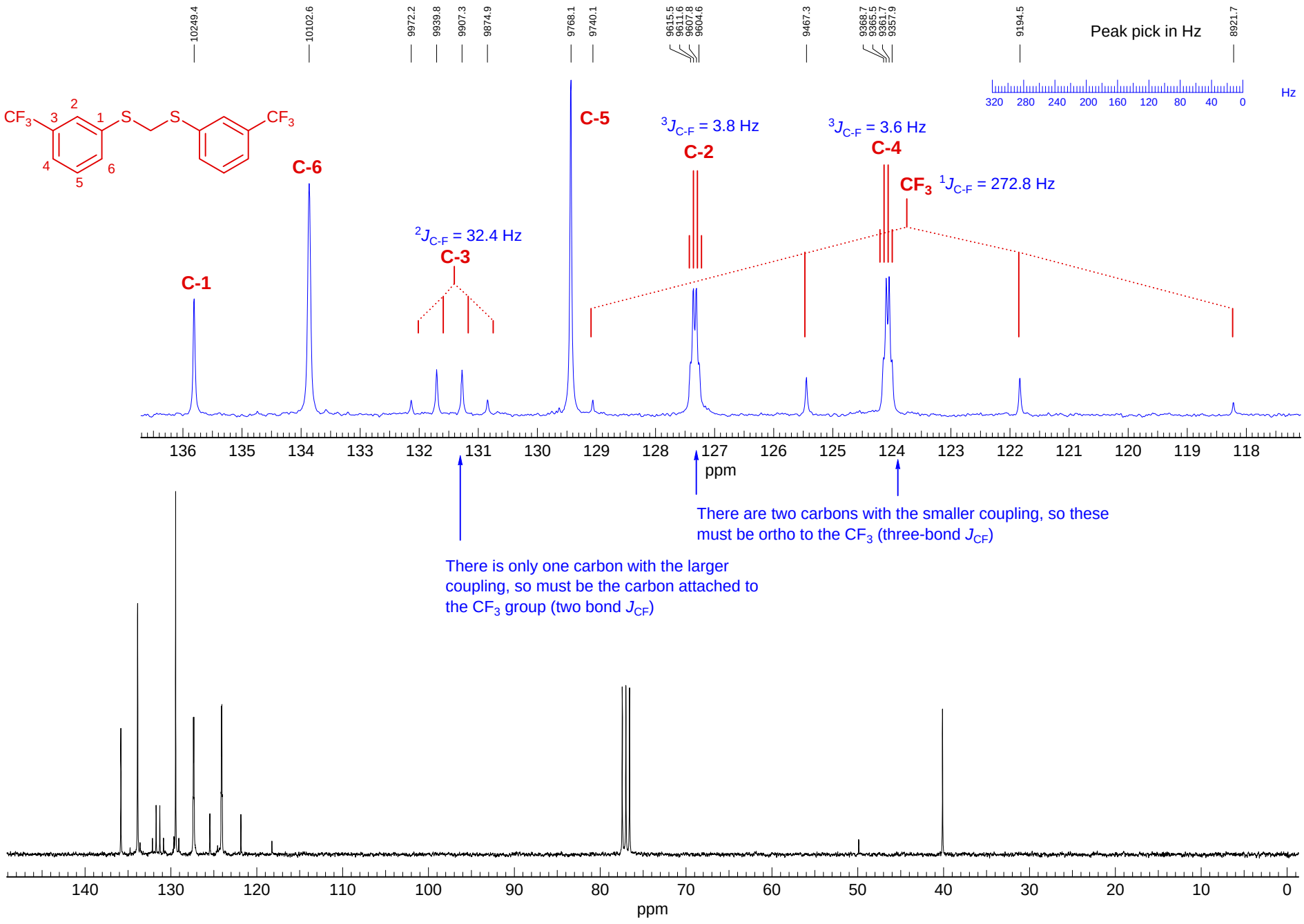

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