Synthesis of Differently Fused Thienoacenes by Control of Halogen Dance

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Thienoacenes have received considerable attention as organic semiconductor materials. Since they possess divergent physical properties due to their differently fused cyclic skeletons, a method for synthesizing various thienoacenes has been strongly required. Herein, we report a synthetic method for the differently fused thienoacenes by controlling halogen dance of 2-bromobenzothiophene (1) that involves switching of the lithium atom at position 3 and the bromo group.

After deprotonation of benzothiophene 1 using LDA, the resulting β-thienyllithium 2 underwent halogen dance to result in exchange of the lithium atom and the bromo group. This α-thienyllithium 3 reacted with diphenyl disulfide to provide 4. The transient β-thienyllithium 2 was also trapped by in situ transmetalation using zinc chloride diamine complex, and the isomeric 5 was obtained in a similar manner. These sulfides were converted to the corresponding thienoacenes 6 and 7 by the palladium-catalyzed cyclization. We applied this method to thienothiophene 8, and the three possible constitutional isomers were regioselectively synthesized as the precursors of the thienoacenes.