

Supplementary Material

Metal-free synthesis of α,α -difluorocyclopentanone derivatives via regioselective difluorocyclopropanation/VCP rearrangement of silyl dienol ethers

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¹H NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**)

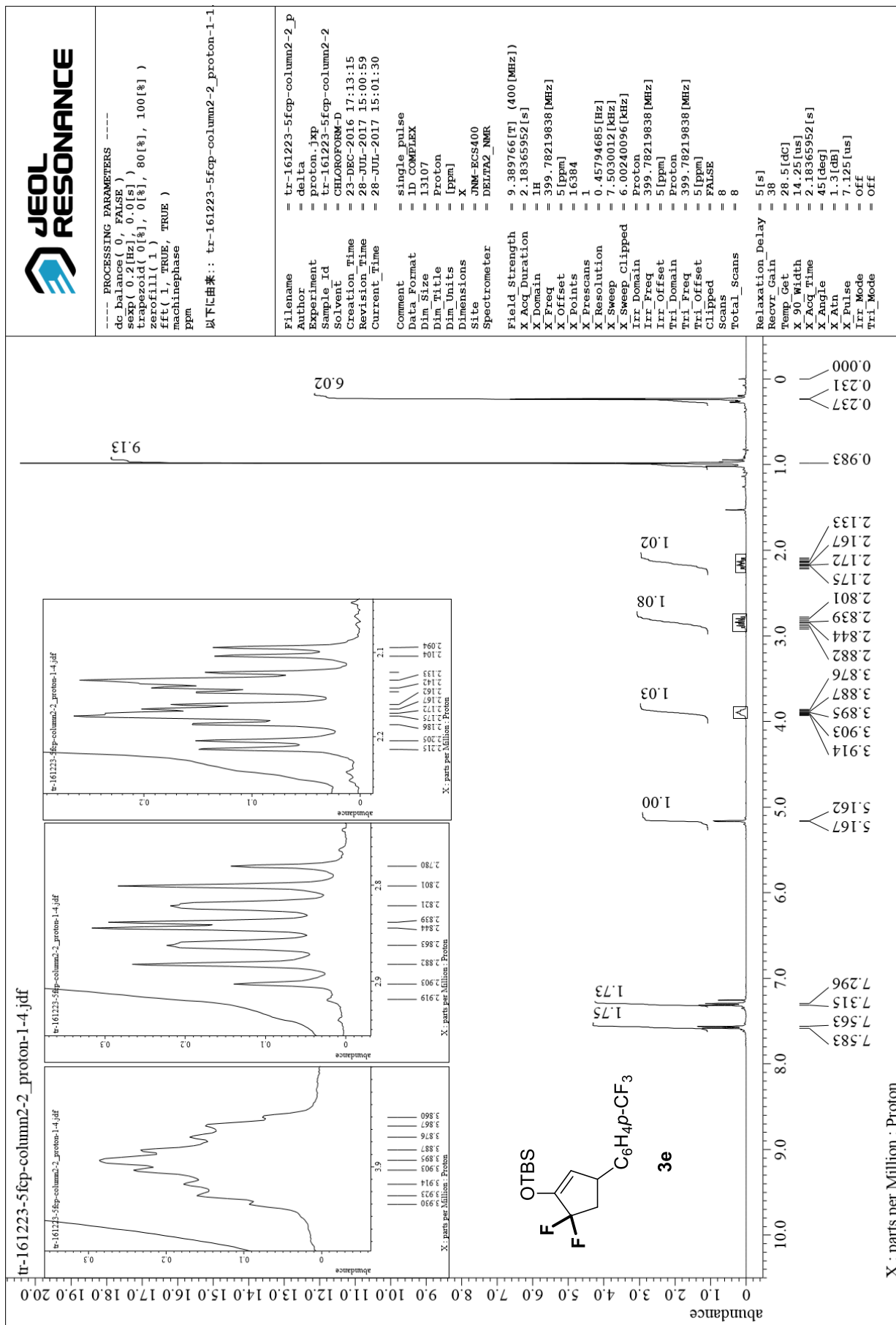
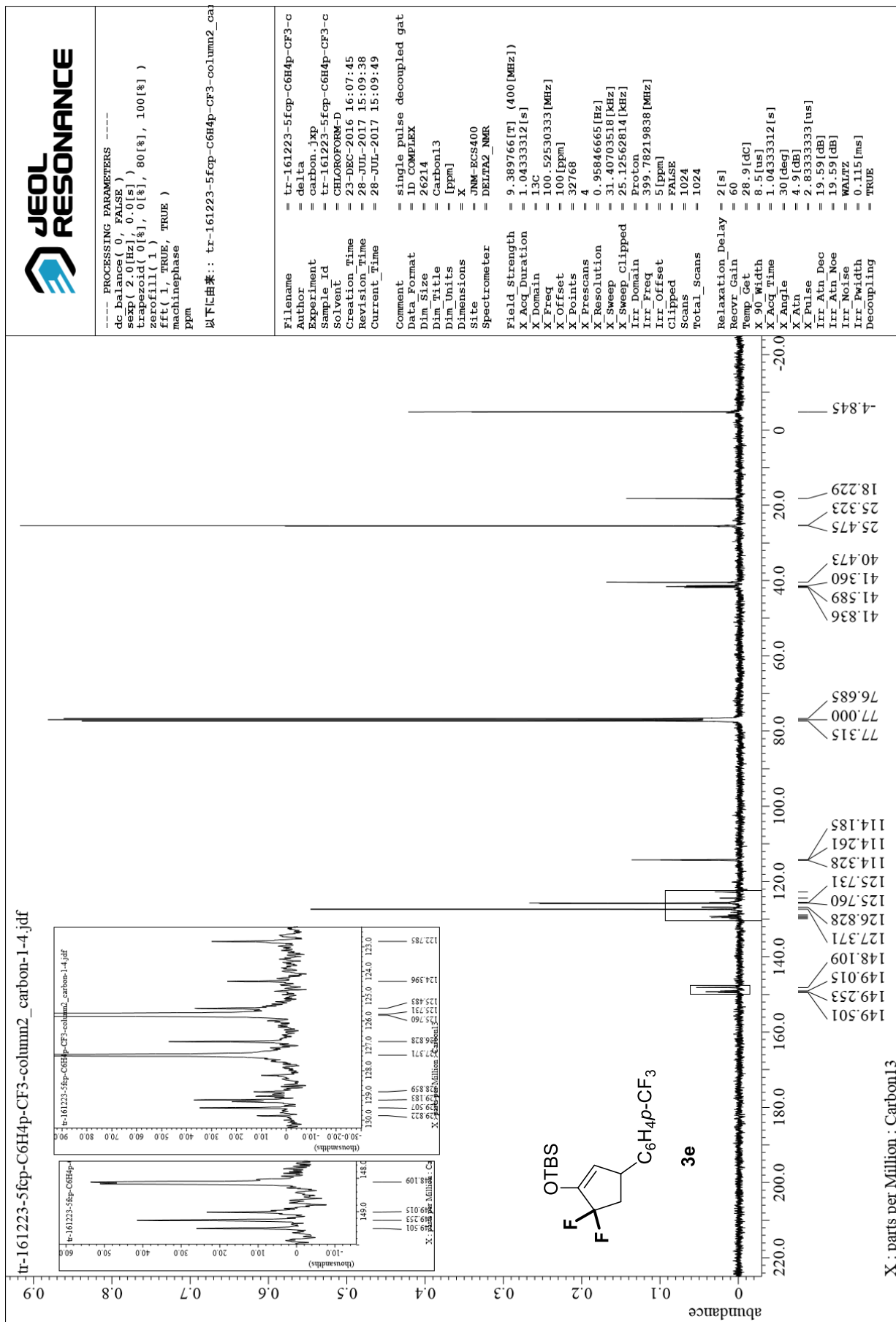


Figure S1. ¹H NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**).

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

¹⁹F NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**)

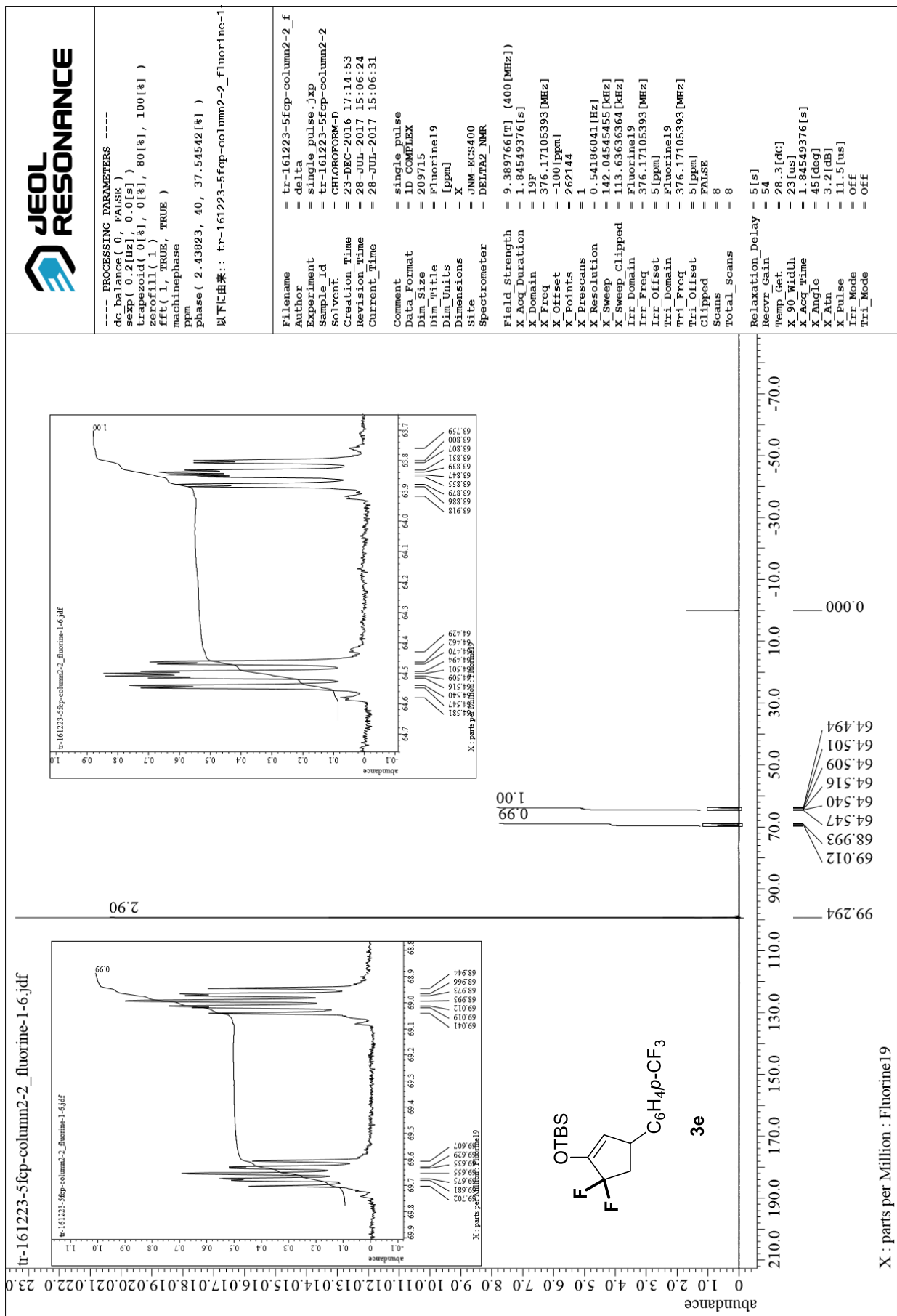


Figure S3. ¹⁹F NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-(4-trifluoromethylphenyl)cyclopent-1-ene (**3e**).

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

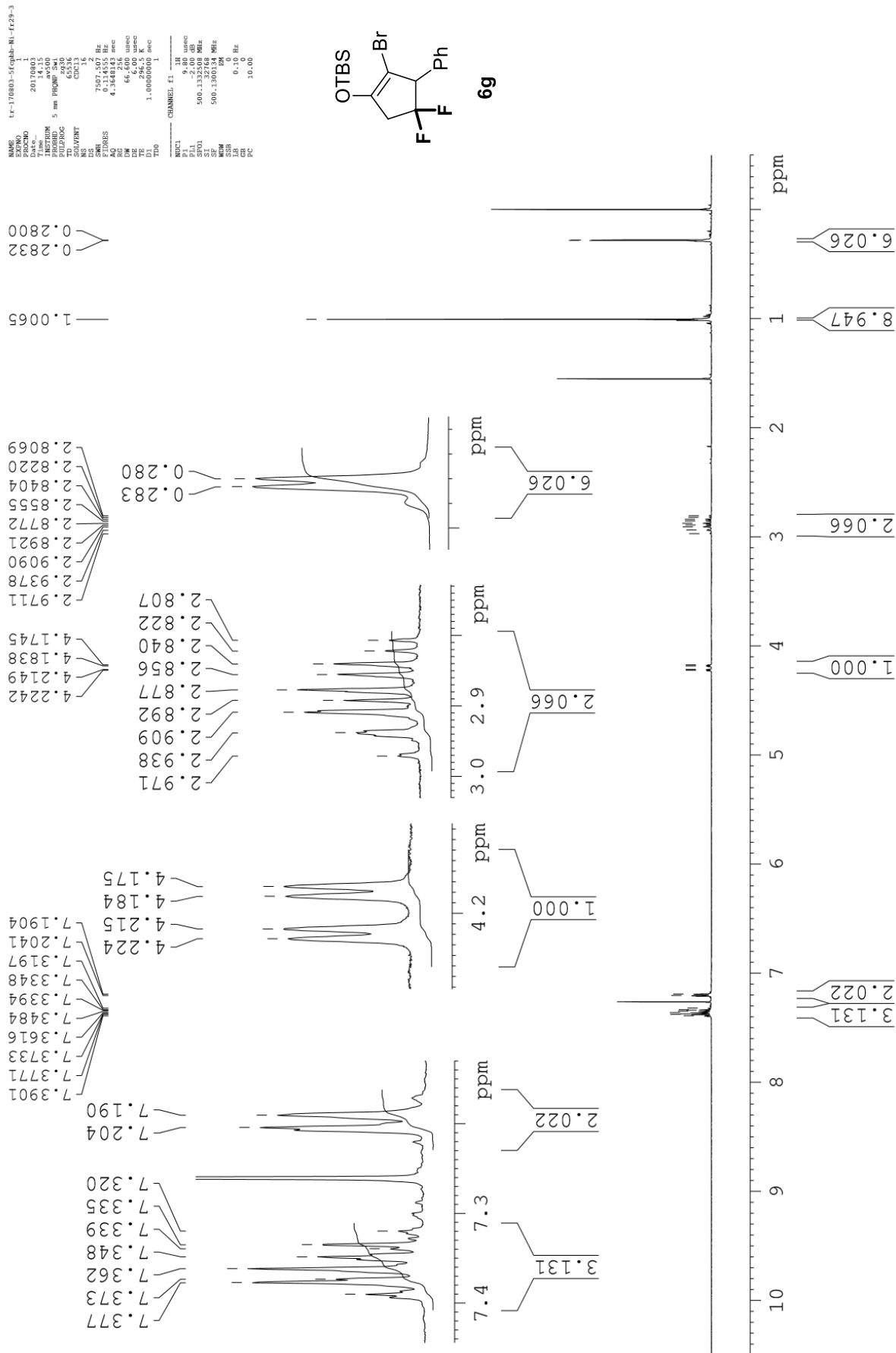
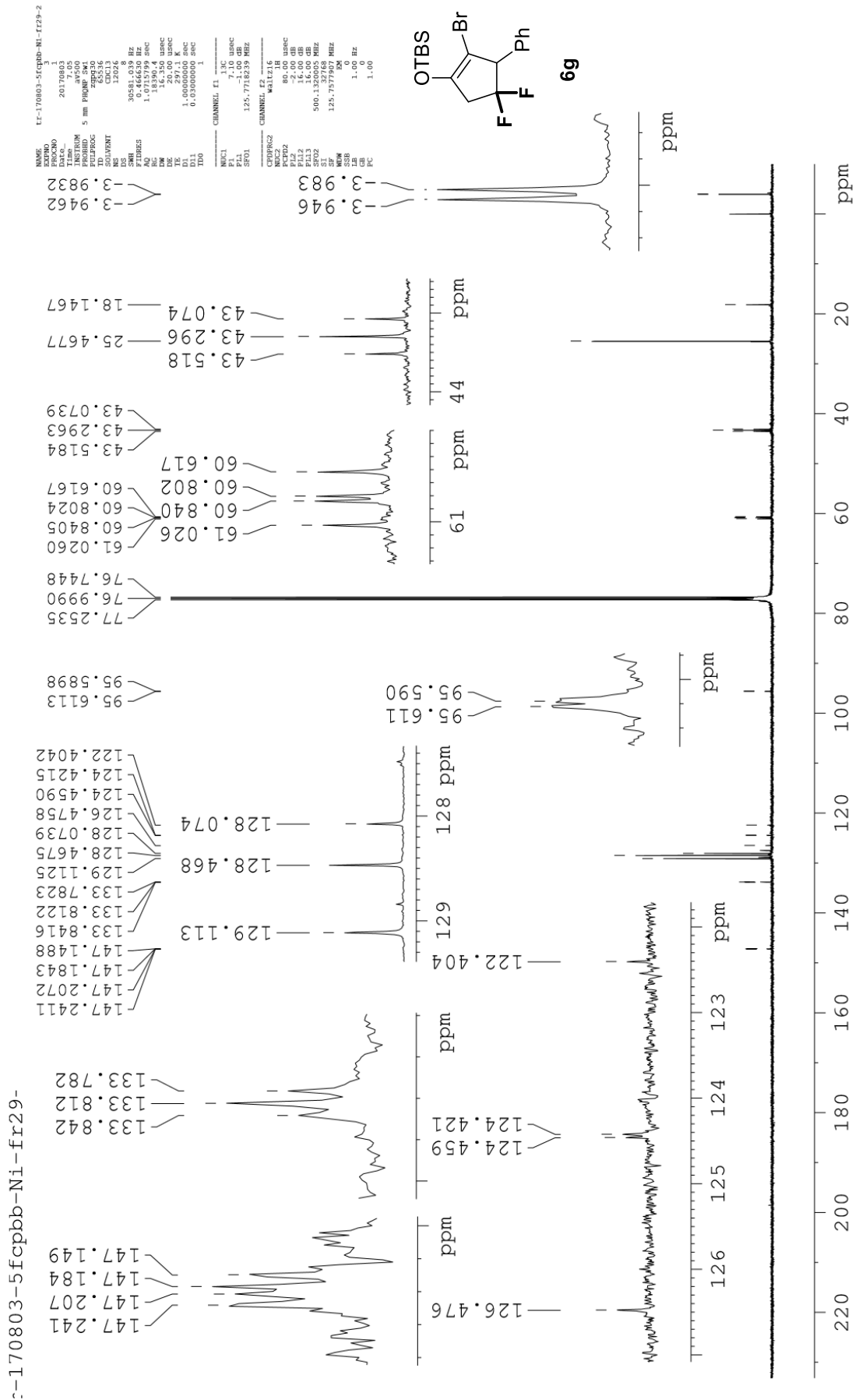
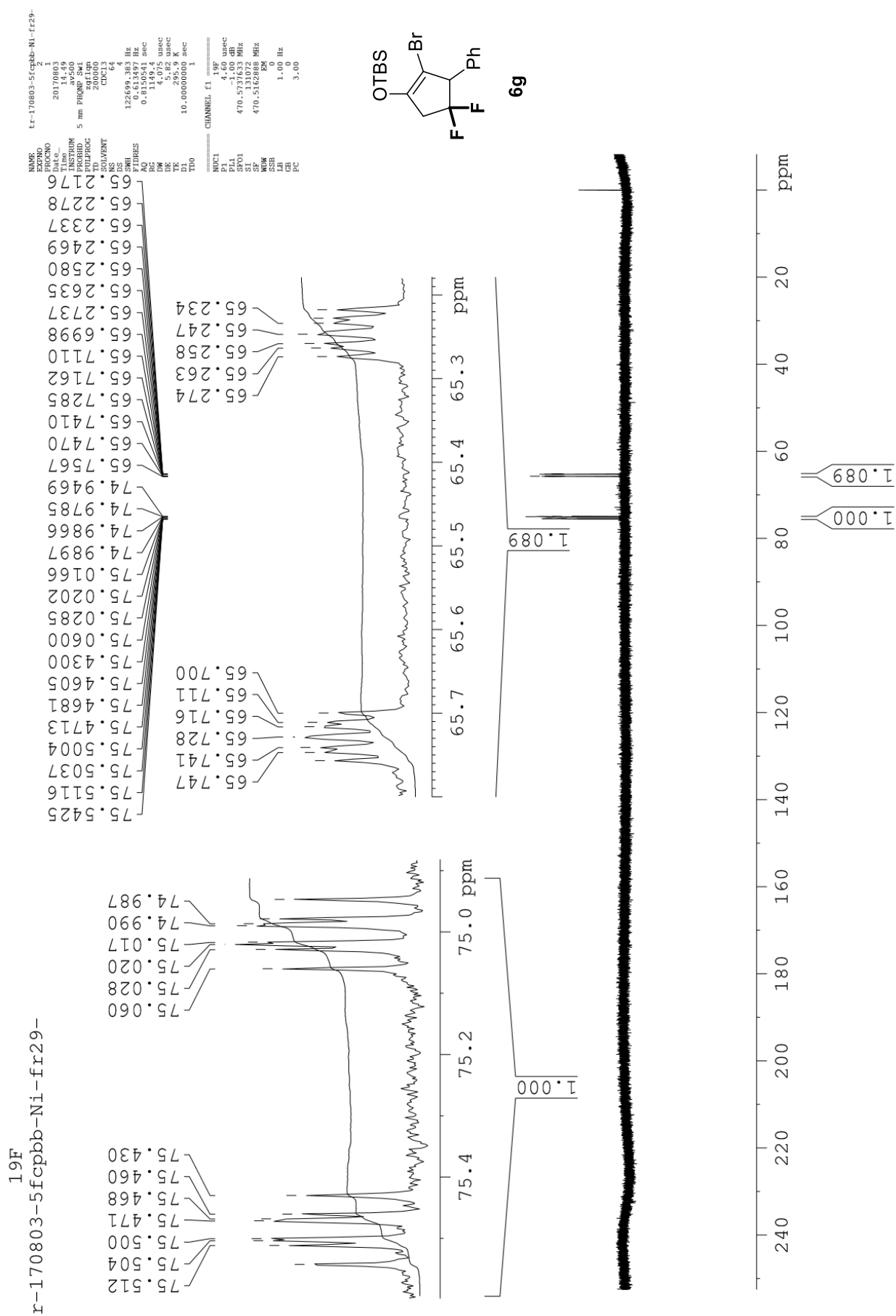


Figure S4. ¹H NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**).

^{13}C NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**)Figure S5. ^{13}C NMR of 2-Bromo-1-[*tert*-butyl(dimethyl)silyloxy]-4,4-difluoro-3-phenylcyclopent-1-ene (**6g**).

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

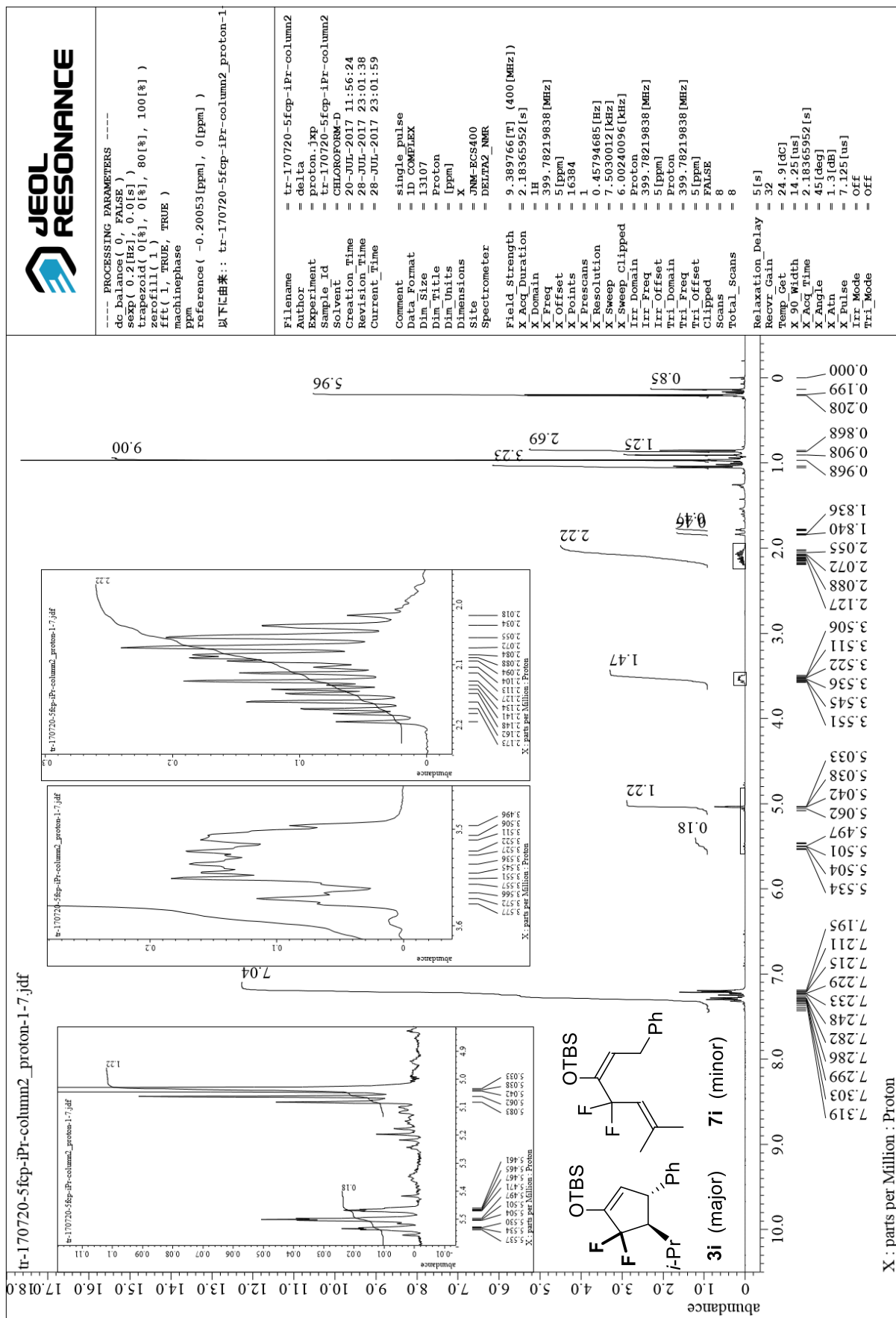
¹H NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-isopropyl-4-phenylcyclopent-1-ene (**3i**) and 3-[*tert*-Butyl(dimethyl)silyloxy]-4,4-difluoro-6-methyl-1-phenylhepta-2,5-diene (**7i**)

Figure S7. ¹H 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**).

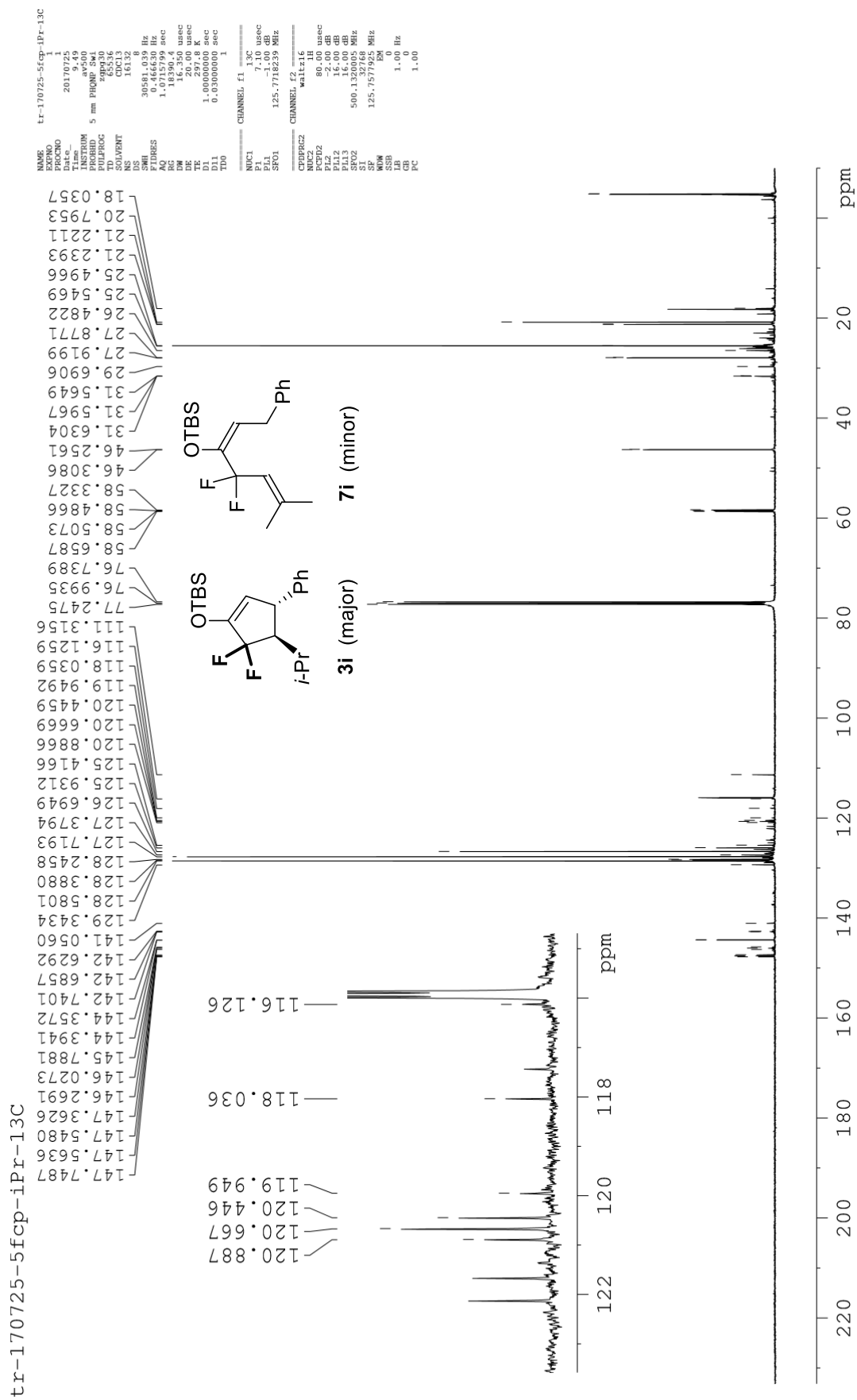
¹³C NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-isopropyl-4-phenylcyclopent-1-ene (**3i**) and 3-[*tert*-Butyl(dimethyl)silyloxy]-4,4-difluoro-6-methyl-1-phenylhepta-2,5-diene (**7i**)

Figure S8. ¹³C 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**).

^{19}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**)

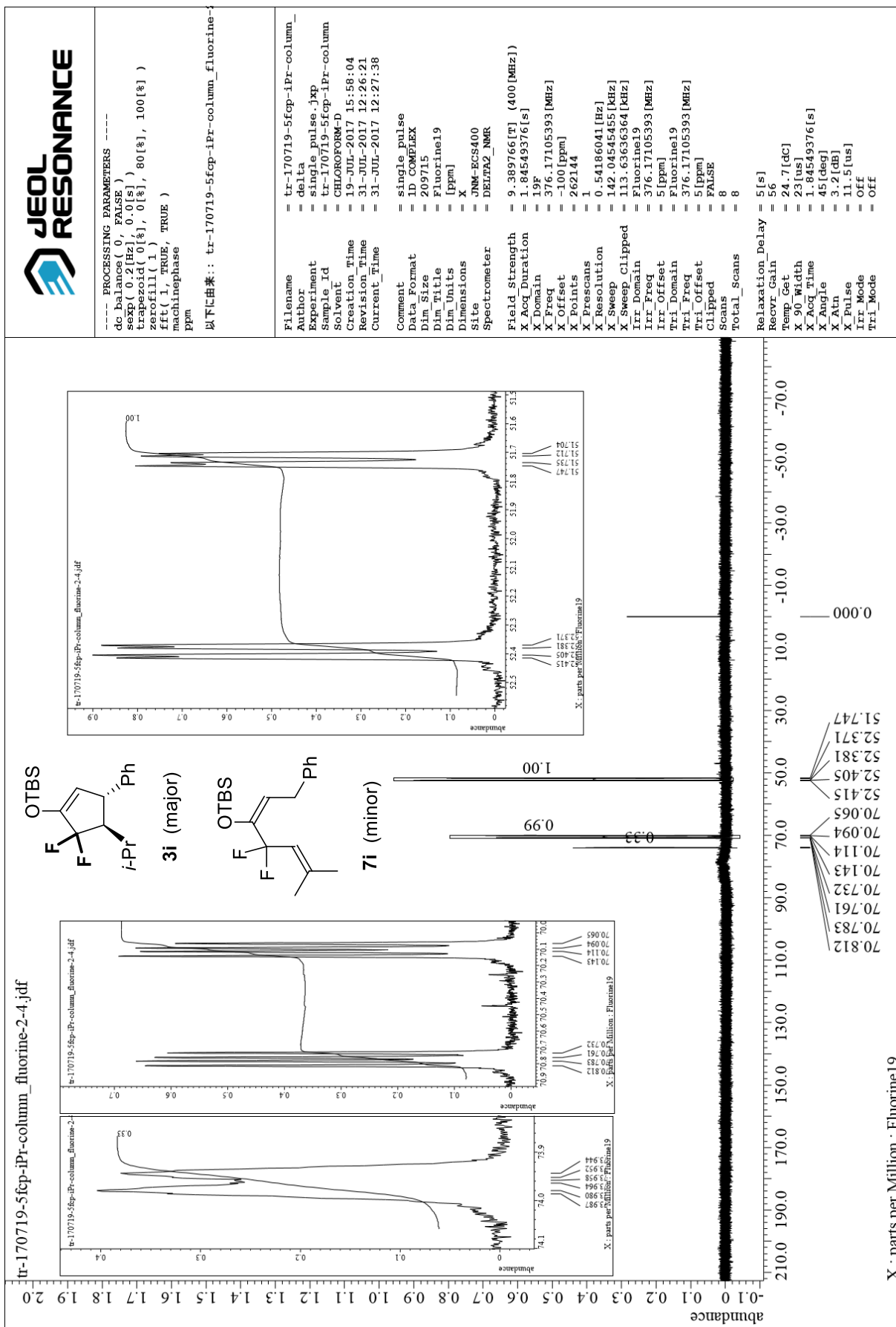
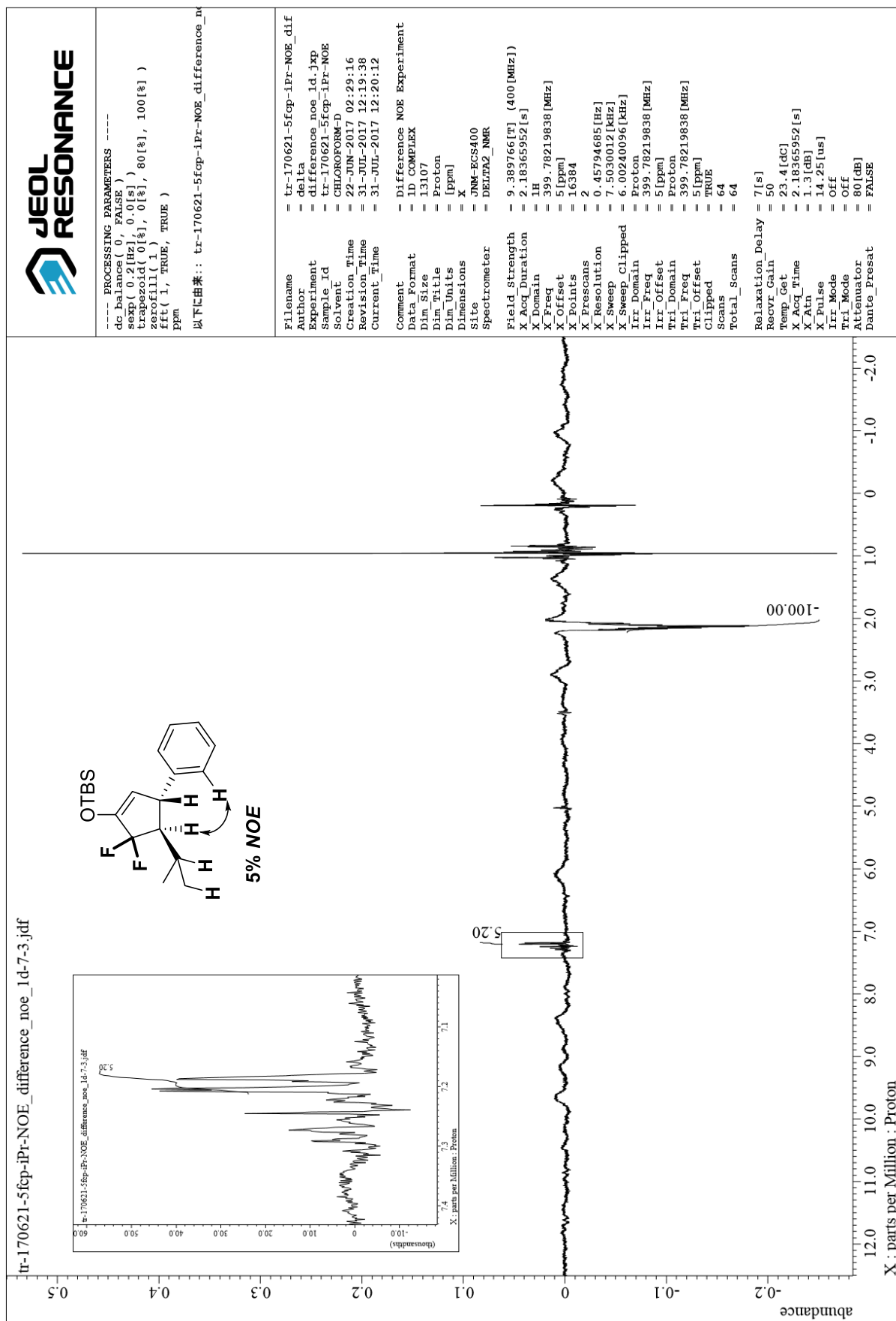


Figure S9. ^{19}F NMR of 1-[*tert*-Butyl(dimethyl)silyloxy]-5,5-difluoro-3-isopropyl-4-phenylcyclopent-1-ene (**3i**) and 3-[*tert*-Butyl(dimethyl)silyloxy]-4,4-difluoro-6-methyl-1-phenylhepta-2,5-diene (**7i**).

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

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

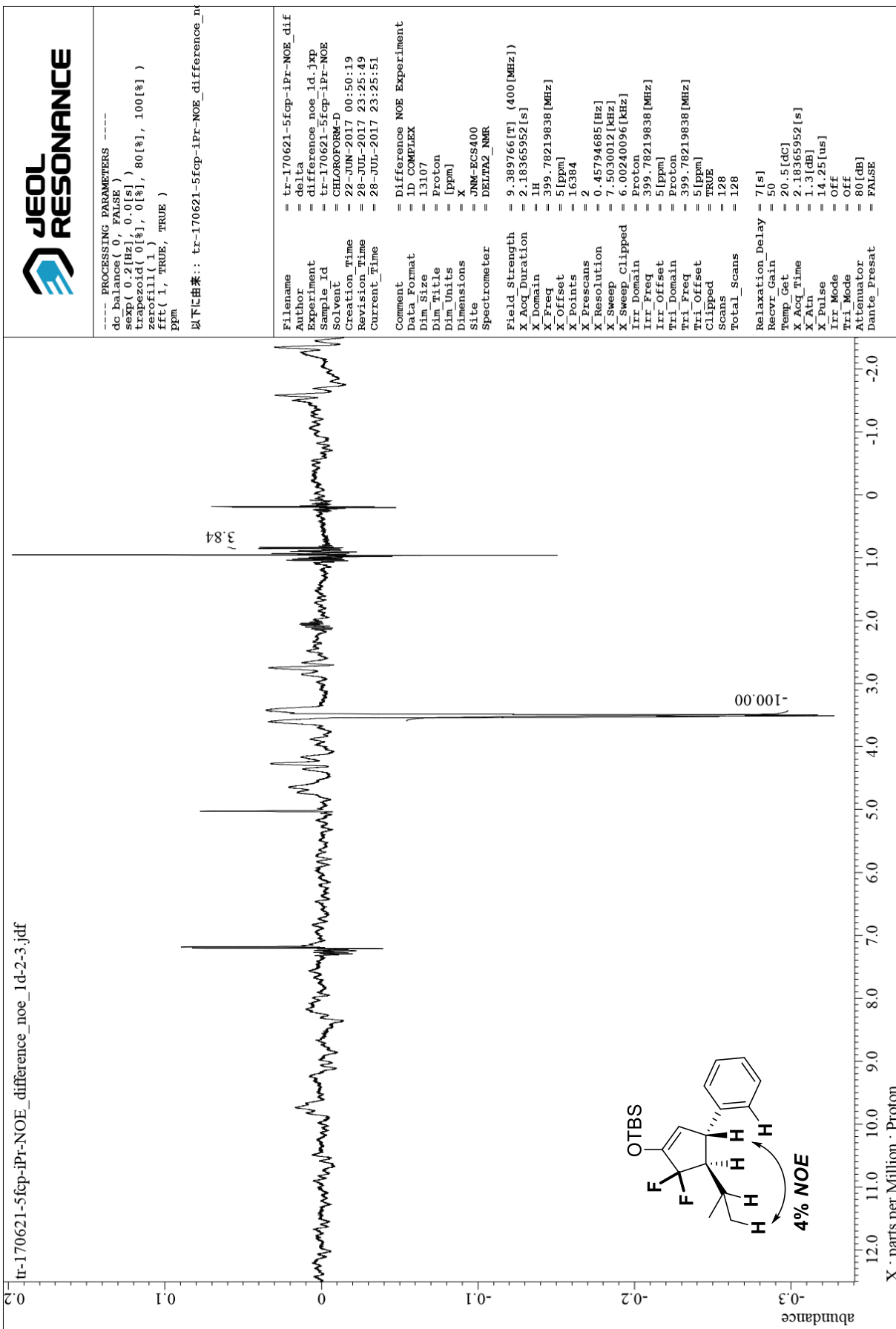


Figure S11. NOE spectrum II of 5,5-difluorocyclopent-1-en-1-yl silyl ether **3i**.

^1H 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**)

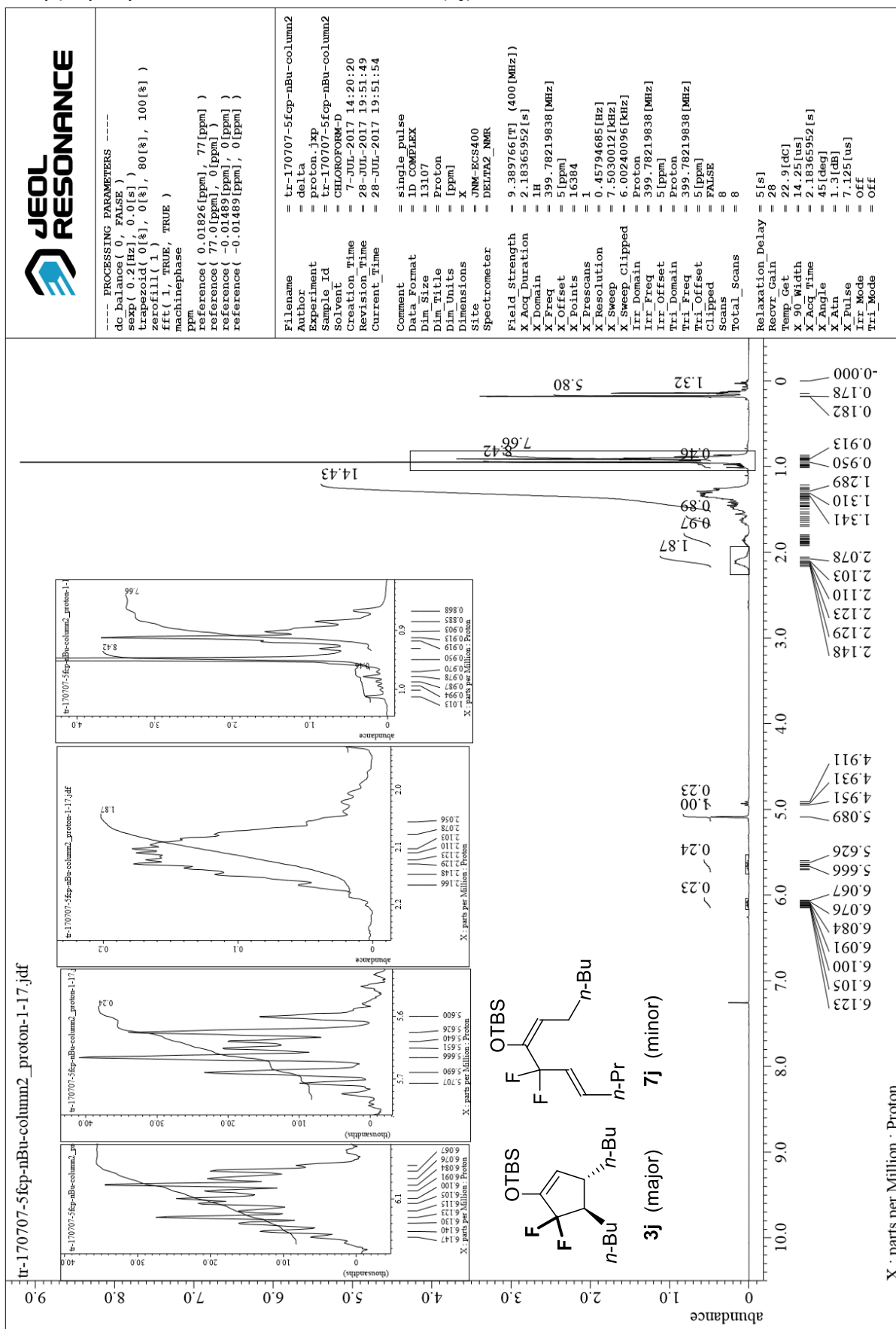


Figure S12. ^1H NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**).

¹³C 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**)

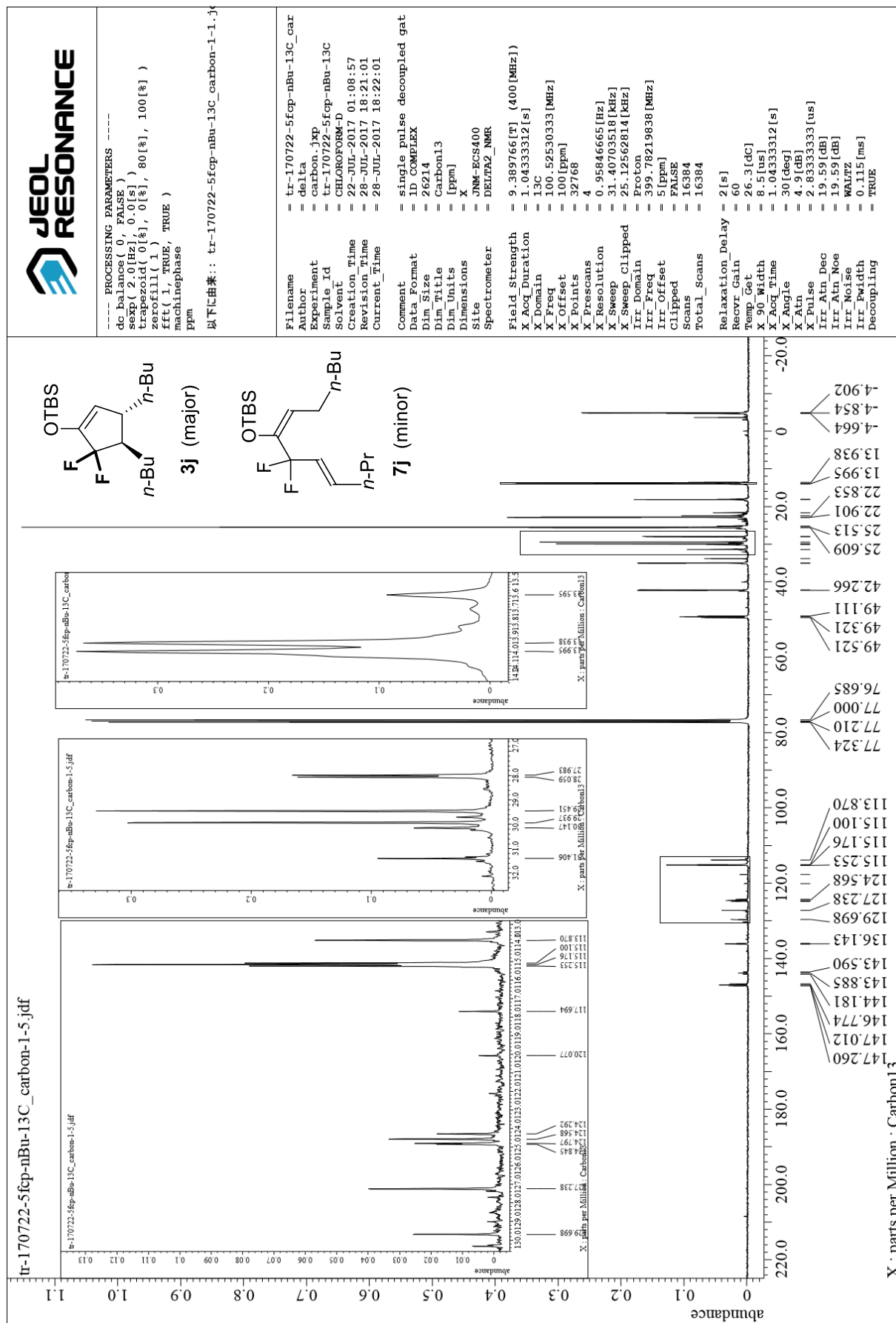


Figure S13. ¹³C NMR of 3,4-Dibutyl-1-[*tert*-butyl(dimethyl)silyloxy]-5,5-difluorocyclopent-1-ene (**3j**) and 7-[*tert*-Butyl(dimethyl)silyloxy]-6,6-difluorotrideca-4,7-diene (**7j**).

