SYNTHESIS AND APPLICATION OF
TETRAFLUOROETHYLENATED ACETYLENE DERIVATIVES

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Our recent effort has been devoted to the synthesis of internal alkynes having a CF₃ group on the sp-carbon because they have been proved to be promising synthetic intermediates for versatile organofluorine compounds via highly stereoselective hydrometallation, carbometallation, bismetallation involving transition metal.¹ In the field of organofluorine chemistry, subsequently, development of new internal alkynes bearing perfluoroalkylene moiety, e.g. CF₂CF₂, at the sp-carbon have become occupied a central position on the synthetic interest due to the potent synthetic diversity to novel fluorine-containing optoelectronic materials as well as pharmaceuticals.

In our group, recently, intensive studies toward the effective synthesis of novel CF₂CF₂-containing organic molecules have been carried out, and we successfully revealed several practical synthetic protocols for such tetrafluoroethylenated compounds so far.²,³ However, no attention has been paid to the internal alkynes with a CF₂CF₂ fragment at the sp-carbon although they can be promising synthetic intermediates to synthesize various organofluorine compounds. Therefore, our research subjects were expanded to development and synthetic application of novel tetrafluoroethylenated alkynes.

Thus, bromination of commercially available 4-bromo-3,3,4,4-tetrafluorobuten-1-ene (1) gave the corresponding brominated 2, which was converted to the corresponding propargyl alcohol 3 in high yield after treating LHMDS, followed by benzaldehyde. On the other hand, treatment of 2 with NaOH took place nicely to provide the corresponding vinyl bromide 6, which was subjected to Pd(0)-catalyzed Negishi cross-coupling reaction, leading to the corresponding phenylacetylene derivative 7 bearing CF₂CF₂ unit. As a typical synthetic application, thus obtained internal alkynes 3 and 7 were heated with 2,3-dimethylbuta-1,4-diene in xylene at 150 °C for 24 h in a sealed tube. As a result, the Diels-Alder reaction proceeded very well to give the corresponding cycloadduct 4 and 8 in high yields. Subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) successfully provided the corresponding aromatic compounds with a CF₂CF₂ moiety. In this presentation, we would report the detail of the synthesis of novel tetrafluoroethylenated acetylene derivatives and their synthetic applications.

**Scheme 1.** Preparation of Novel Tetrafluoroethylenated Acetylene Derivatives and their Synthetic Application to CF₂CF₂-containing Aromatics

References
1) For review, see: T. Konno, Synlett 2014, 1350–1370.