SYNTHESIS OF TERT-BUTYL PENT-4-YN-1-YLCARBAMATE AND (2*Z*)-3-IODO-2-METHYLACRYLIC ACID COMPOUNDS AS THE STARTING MATERIALS FOR THE TOTAL SYNTHESIS OF PANDAMARINE

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ABSTRACT

The undergraduate thesis entitled "Synthesis of *tert*-butyl pent-4-yn-1-ylcarbamate and (2*Z*)-3-iodo-2-methylacrylic Acid Compounds as the Starting Materials for the Total Synthesis of Pandamarine" has been conducted. This research was aimed to synthesize the starting materials such as *tert*-butyl pent-4-yn-1-ylcarbamate compounds and (2*Z*)-3-iodo-2-methylacrylic acid compounds for the synthesis of Pandamarine compound through a series of reaction that involved the utilization of Grignard reagent and copper(I) catalyst for the carbometallation of primary propargyl alcohol, the oxidation of primary alcohol through TEMPO catalyst, an oxidation of aldehyde subtrate into its correspondence carboxylic acid through Pinnick's Oxidation reaction.

The formation of *tert*-butyl pent-4-yn-1-ylcarbamate compound through Curtius Rearrangement using DPPA reagent. The reasearch began by reacting a commercially available 5-hexynoic acid with DPPA that resulting an acyl azide that underwent of Curtius Rearrangement that lead to the formation isocyanate intermediate that reacted with alcohol to produced carbamate compound. The synthesis was proceeded with the formation of (2*Z*)-3-iodo-2-methylacrylic Acid Compounds through the *anti*-additon of primary propargyl alcohol utilizing an organocatalyst and Grignard reagent and subsequently an iodonolysis to formed a halogen substituted vinyl alcohol. Finally the oxidation of vinyl alcohol using TEMPO catalyst and followed by the oxidation of aldehyde compound through Pinnick's Oxidation that lead to the formation of an acrylic acid. All of the synthesized compounds were elucidated using ^{1}H-NMR spectrometer.

The resulting *tert*-butyl pent-4-yn-1-ylcarbamate compound from Curtius Rearrangement appeared initially as an orange liquid, therefore purification by FCC liquid deposit (10% Et_2O in PE) was obtained as a white solid in a 44% yield. The carbometallation and iodonolysis of primary propargyl alcohol resulted (2*Z*)-3-Iodo-2-methyl-2-propen-1-ol compound as an orange oil with 51%. Lastly, the oxidation of (2*Z*)-3-Iodo-2-methyl-2-propen-1-ol compounds generated (2*Z*)-3-iodo-2-methylacrylic Acid compounds in the form of crude white solid with 99.3% yield.

Keywords : Carbometallation, Curtius Rearrangement, Iodonolysis, Isocyanate, Pinnick's Oxidation and TEMPO Catalyst.

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INTISARI

Telah dilakukan penelitian skripsi yang berjudul "Sintesis Senyawa Asam Tert-butil pent-4-yn-1-ilkarbamat dan (2Z)-3-iodo-2-metilakrilat sebagai Bahan Awal Sintesis Total Pandamarine". Penelitian ini bertujuan untuk mensintesis bahan awal senyawa Pandamarine melalui serangkaian reaksi yang melibatkan penggunaan reagen Grignard dan katalis copper(I) untuk karbometalasi propargil alkohol primer, oksidasi alkohol primer melalui katalis TEMPO, dan oksidasi alkohol primer. aldehida subtrat menjadi asam karboksilat melalui reaksi Oksidasi Pinnick dan pembentukan senyawa karbamat melalui *Curtius Rearrangement* menggunakan reagen DPPA. Penelitian diawali dengan mereaksikan asam 5-heksinoat yang tersedia secara komersial dengan DPPA sehingga menghasilkan asil azida yang mengalami *Curtius Rearrangement* yang menghasilkan pembentukan zat antara isosianat yang direaksikan dengan alkohol menghasilkan senyawa karbamat. Kemudian dilanjutkan dengan anti-adisi propargil alkohol primer menggunakan organokatalis dan reagen Grignard dan selanjutnya dilakukan iodonolisis hingga membentuk vinil alkohol tersubstitusi halogen. Terakhir dilakukan oksidasi vinil alkohol menggunakan katalis TEMPO dan dilanjutkan dengan oksidasi senyawa aldehida melalui Oksidasi Pinnick yang menghasilkan pembentukan asam akrilat. Seluruh senyawa hasil sintesis dielusidasi menggunakan spektrometer ^{1}H-NMR.

Senyawa tert-butil pent-4-yn-1-ilkarbamat yang dihasilkan dari *Curtius Rearrangement* tampak sebagai cairan berwarna oranye, oleh karena itu purifikasi dengan *liquid deposit* FCC (10% Et2O dalam PE) menghasilkan produk berupa padatan putih dengan rendemen sebesar 44%. Karbometalasi dan iodonolisis propargil alkohol primer menghasilkan senyawa (2Z)-3-Iodo-2-metil-2-propen-1-ol yang dimurnikan menggunakan silika gel FCC dengan metode *liquid deposit* menggunakan eluen gradien dari 5% hingga 30% Et2O di PE menghasilkan cairan berwarna oranye dengan 50,8%. Terakhir, oksidasi senyawa (2Z)-3-Iodo-2-metil-2-propen-1-ol menjadi senyawa Asam (2Z)-3-iodo-2-metilakrilat berupa padatan putih dengan rendemen 99,3%. yang tidak memerlukan pemurnian lebih lanjut.

Kata kunci : *Curtius Rearrangement*, Iodonolisis, Isosianat, Karbometalasi, TEMPO dan Oksidasi Pinnick