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## SYNTHESIS OF ACRYLATES OF SOME ACETYLENE DIOLS BY ESTERIFICATION REACTION

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**Abstract**

For the first time, the synthesis of complex esters was carried out using the etherification reaction of acetylene diols with acrylic acid under the catalysis of $C_6H_6$ and concentrated $H_2SO_4$ solvents. The factors affecting the yield of the synthesized complex esters, including the ratios of starting materials, temperature, reaction time, catalysts and solvents, were determined and analyzed. Based on the results obtained, the $^1H$ NMR spectra of the synthesized complex esters were analyzed. Based on the results obtained, the most optimal conditions for the process were studied, and the composition, purity, structure and quantum-chemical properties and Rf values of the synthesized complex esters were proven by modern physico-chemical research methods, and the efficiency range was determined.

**Keywords:** acetylene diols, esters, acrylic acid, sulfuric acid, benzene etherification reaction, reaction mechanism, product yield, catalyst and solvent.

**Introduction:** Currently, the synthesis of complex esters based on the esterification reaction of carbon acids with acetylene alcohols is being carried out worldwide and is being widely used in various sectors of society. This includes significant applications in agriculture, medicine, and perfumery [1-3]. For this reason, deep scientific research is being conducted by scientists around the world on the synthesis of complex esters of acetylene diols with carbon acids and their applications [4. 6-10] Among these, the complex esters of acetylene alcohols with saturated carbon acids, as well as those with unsaturated carbon acids, are of great importance [5. 11-14]. The complex esters of acrylic acid, which is an unsaturated carbon acid, are being widely used in many fields [15-17]. Considering these needs, the synthesis of complex esters of acetylene diols was carried out, and their analysis was conducted using physico-chemical research methods [18-21].

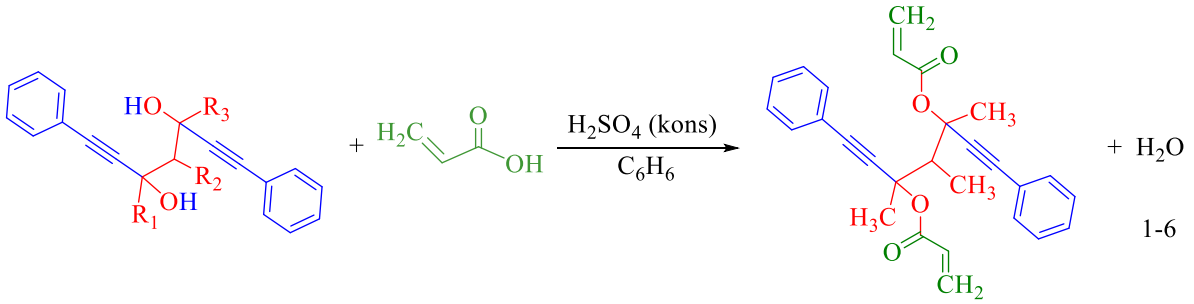
**Experimental Section:** (As an example, the synthesis of 3,4-dimethyl-1,6-diphenylhexa-1,5-diene-3,4-diol diacrylate is presented.) The synthesis of complex esters was carried out in a double-layer reactor made of thermally and mechanically strong quartz glass with a capacity of 500 ml. The reactor was equipped with a mechanical stirrer, two spray nozzles, a reflux condenser, and a Dean-Stark apparatus. Initially, 130 ml of $C_6H_6$ and 1.47 ml (0.015 mol) of concentrated sulfuric acid ($H_2SO_4$) were added to the reactor while stirring for 1 hour. The resulting catalytic system was maintained at 75-80°C with $H_2SO_4/C_6H_6$, and 95.22 ml (0.3 mol) of 3,4,5-trimethyl-1,7-diphenylheptadiyne-1,6-diol-3,5 and 28.8 ml (0.4 mol) of acrylic acid were added dropwise through the nozzle over 6 hours. To prevent the water produced from hydrolyzing the expected product, the Dean-Stark apparatus continuously separated it from the system. After the water separation was complete, the resulting reaction mixture was dried for 24 hours with $MgSO_4$ and extracted with DEE (3×50). The mixture was then fractionated under vacuum. Based on the experimental results, 99.5 grams of 3,4,5-trimethyl-1,7-diphenylhepta-1,6-diene-3,5-diol diacrylate was synthesized with a yield of 80.2%, along with 8% of starting materials, 6% of by-products, and 4% of waste.

We also synthesized the following complex esters using the same method:

1. 82% yield of 3,4-dimethyl-1,6-diphenylhexa-1,5-diene-3,4-diol diacrylate,
2. 80.6% yield of 3,5-dimethyl-1,7-diphenylhepta-1,6-diene-3,5-diol diacrylate,
3. 80.2% yield of 3,4,5-trimethyl-1,7-diphenylhepta-1,6-diene-3,5-diol diacrylate,
4. 78.5% yield of 3,6-dimethyl-1,8-diphenylocta-1,7-diene-3,6-diol diacrylate,
5. 77.2% yield of 3-methyl-1,7-diphenyl-5-(thiophenyl-2)hepta-1,6-diene-3,5-diol diacrylate, and
6. 75.3% yield of 1,7-diphenyl-3-(thiophenyl-2)-5-(trifluoromethyl)hepta-1,6-diene-3,5-diol diacrylate.

**Reaction Scheme and Mechanism:** The acetylene diol molecules participate in the esterification reaction with carbon acids due to the presence of substituents, three bonds, and the reactive hydroxyl (OH) group. In this work, the esterification reactions of the

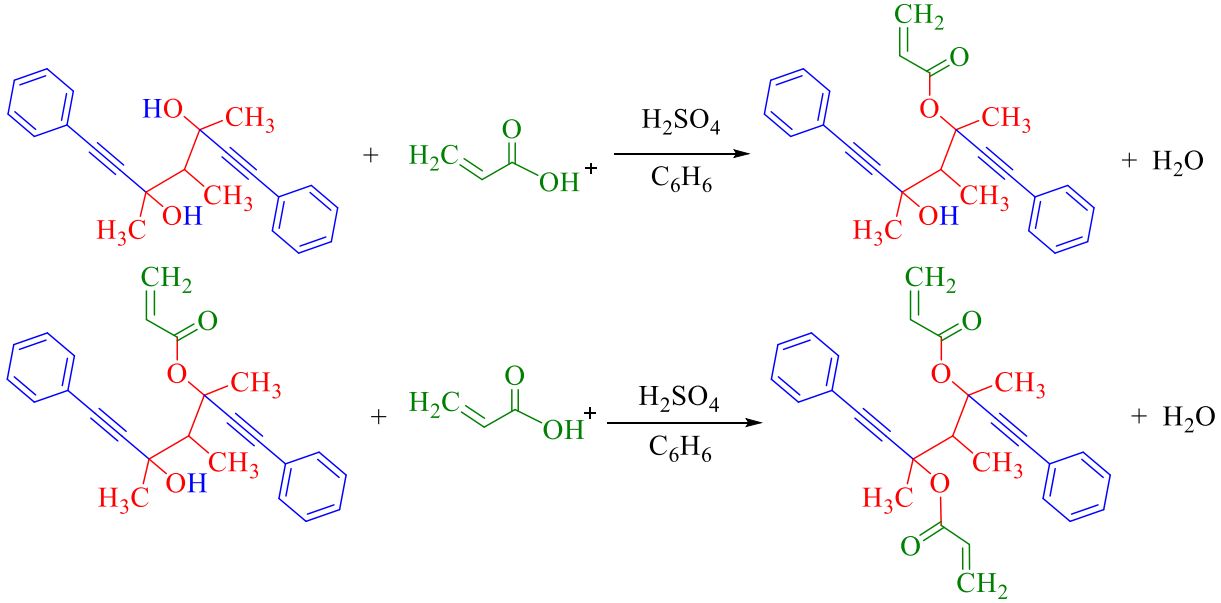
following diols with acrylic acid are presented: 3,4-dimethyl-1,6-diphenylhexa1z2-1,5-diol-3,4; 3,5-dimethyl-1,7-diphenylhepta-1,6-diol-3,5; 3,4,5-trimethyl-1,7-diphenylhepta-1,6-diol-3,5; 3,6-dimethyl-1,8-diphenylocta-1,7-diol-3,6; 3-methyl-1,7-diphenyl-5-(thiophenyl-2)hepta-1,6-diol-3,5; and 1,7-diphenyl-3-(thiophenyl-2)-5-(trifluoromethyl)hepta-1,6-diol-3,5. The reaction mechanism is proposed based on literature sources as follows [13,18-19].




**1.** R1= Me, $R_3$= Me,
**2.** R2= Me, $R_2$= H, $R_3$= Me,
**3.** R3= Me, $R_2$= Me, $R_3$= Me,
**4.** R4= Me, $R_2$= 2H, $R_3$= Me,
**5.** R5= Th, $R_2$= H, $R_3$= Me,
**6.** R6= Th, $R_2$= H, $R_3$= $CF_3$,

First, sulfuric acid protonates acrylic acid and increases its electrophilicity. The oxygen atom of the acetylene diol attacks the carbonyl group of the protonated acrylic acid, resulting in the formation of a complex ester and water.

In the case of 3,4,5-trimethyl-1,7-diphenylhepta-diene-1,6-diol-3,5, the oxygen atoms in the two OH hydroxyl groups undergo stepwise electrophilic attack by the protonated acrylic acid, leading to the expected formation of a complex ester and water.




To synthesize complex esters with high efficiency, the nature and structure of substituents in acetylene diols and acrylic acid molecules, as well as the effects of temperature, reaction duration, catalyst, and solvent nature were systematically analyzed and studied [19-21].

Initially, the effect of temperature on the yield of complex esters was investigated. The process was conducted over 6 hours at temperatures ranging from 60 to 100 °C, using benzene as the solvent and sulfuric acid as the catalyst, with acetylene diol and acrylic acid reacting at molar ratios of 0.3 and 0.4. At 80 °C, the catalyst $H_2SO_4$ interacted with the carbonyl group of acrylic acid, forming an intermediate compound that facilitated an easy reaction with acetylene diols, resulting in a favorable environment for high product yields. However, when the temperature was increased to 100 °C, a decrease in product yield was observed due to the reversion of the synthesized complex esters back to the starting materials or the dehydration of acetylene diols, leading to the formation of by-products.

Table 1

Effect of temperature on the synthesis of esters (catalyst $H_2SO_4$)

| Complex Ester | Product Yield, % | | |
|---|---|---|---|
| | 60 °C | 80 °C | 100 °C |
| 1 | 74 | 82 | 44 |
| 2 | 73 | 80,6 | 39 |
| 3 | 72 | 80,2 | 42 |
| 4 | 70 | 78,5 | 40 |
| 5 | 69 | 77,2 | 35 |
| 6 | 60 | 75,3 | 29 |

The duration of the reaction for the esterification of acetylene diols with acrylic acid was conducted at 80 °C in a benzene solution for periods ranging from 3 to 8 hours (see Table 2). When the process was carried out for 6 hours, it was observed that only a small amount of intermediate and by-products were formed, and the synthesized product had a low conversion to complex esters and minimal reversion to starting materials. During the reaction, water was continuously collected in a Dean-Stark apparatus, which prevented the hydrolysis of the complex ester by water and achieved high yields.

When the reaction duration was increased to 8 hours, the protons from sulfuric acid attacked the unshared electrons on the oxygen atom of the hydroxyl group in the acetylene diol, resulting in the protonation of the OH group and a decrease in the nucleophilicity of the diol as well as the activity of the catalyst. This led to a decrease in the expected yield of the complex ester. The maximum yield of the product was determined when the reaction time increased from 3 to 5 hours at 80 °C with $H_2SO_4$ as the catalyst in benzene solution, but a decrease in yield was observed when extending the reaction time from 5 to 8 hours.

Table 2

Effect of Reaction Duration on the Yield of Complex Esters
(Temperature: 100 °C, Catalyst: $H_2SO_4$, Solvent: $C_6H_6$)

| Complex Ester | Product Yield, % | | | |
|---|---|---|---|---|
| | 3 hours | 4 hours | 6 hours | 8 hours |
| 1 | 38 | 72 | 82 | 66 |
| 2 | 33 | 68 | 80,6 | 61 |
| 3 | 36 | 71 | 80,2 | 63 |
| 4 | 34 | 70 | 78,5 | 60 |
| 5 | 29 | 60 | 77,2 | 53 |
| 6 | 25 | 52 | 75,3 | 46 |

The amount of starting materials in the esterification reaction of acetylene diols with acrylic acid was also studied (see Table 3). Initially, when the starting materials 3,4,5-trimethyl-1,7-diphenylheptadiene-1,6-diol-3,5 and acrylic acid were taken in molar ratios of 0.3:0.2 and 0.3:0.3, a deficiency of acrylic acid was observed after the process stopped, which led to a decrease in product yield due to excess acetylene diols remaining in the system. When the molar ratio of the starting materials was adjusted to 0.3:0.4, a higher yield of the product was achieved. This increase in yield was attributed to the complete ionization of acetylene diol and acrylic acid molecules, which enhanced the activity of the intermediate complex compounds, resulting in higher yields of complex esters. However, when the amounts of the reagents and substrates were set to 0.2:0.4 mol, a decrease in product yield was also observed.

Table 3.

Effect of Starting Materials on the Yield of Complex Esters
(Temperature: 100 °C, Solvent: $C_6H_6$)

| Complex Ester | Product Yield, % in molar ratios of | | | |
|---|---|---|---|---|
| | 0,3:0,2 | 0,3:0,3 | 0,3:0,4 | 0,2:0,4 |
| 1 | 38,2 | 63,6 | 82 | 65 |
| 2 | 35,8 | 61,4 | 80,6 | 61,6 |
| 3 | 36,4 | 60,5 | 80,2 | 63,4 |
| 4 | 34,6 | 59,4 | 78,5 | 60 |
| 5 | 29,5 | 57,7 | 77,2 | 53,5 |
| 6 | 25,7 | 52 | 75,3 | 46,8 |

The composition, purity, structure, and physicochemical properties of the synthesized complex esters were determined using modern methods such as $^1$H-NMR, spectroscopy, mass spectrometry, chromatographic techniques (TLC, HPLC), quantum-chemical methods, and other physicochemical research methods (see Figures 1, 2, and 3). Based on the research results, the composition of the synthesized complex esters was calculated (see Table 3).

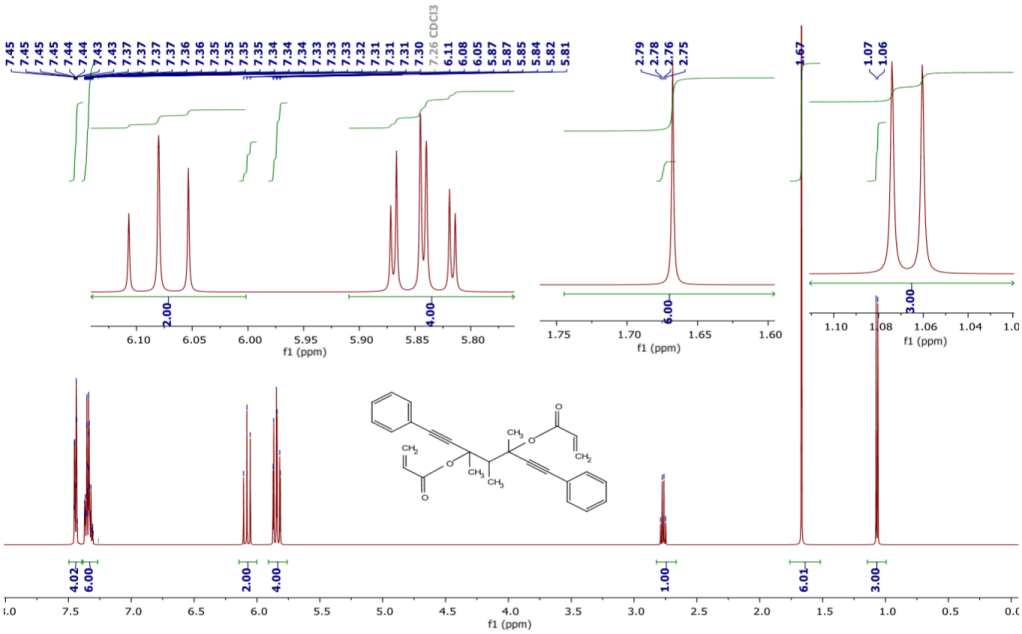


*Figure 1. [1]H NMR Spectrum of 3,4,5-Trimethyl-1,7-Diphenylhepta-1,6-diene-3,5-diol Diacrylate.*

Analysis of the [1]H NMR Spectrum of 3,4,5-Trimethyl-1,7-Diphenylhepta-1,6-diene-3,5-diol Diacrylate.
[1]H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.38 (m, 4H), 7.39 – 7.27 (m, 6H), 6.08 (t, J = 13.4 Hz, 2H), 5.84 (td, J = 13.2, 2.6 Hz, 4H), 2.77 (q, J = 6.8 Hz, 1H), 1.67 (s, 6H), 1.07 (d, J = 6.8 Hz, 3H).

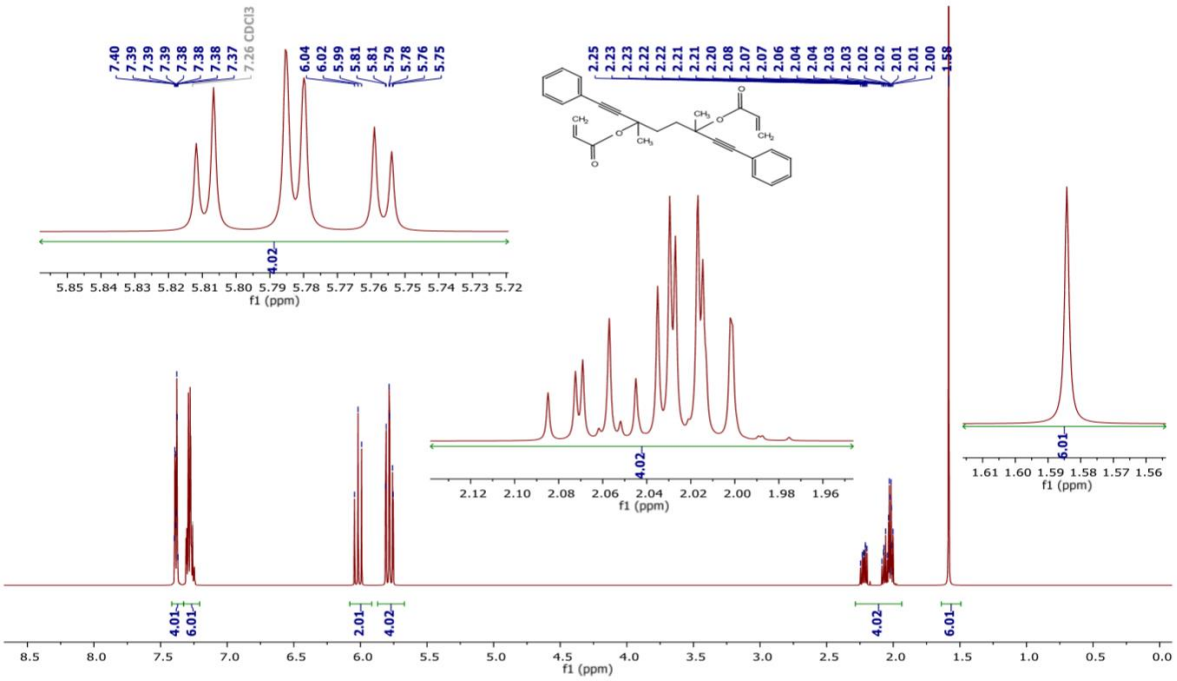


*Figure 2. [1]H NMR Spectrum of 3,6-Dimethyl-1,8-Diphenylocta-1,7-diene-3,6-diol Diacrylate.*

Analysis of the [1]H NMR Spectrum of 3,6-Dimethyl-1,8-Diphenylocta-1,7-diene-3,6-diol Diacrylate.
[1]H NMR (500 MHz, Chloroform-d) δ 7.42 – 7.33 (m, 4H), 7.33 – 7.21 (m, 6H), 6.08 – 5.91 (m, 2H), 5.78 (td, J = 13.2, 2.6 Hz, 4H), 2.28 – 1.94 (m, 4H), 1.58 (s, 6H).

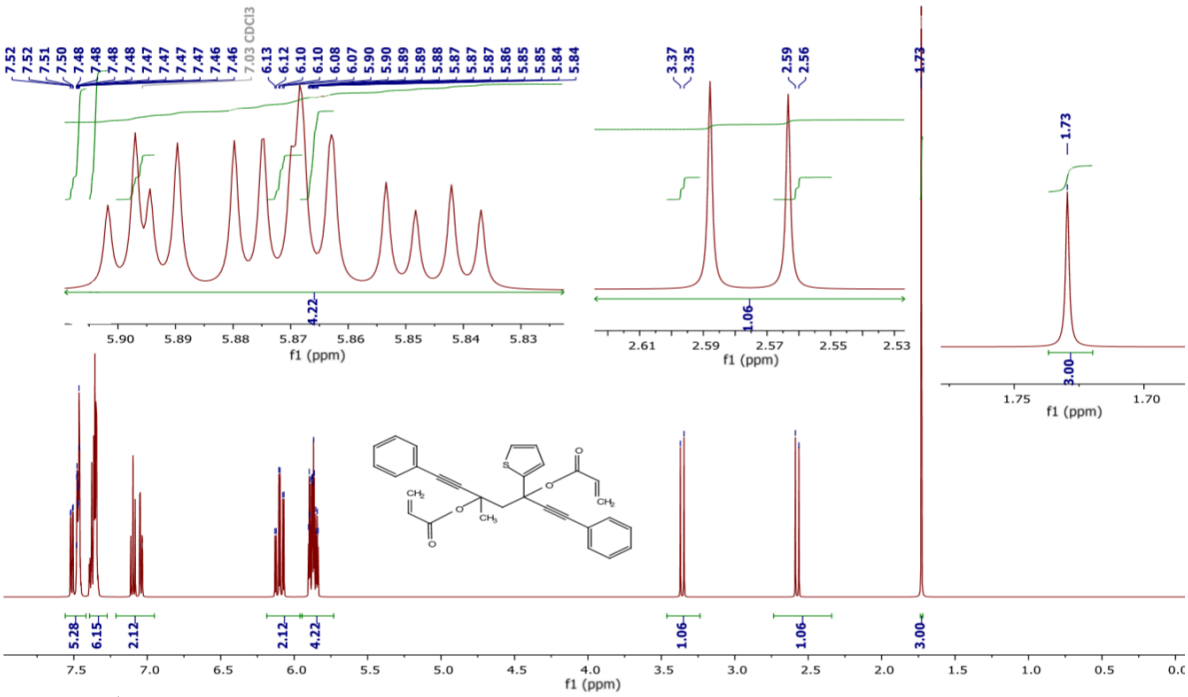



*Figure 3. [1]H NMR Spectrum of 3-Methyl-1,7-Diphenyl-5-(Thienyl-2) Hepta-1,6-Diene-3,5-Diol Diacrylate.*

Analysis of the [1]H NMR Spectrum of 3-Methyl-1,7-Diphenyl-5-(Thienyl-2) Hepta-1,6-Diene-3,5-Diol Diacrylate.

[1]H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.42 (m, 5H), 7.39 – 7.27 (m, 6H), 7.21 – 6.95 (m, 2H), 6.10 (td, J = 13.4, 4.0 Hz, 2H), 5.96 – 5.73 (m, 4H), 3.36 (d, J = 12.4 Hz, 1H), 2.58 (d, J = 12.3 Hz, 1H), 1.73.

Table 4

Elemental Analysis Results of Synthesized Complex Esters

| Complex esters | Brutto formula | Molecular Mass, g/mol | Analysis Results | Element Name and Analysis | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | O | S | F |
| **1** | $C_{26}H_{22}O_4$ | 398,48 | Calculated | 78,5 | 5,8 | 15,9 | - | - |
| | | | Identefied | 78,3 | 5,6 | 16,1 | - | - |
| **2** | $C_{27}H_{24}O_4$ | 412,51 | Calculated | 78,25 | 5,54 | 15,30 | - | - |
| | | | Identefied | 78,6 | 5,9 | 15,5 | - | - |
| **3** | $C_{28}H_{26}O_4$ | 426,54 | Calculated | 79,21 | 6,18 | 15,82 | - | - |
| | | | Identefied | 78,8 | 6,1 | 15,0 | - | - |
| **4** | $C_{28}H_{26}O_4$ | 426,54 | Calculated | 79,21 | 6,18 | 15,82 | - | - |
| | | | Identefied | 78,8 | 6,1 | 15,0 | - | - |
| **5** | $C_{30}H_{24}O_4S$ | 480,61 | Calculated | 75,87 | 5,38 | 13,31 | 6,8 | - |
| | | | Identefied | 75,0 | 5,0 | 13,3 | 6,7 | - |
| **6** | $C_{30}H_{21}O_4$ SF3 | 534,58 | Calculated | 66,9 | 4,17 | 11,97 | 5,95 | 10,15 |
| | | | Identefied | 67,4 | 4,0 | 12,0 | 6,0 | 10,7 |

**Conclusion:** The synthesis of complex esters was conducted for the first time through the esterification reaction of acetylene diols using concentrated sulfuric acid as a catalyst and benzene as a solvent, with acrylic acid involved. The reaction mechanisms were proposed based on literature sources, and the structure, composition, and Rf values of the synthesized complex esters were determined using modern physicochemical research methods.

As a result, the following complex esters were synthesized:

1. 3,4-Dimethyl-1,6-Diphenylhexa-1,5-diene-3,4-diol diacrylate,
2. 3,5-Dimethyl-1,7-Diphenylhepta-1,6-diene-3,5-diol diacrylate,
3. 3,4,5-Trimethyl-1,7-Diphenylhepta-1,6-diene-3,5-diol diacrylate,
4. 3,6-Dimethyl-1,8-Diphenylocta-1,7-diene-3,6-diol diacrylate,
5. 3-Methyl-1,7-Diphenyl-5-(Thienyl-2) Hepta-1,6-diene-3,5-diol diacrylate, and
6. 1,7-Diphenyl-3-(Thienyl-2)-5-(Trifluoromethyl) Hepta-1,6-diene-3,5-diol diacrylate.

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