

## Supplementary Material

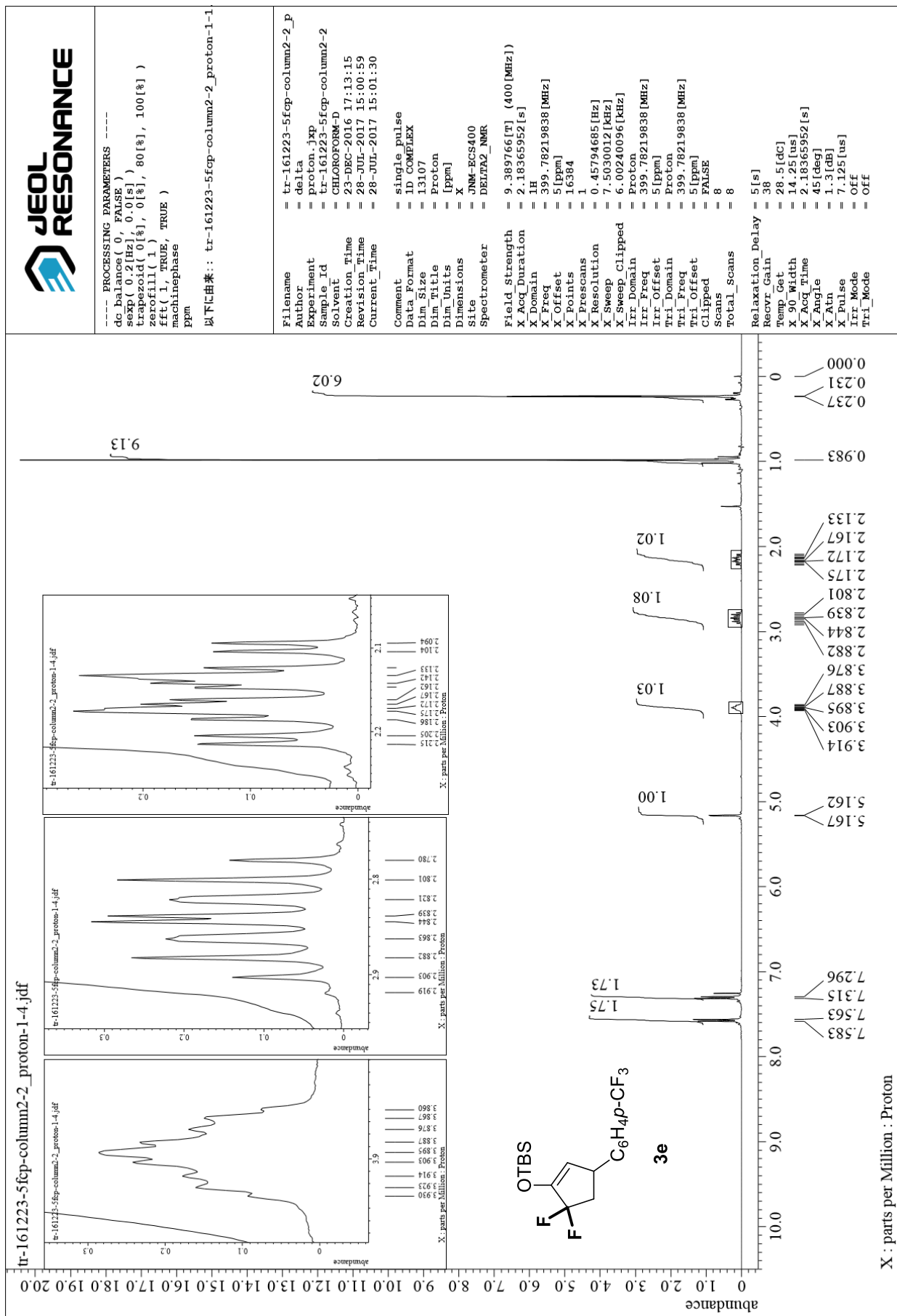
### Metal-free synthesis of $\alpha,\alpha$ -difluorocyclopentanone derivatives via regioselective difluorocyclopropanation/VCP rearrangement of silyl dienol ethers

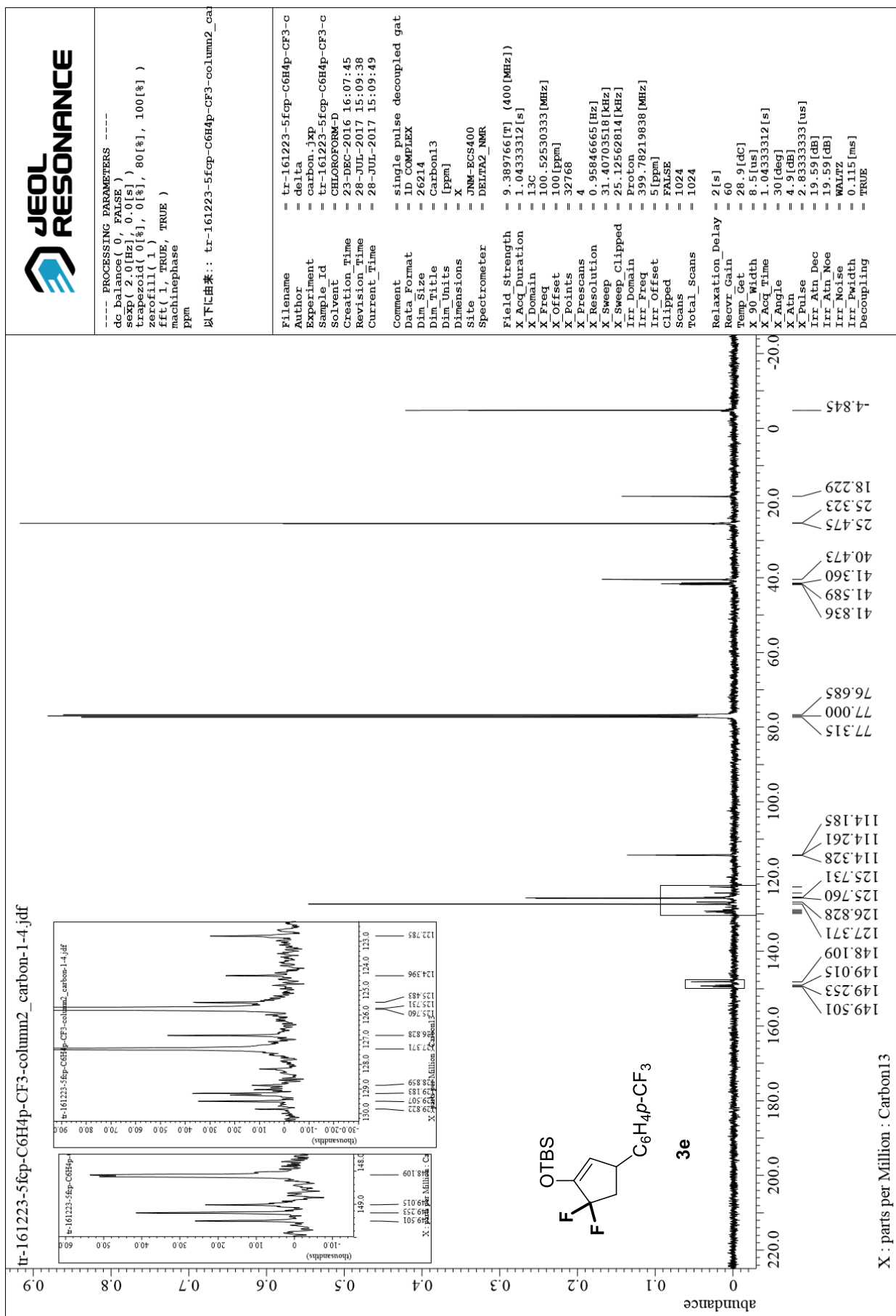
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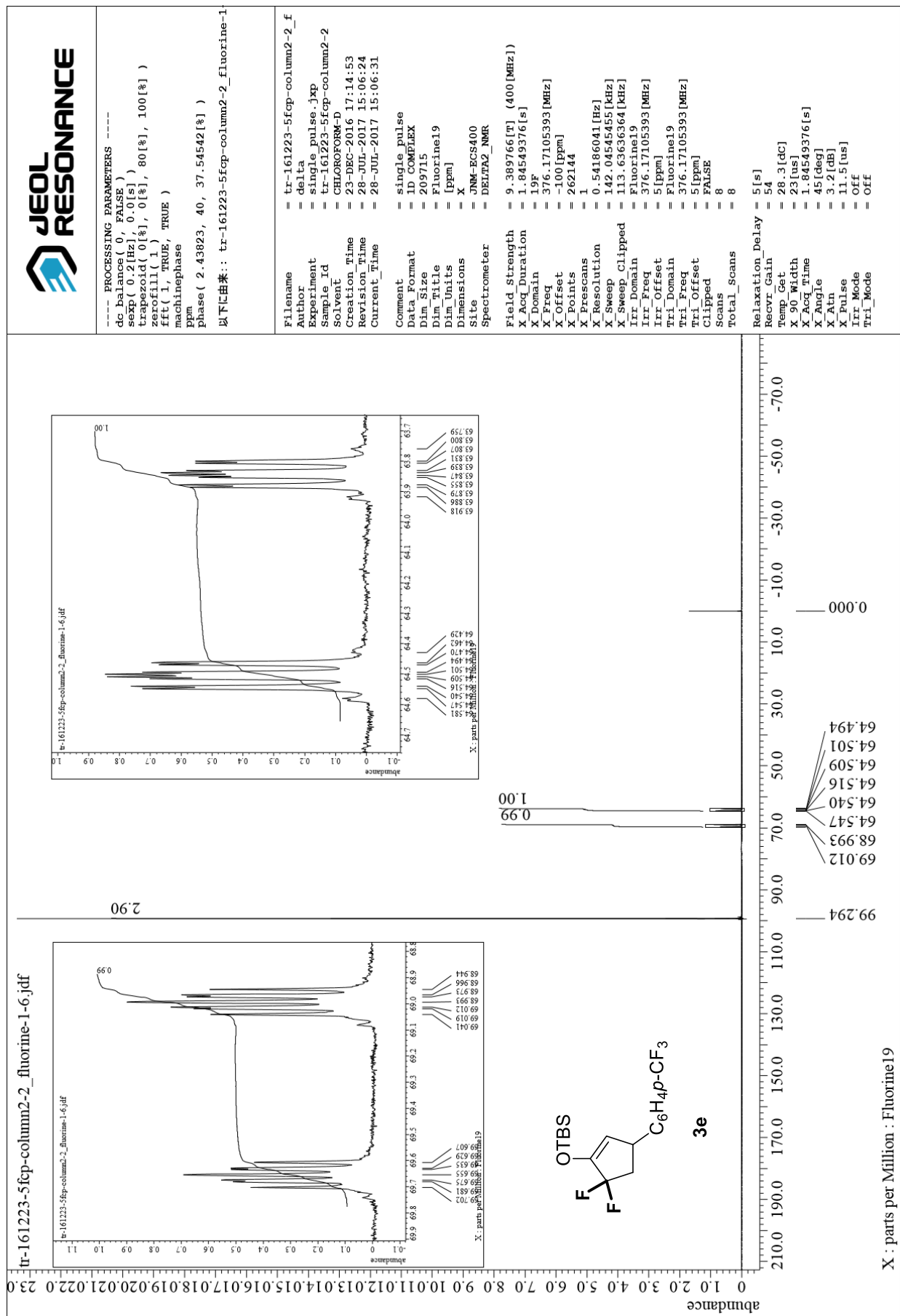
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<sup>1</sup>H NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**)Figure S1. <sup>1</sup>H NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**).

<sup>13</sup>C NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**)Figure S2. <sup>13</sup>C NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**).

<sup>19</sup>F NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**)Figure S3. <sup>19</sup>F NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**).

<sup>1</sup>H NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**)

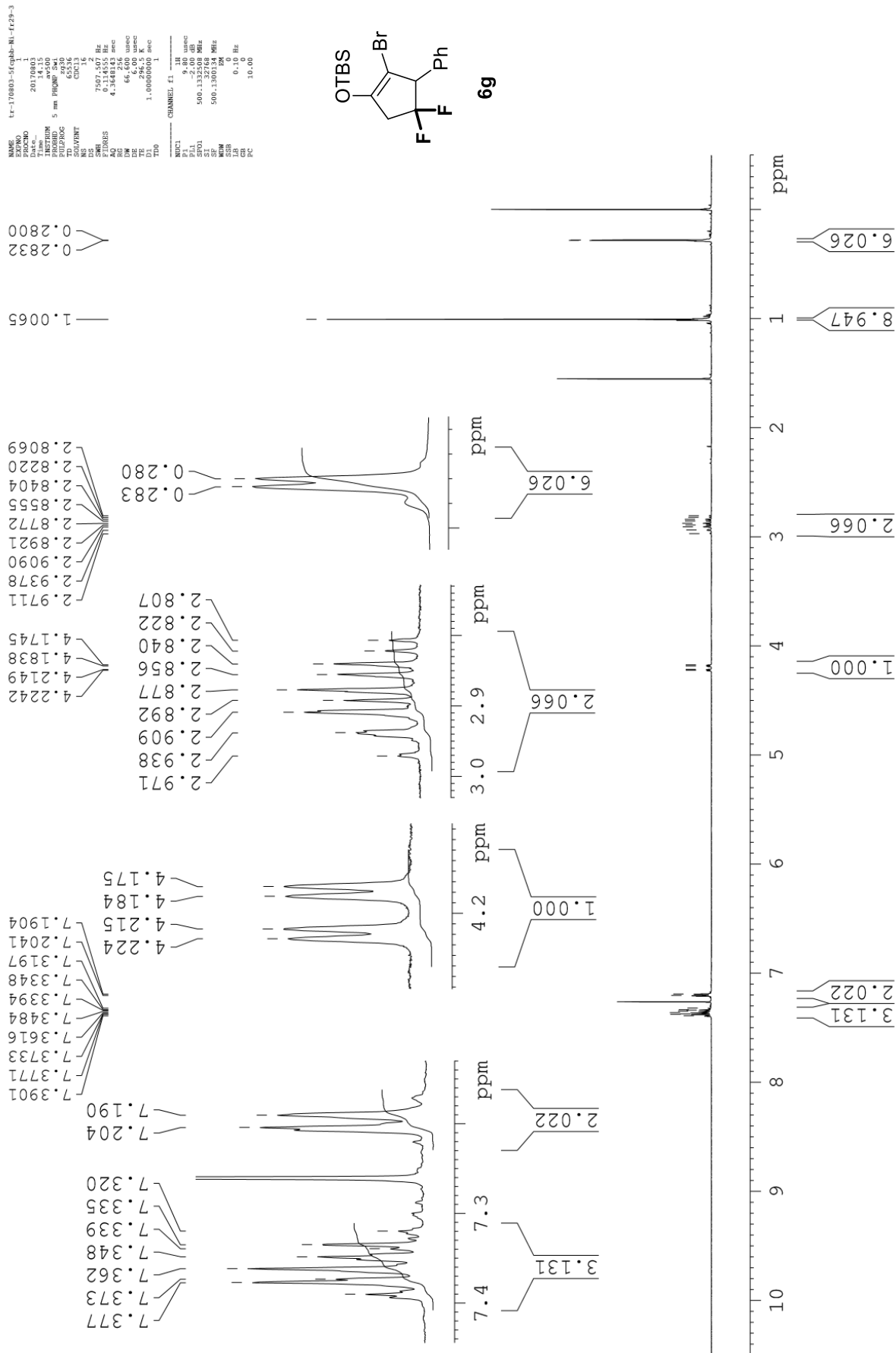
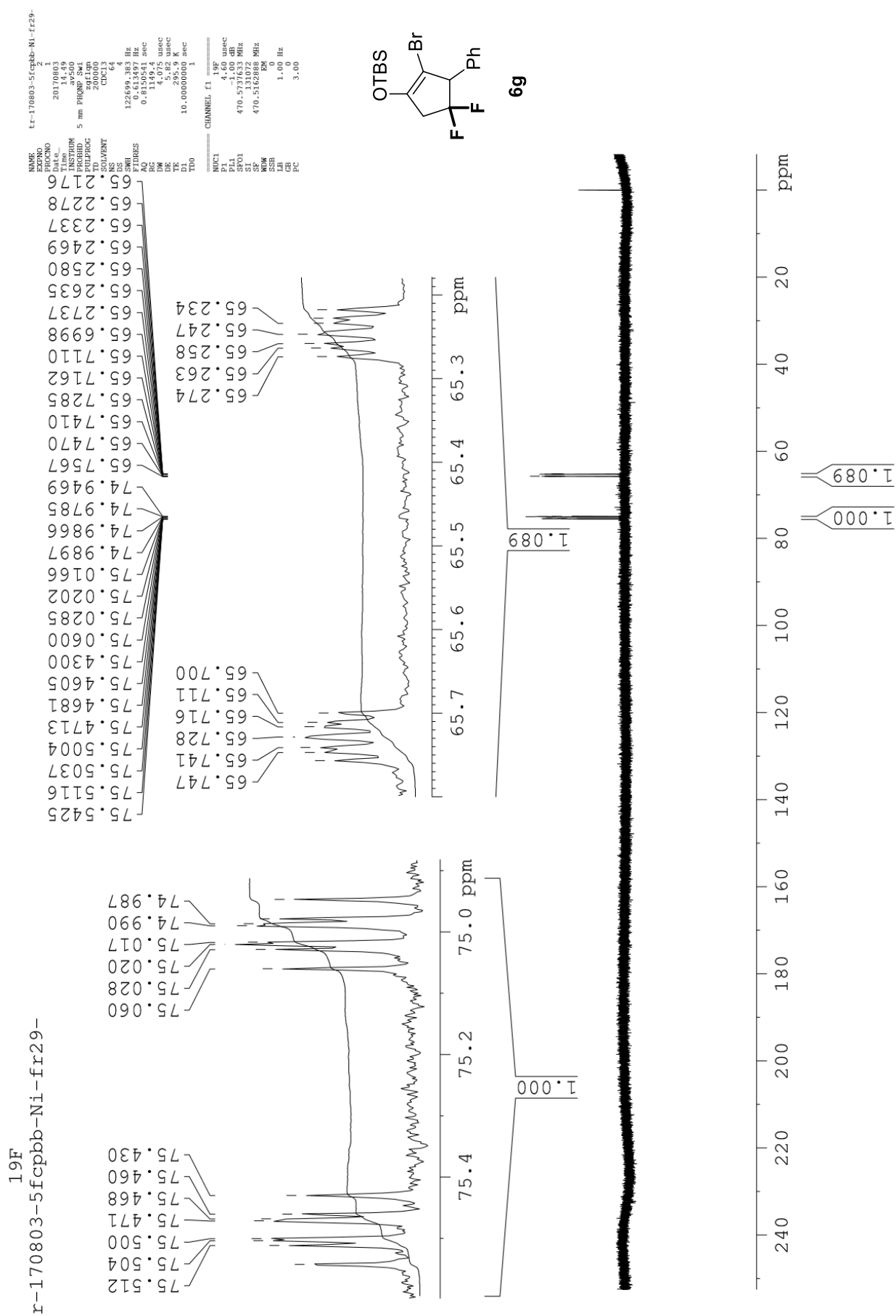


Figure S4. <sup>1</sup>H NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**).



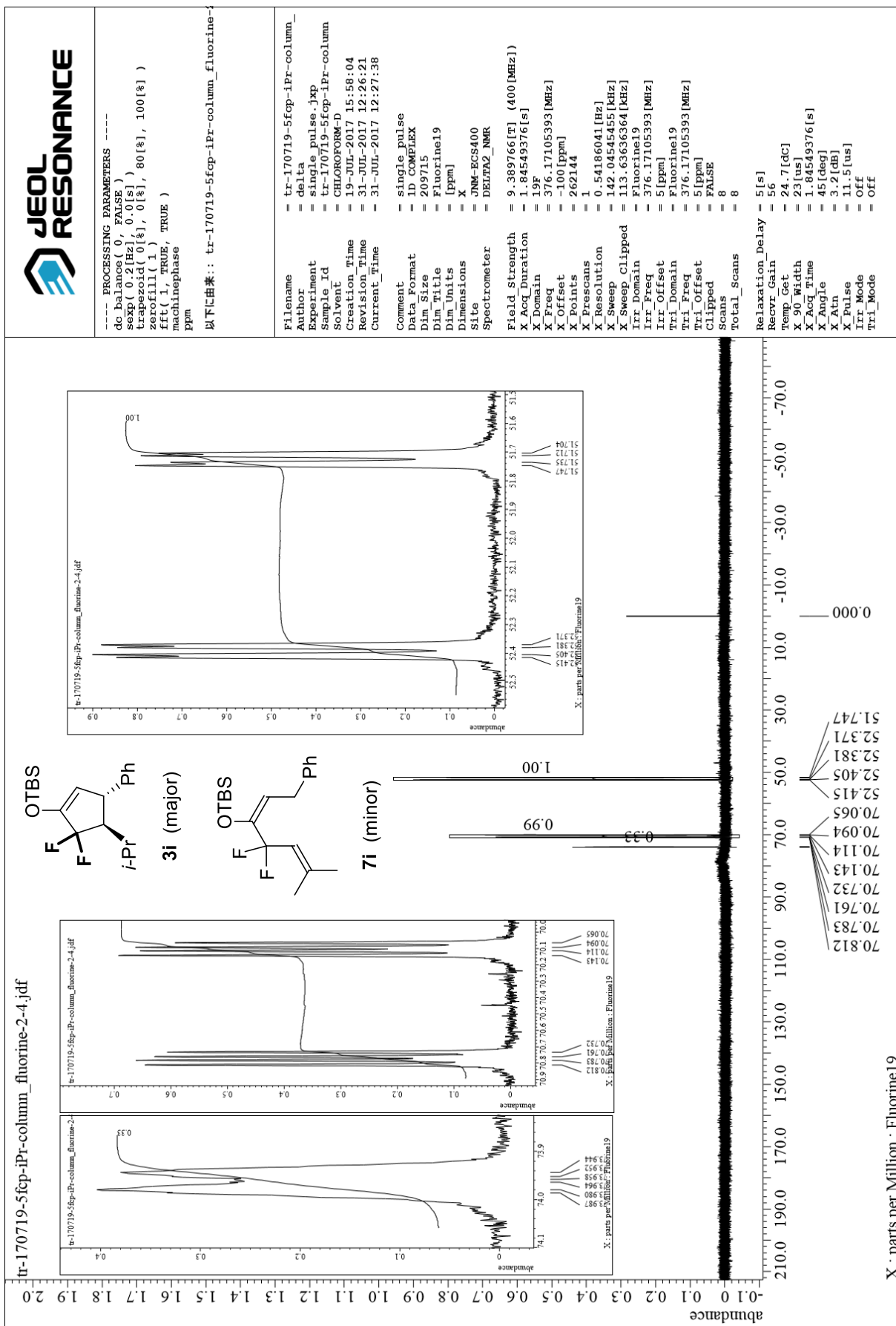
$^{19}\text{F}$  NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**)Figure S6.  $^{19}\text{F}$  NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**).



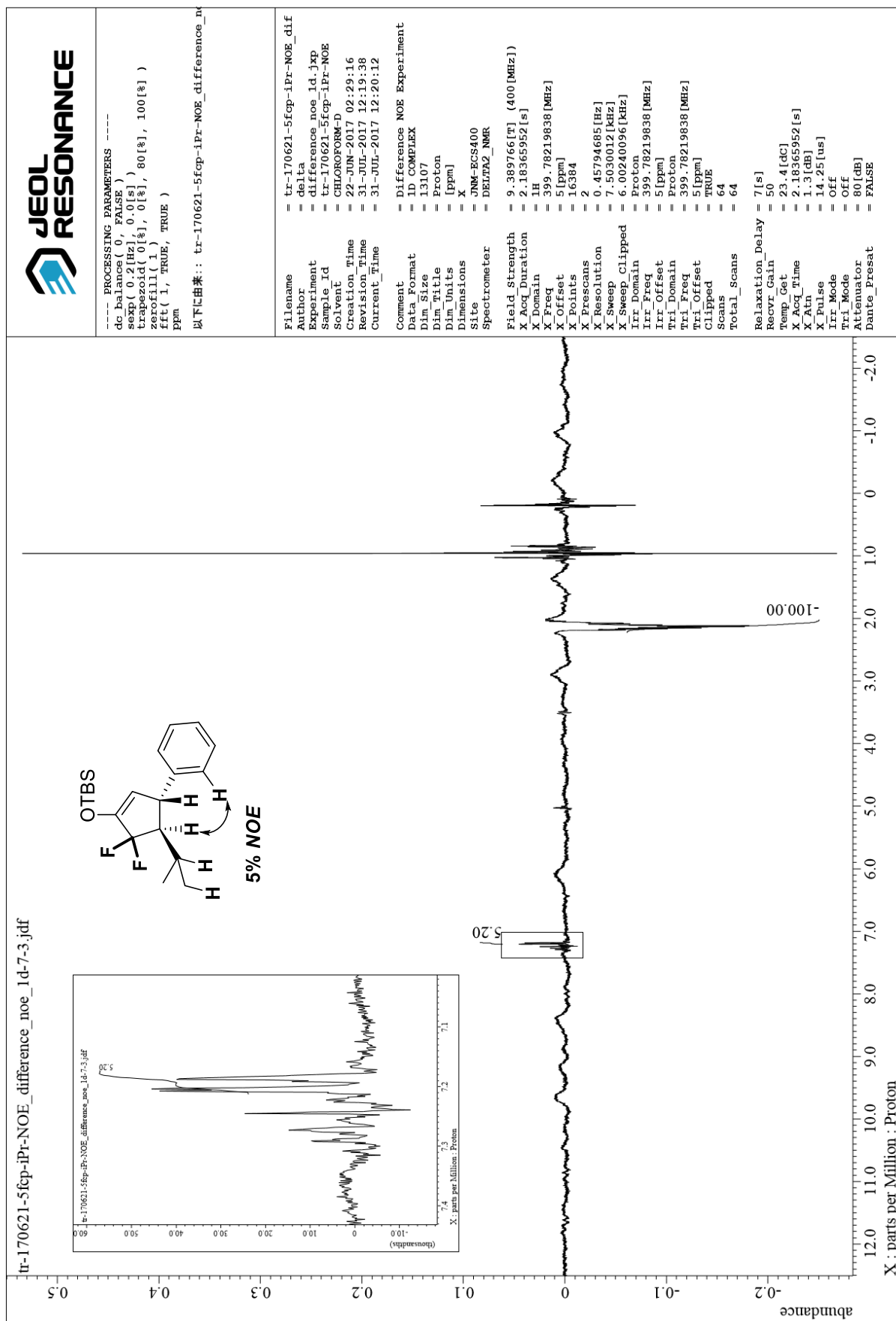




$^{19}\text{F}$  NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-isopropyl-4-phenylcyclopent-1-ene (**3i**) and 3-[*tert*-Butyl(dimethyl)silyloxy]-4,4-difluoro-6-methyl-1-phenylhepta-2,5-diene (**7i**)



**Figure S9.**  $^{19}\text{F}$  NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-isopropyl-4-phenylcyclopent-1-ene (**3i**) and 3-[*tert*-Butyl(dimethyl)silyloxy]-4,4-difluoro-6-methyl-1-phenylhepta-2,5-diene (**7i**).

NOE spectrum I of 5,5-difluorocyclopent-1-en-1-yl silyl ether **3i**Figure S10. NOE spectrum I of 5,5-difluorocyclopent-1-en-1-yl silyl ether **3i**.

NOE spectrum II of 5,5-difluorocyclopent-1-en-1-yl silyl ether **3i**

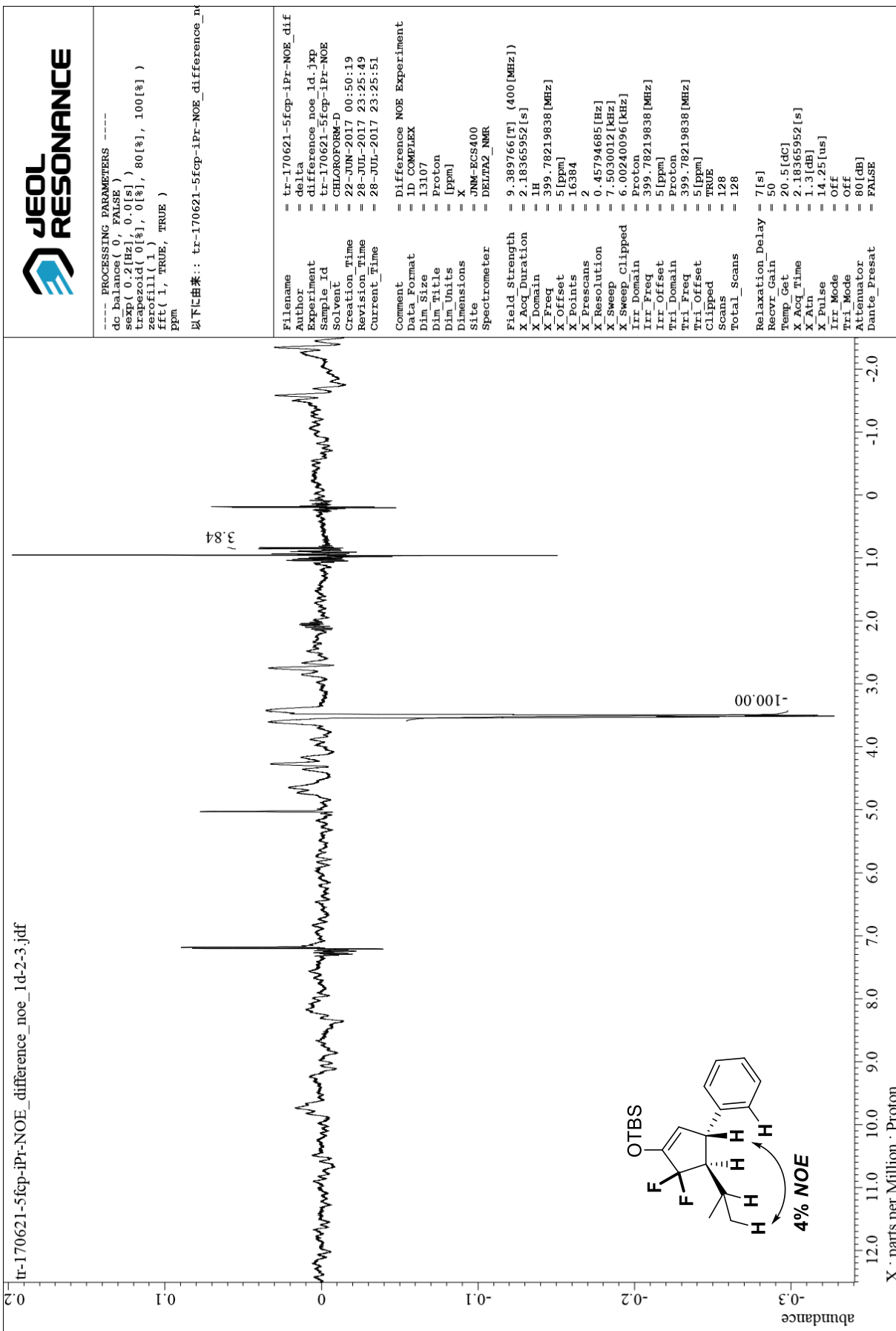


Figure S11. NOE spectrum II of 5,5-difluorocyclopent-1-en-1-yl silyl ether **3i**.

$^1\text{H}$  NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**)

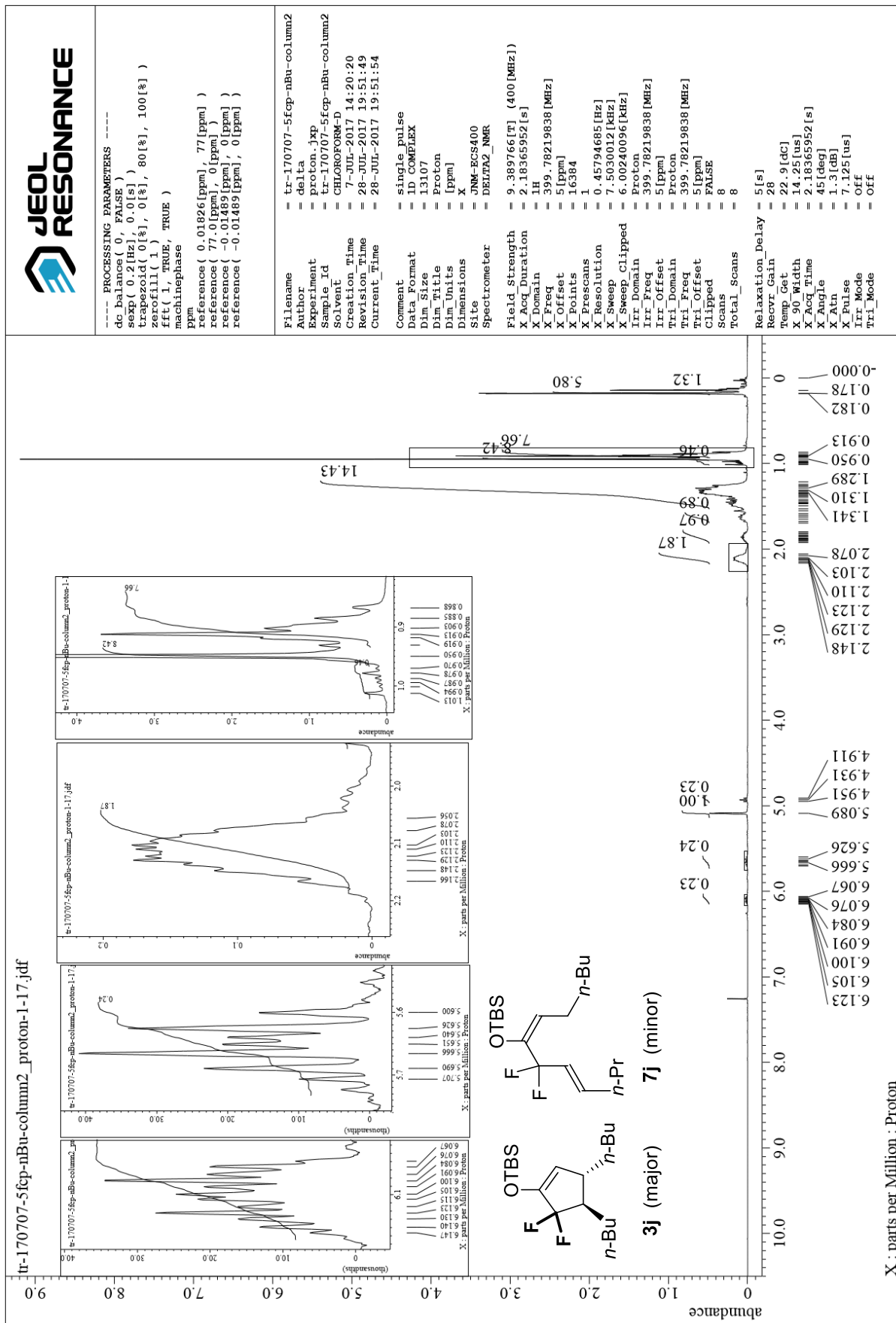
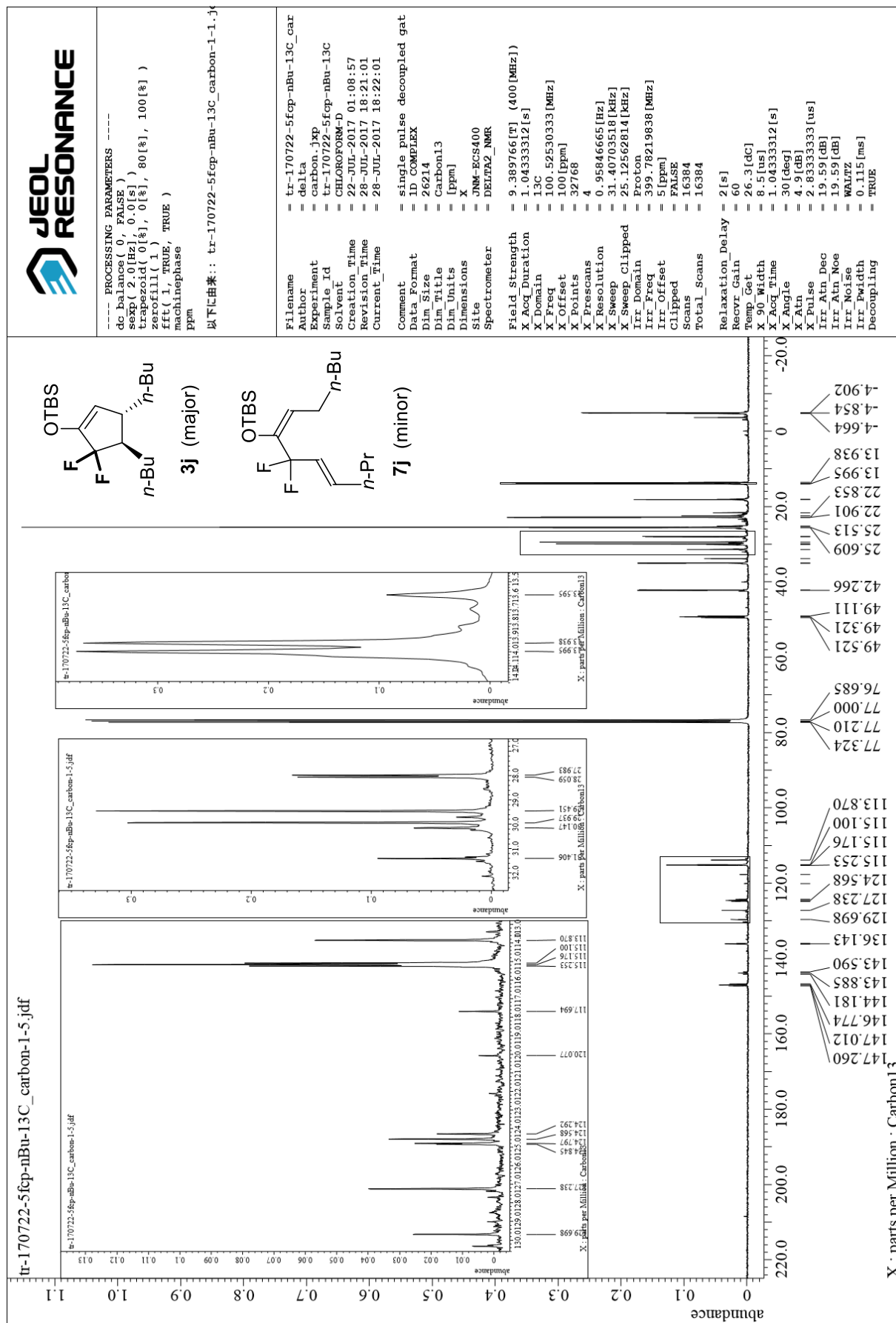


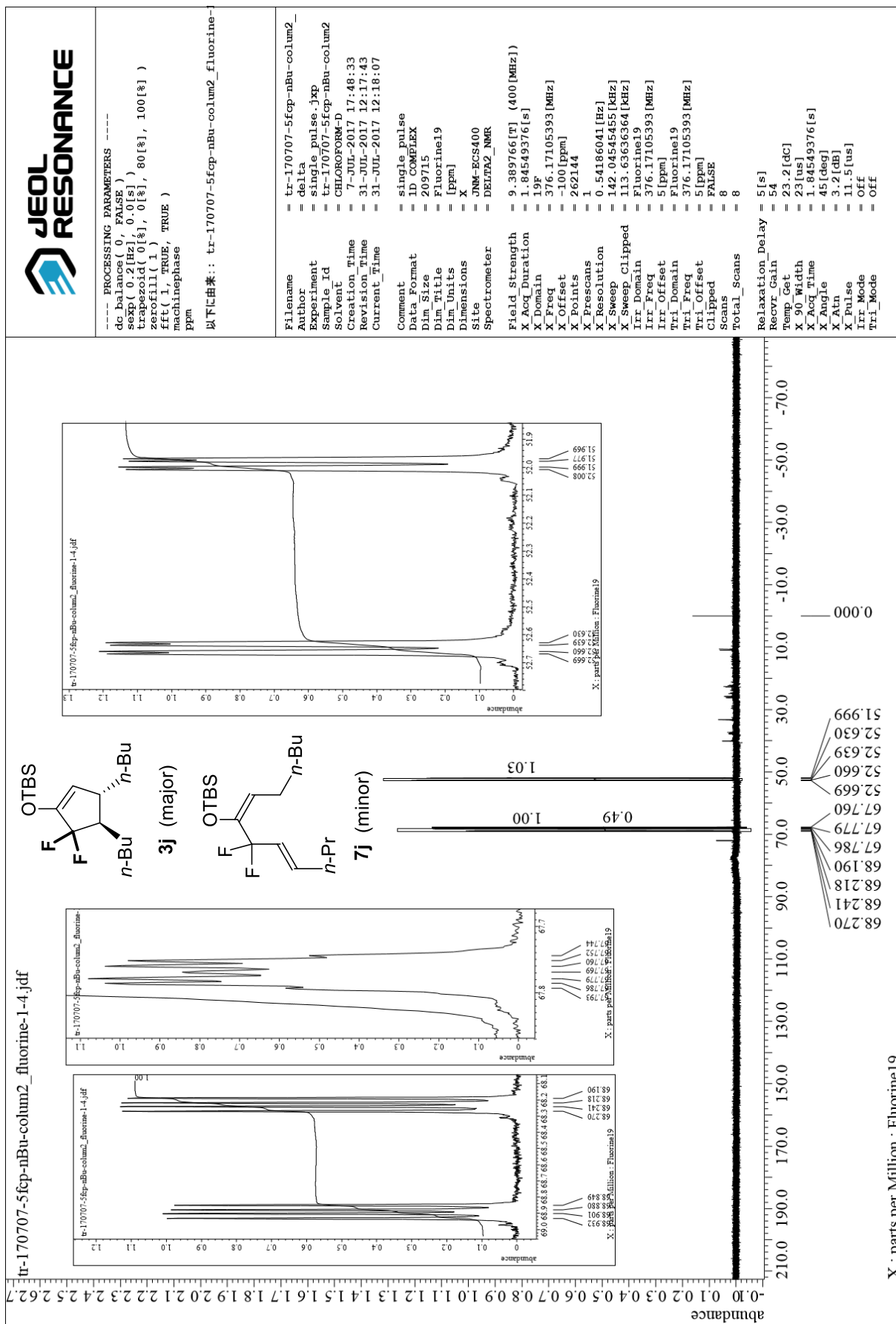
Figure S12.  $^1\text{H}$  NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**).

<sup>13</sup>C NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**)



**Figure S13.** <sup>13</sup>C NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**).

$^{19}\text{F}$  NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**)



**Figure S14.**  $^{19}\text{F}$  NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**).