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O. I. Shamrai[1,2], E. V. Zarudnitskii[1,3]

[1] Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, 5 Akademik Kuhar str., 02094 Kyiv, Ukraine
[2] Enamine Ltd, 78, Winston Churchill str., 02094 Kyiv, Ukraine
[3] National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", 37 Beresteiskyi ave., 03056 Kyiv, Ukraine

Danishefsky's Diene *vs* Rawal's Diene in [4+2] *Hetero*-Diels-Alder Reactions with Aldehydes

Abstract

The Diels-Alder reaction remains one of the most versatile and widely employed cycloaddition strategies in synthetic organic chemistry. The development of functionalized dienes, particularly Danishefsky's diene (DD) and Rawal's diene (RD), has significantly expanded the synthetic potential of this reaction. A comparative analysis of these two dienes has been performed in this study; in particular their reactivity with aldehyde dienophiles, leading to pyran derivatives – key intermediates in the pharmaceutical synthesis, has been analyzed. The reactivity, scope, and reaction conditions for both dienes have been assessed. Although DD is well studied and widely used in synthetic protocols, RD exhibits higher reactivity, especially under mild thermal conditions, eliminating the need for the Lewis acid catalysis. Experimental results for eight aldehyde substrates have revealed key differences in their efficiency and scalability. The data obtained emphasize the complementary nature of DD and RD in synthetic applications, providing valuable recommendations for optimizing diene selection in complex organic transformations.

Keywords: Danishefsky's diene; Rawal's diene; Diels-Alder reaction; aldehyde; pyran

О. І. Шамрай[1,2], Є. В. Зарудницький[1,3]

[1] Інститут органічної хімії Національної академії наук України, вул. Академіка Кухаря, 5, м. Київ, 02094, Україна
[2] ТОВ НВП «Єнамін», вул. Вінстона Черчилля, 78, м. Київ, 02094, Україна
[3] Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», Берестейський просп., 37, 03056, м. Київ, Україна

Дієн Данішефського та дієн Раваля в реакціях [4+2] *гетеро*-Дільса-Альдера з альдегідами

Анотація

Реакція Дільса-Альдера залишається однією з найуніверсальніших і найширше застосовуваних стратегій циклоприєднання в синтетичній органічній хімії. Розвиток функціоналізованих дієнів, зокрема дієну Данішефського (DD) і дієну Раваля (RD), суттєво розширив синтетичний потенціал цієї реакції. У цьому дослідженні проведено порівняльний аналіз цих двох дієнів, зокрема їхньої реакційної здатності з альдегідними дієнофілами, що дозволяє одержати похідні піранів – ключові проміжні сполуки у фармацевтичному синтезі. Було оцінено реакційну здатність, сферу застосування та умови проведення реакцій для обох дієнів. Хоча DD добре вивчений і широко використовуваний у синтетичних протоколах, RD демонструє вищу реакційну здатність, особливо у м'яких термічних умовах, усуваючи потребу в каталізі кислотами Льюїса. Експериментальні результати для восьми альдегідних субстратів виявили ключові відмінності у їхній ефективності та масштабованості. Отримані дані підкреслюють взаємодоповняльний характер DD і RD у синтетичних застосуваннях, надаючи цінні рекомендації для оптимального вибору дієну в складних органічних перетвореннях.

Ключові слова: дієн Данішефського; дієн Раваля; реакція Дільса-Альдера; альдегід; піран

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Supporting information: Copies of ^{1}H, ^{13}C NMR spectra of dihydropyranones and ^{1}H NMR spectra of crude mixtures.
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Introduction

Since its discovery by Diels and Alder in 1928 [1], the synthetic potential of the Diels-Alder reaction has been significantly expanded through modifications of both the diene and dienophile components [2]. While a vast array of dienophiles has been explored, the key challenge often lies in selecting or designing a suitable diene that ensures the sufficient reactivity toward diverse dienophiles [3]. Early empirical observations, later supported by theoretical and computational studies, showed that incorporating lone-pair-containing heteroatoms into the diene framework increases the rate and regioselectivity of cycloaddition reactions [4, 5]. This understanding played an important role in the development of more reactive and functionally diverse dienes.

Among the first heteroatom-substituted dienes used in [4+2] cycloadditions were simple dialkoxy dienes, followed soon by monoalkoxy variants (**Figure**, *A*, upper row) [6]. However, the synthetic applications of these dienes were significantly limited, primarily due to the challenges associated with their preparation. A major breakthrough came with the discovery of efficient methods for converting carbonyl compounds into silyl enol ethers, which facilitated the synthesis of various siloxydienes – a class that ultimately surpassed simple alkoxy dienes in popularity.

One of the most significant advances in siloxy dienes was the development of 1-methoxy-3-trimethylsiloxy-1,3-butadiene in 1974 [6f], commonly known after its inventor as Danishefsky's diene. This diene gained the widespread use due to its high reactivity toward a variety of dienophiles, including heterodienophiles [7]. Its introduction marked a major milestone in *hetero*-Diels-Alder reactions, enabling the regioselective synthesis of pyrans and piperidines while allowing for further functional group manipulations. These advantages have led to extensive research efforts aimed at refining its reactivity profile.

Parallel to the development of alkoxy and siloxy dienes, researchers explored amino-substituted dienes (**Figure**, *A*, lower row), which also played a crucial role in the evolution of the Diels-Alder reaction. The first simple 1-amino-substituted diene, despite its relative instability, was found to be highly reactive toward various dienophiles [8]. The synthesis of 1-*N*-acylamino-1,3-butadienes provided a more stable alternative, enabling applications in the alkaloid synthesis [9]. Later, 2-aminodienes demonstrated promising results in asymmetric Diels-Alder reactions [10]. Despite their significance, the combination of siloxy and amino groups in a single diene received little attention. Rare examples included cyclopentene-containing diene [11] and cyclic *N*-acylamino dienes [12]. That was until 1997, when *Rawal* carefully investigated this approach to increasing the diene's reactivity [13]. The Rawal's subsequent studies emphasized unique structural features of the aminosiloxy molecular platform, its potential as a building block, and a promising alternative to Danishefsky-type dienes [14].

Over the decades of experiments, exactly two dienes – Danishefsky's diene and Rawal's diene – have emerged as the most prominent choices for the Diels-Alder type transformations due to their distinct reactivity patterns and broad synthetic utility. Despite their structural differences, both dienes efficiently interact with electron-deficient π-systems to yield diverse and functionally rich products. Nevertheless, there are three distinct points that make these two dienes unequal in terms of synthetic applicability – reactivity, substrate scope, and reaction conditions (**Figure**, *B*). The initial and follow-up evaluations of the relative reactivity of Rawal's and Danishefsky's dienes determined that the aminosiloxy diene was 25 to 3000 times more reactive than the 1-methoxy-3-siloxy diene in the reaction with alkenes activated with EWGs [14, 15]. Moreover, the presence of more nucleophilic amine group, and advantageous positioning of enamine and enol ether units in Rawal's diene enhances its reactivity in Diels-Alder reactions, enabling it to overcome synthetic challenges that Danishefsky's diene cannot address. One of such cases was reported by *Gagnon* and *Danishefsky* in the project aimed to reach a polycyclic alkaloid Xestocyclamine A isolated from a marine sponge *Xestospongia sp.* [16]. In this work, the dienes were found to have different activity toward the enone moiety. Less pronounced electron-rich nature of Danishefsky's diene compared to the Rawal's counterpart cut off some dienophile substrates from its scope. Thus, while both dienes are still viable options for alkene, alkyne, and aldehyde dienophiles, ketones are a tough nut to crack for Danishefsky's diene and remain a privilege option of the aminosiloxy diene. A direct consequence of the lower reactivity of the siloxy diene is the need for specific reaction conditions when engaging with aldehyde dienophiles and their *aza*-analogs. In these cases, a Lewis acid catalyst is essential to facilitate the effective interaction between the

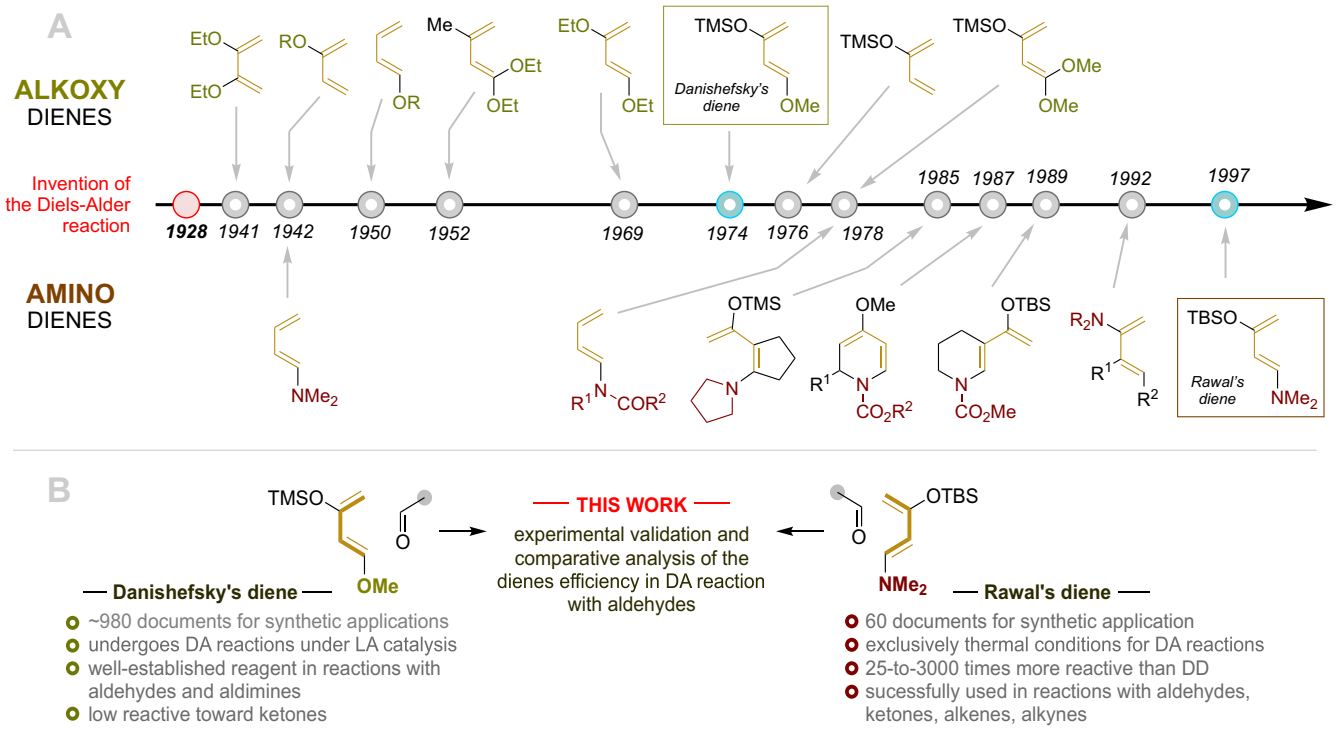

Figure. (**A**) The timeline of selected works related to electron-rich dienes used in the Diels-Alder reaction; (**B**) The synopsis of Danishefsky's and Rawal's dienes and the aim of the work

siloxy diene and the C=O(N) dienophile [7]. In contrast, Rawal's diene operates exclusively under thermal conditions, regardless of the dienophile, making it particularly advantageous for acid-sensitive substrates and challenging synthetic targets.

For borderline cases in synthetic organic chemistry, where several options are possible, choosing the optimal reagent for the reaction is crucial to achieve high yield, selectivity, and efficiency while minimizing side reactions and waste. The right choice ensures cost-effectiveness, scalability, and reproducibility, ultimately enhancing the success of synthetic methodologies in drug discovery, materials science, and industrial applications. From the discussion above, aldehydes are a typical substrate in hetero-Diels-Alder reactions posing a problem of choice of a diene counterpart. While Rawal's diene is seemingly a better variant owing to its higher reactivity, it must be acknowledged that Danishefsky's diene has been far more extensively studied, with over 15 times as many publications dedicated to its reactivity in Diels-Alder reactions (**Figure**, *B*). From years of experience of our synthetic group, most researchers tend to choose the more studied and reliable Danishefsky's diene rather than its powerful alternative. In this work, we are willing to present a comparative analysis of these two dienes, examining and re-evaluating their substrate scope, reaction conditions, yields, and selectivity in the *hetero*-Diels-Alder reaction with aldehydes. By evaluating their advantages and limitations, we aim to emphasize their complementary nature and give an idea of their optimal use in synthetic applications.

This work is further enriched by two key factors. First, to the best of our knowledge, there are currently no studies that specifically compare Danishefsky's diene (DD) and Rawal's diene (RD) in reactions with aldehydes. Second, the products of the transformation – 2,3-dihydro-4*H*-pyran-4-ones – are valuable intermediates for the synthesis of important pharmaceutical compounds [17].

■ Results and discussion

First and foremost, this paper aims to assess the convenience and efficiency of using dienes specifically for routine work. We did not seek to determine the most optimal reaction conditions, but instead employed the most commonly used ones (**Scheme**). For the reaction of aldehydes with the MeO-substituted siloxydiene, we followed the conditions reported by *Danishefsky* and *Kerwin* in one of their seminal works on the subject [18]. These conditions involve a low-temperature reaction in the presence of boron trifluoride etherate as a Lewis acid catalyst, followed by quenching with sodium bicarbonate. The aminosiloxy diene reacted with aldehydes in a two-step process under conditions we recently described in our work on the scaled synthesis of Rawal's diene [19].

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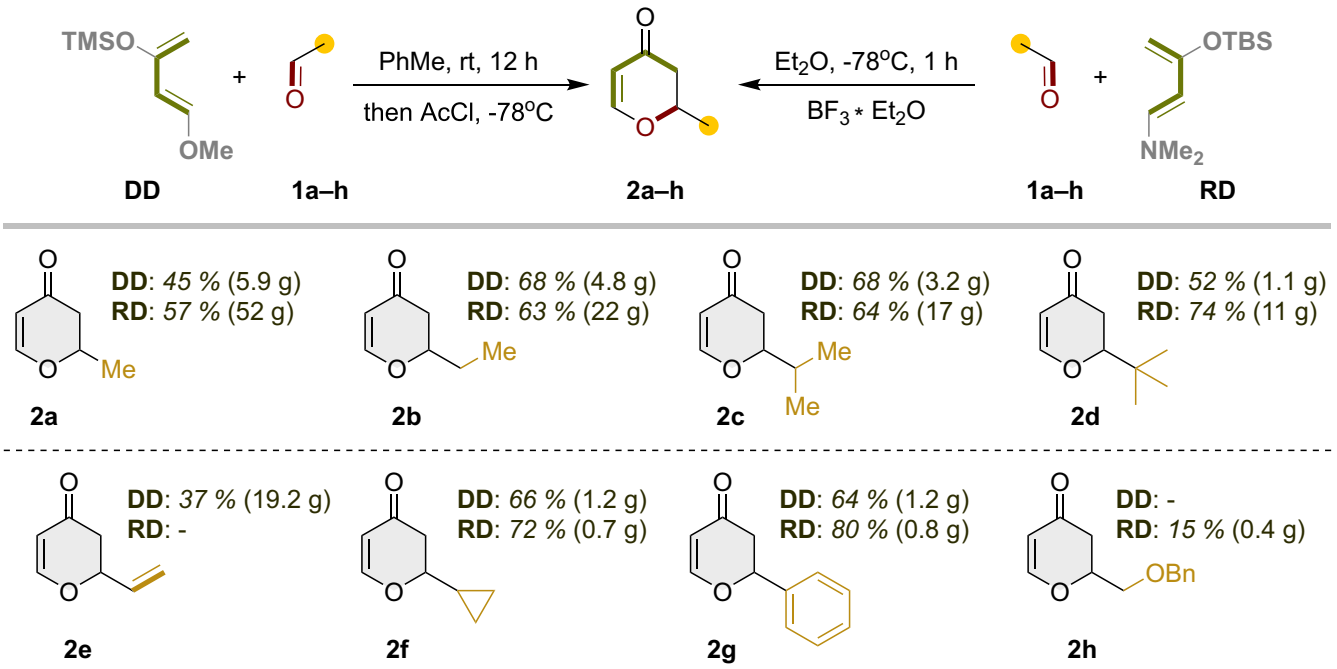

Scheme. The results of *hetero*-DA reactions with Danishefsky's and Rawal's dienes

The first step proceeds under thermal control in a toluene solution at room temperature, without additives, using a 2–4-fold excess of aldehydes. The resulting cycloadduct was not isolated, but directly subjected to the "deprotection" step, efficiently performed with acetyl chloride at low temperature. Crude mixtures obtained from both protocols were analyzed by ^{1}H NMR (see *SI File*), and the final pure products were isolated *via* the column chromatography (see *Experimental Part*).

To ensure the broad substrate coverage and reinforce our conclusions, we selected eight structurally diverse aldehydes. These included simple linear and branched aliphatic aldehydes (**1a–d**), one containing a heteroatom in the carbon chain (**1h**), aromatic benzaldehyde (**1g**), alicyclic cyclopropanecarboxaldehyde (**1f**), and α,ß-unsaturated acrolein (**1e**). The latter was particularly intriguing due to its two electrophilic π-bonds, which could potentially undergo cycloaddition with dienes. Indeed, previous reports described such interactions with DD and RD. However, as stated earlier, our primary focus was on evaluating the practical convenience and efficiency of each diene for synthetic applications.

Our experiments showed that both dienes reacted with aliphatic aldehydes with a comparable efficiency on gram-to-multigram scales. The yields ranged from 45–68% for DD and 57–74% for RD. Notably, RD maintained the consistent efficiency even at a multigram scale, with yields slightly increasing for higher homologs. In contrast, DD exhibited the opposite trend, possibly due to the lower electrophilicity of higher homologs affecting DD more significantly than RD. Interestingly, for linear aliphatic aldehydes **1a,b** under DD conditions, we anticipated and observed substantial amounts of aldehyde trimers in the ^{1}H NMR spectra of crude mixtures. However, these trimers likely originated from the commercial aldehyde source rather than forming during the reaction as the RD crude mixture contained them in exactly the same relative amount as DD.

A surprising finding was that acrolein reacted exclusively with DD, yielding dihydropyranone **2e**. The ^{1}H NMR spectrum of the reaction mixture showed no evidence of an alternative cycloadduct involving the aldehyde's alkene moiety. In contrast, the reaction of RD with acrolein yielded a crude mixture dominated by TBS group signals, with no characteristic peaks corresponding to either the starting materials or expected products. This was unexpected, taking into account that previous reports describe a successful cycloaddition of RD with related substrates, such as methacrolein and acrylic acid derivatives, leading to high-yielding cyclohexene products [13].

Interestingly, cyclopropanecarboxaldehyde (**1f**) has not previously been reported to react with any of the dienes. However, we observed no unusual reaction behavior, and the final dihydropyranone **2f** was isolated with comparable yields on a gram scale for both dienes. Similarly, reactions with benzaldehyde proceeded smoothly, giving the corresponding 5-phenylpyranone in slightly higher yields for RD.

The introduction of an oxygen atom in the α-position of acetaldehyde was expected to

enhance the reactivity of aldehyde **1h** compared to **1a**. However, DD failed to yield the desired product **2h** as its ^{1}H NMR spectrum showed no characteristic pyranone signals. Literature precedents suggest that this failure could be attributed to the inefficiency of the catalyst used. Reports indicate that Zn-based promoters are more effective for this transformation than boron trifluoride [20]. Thus, when using DD, selecting an appropriate catalyst is crucial. Surprisingly, RD also exhibited low efficiency with **1h**, leading to significant tarring and yielding only 15% of **2h**.

While both dienes demonstrated comparable efficiency on a gram scale for aliphatic aldehydes, we identified several experimental factors favoring RD for scaled syntheses of dihydropyranone products. The use of DD requires careful temperature control during the Lewis acid addition. Even a single drop of etherate causes a significant temperature spike, and although larger reaction scales mitigate these fluctuations, the risk of exceeding the acceptable temperature range remains, potentially leading to extensive tarring. Maintaining -78°C throughout the reaction is also critical to prevent side reactions. In contrast, RD follows a straightforward, low-maintenance protocol requiring only reagent mixing at ambient temperature. It lacks an exothermic effect and other complicating factors, remaining unchanged regardless of the reaction scale. The second step of the RD protocol, involving the removal of dimethylamino and TBS groups, does require an exothermic reaction with acetyl chloride at low temperature, which presents some operational challenges. However, the temperature rise is more manageable compared to the boron trifluoride addition, and the exotherm is easily controlled. Additionally, the large-scale isolation of DD products can be cumbersome, requiring careful addition of the reaction mixture into a saturated sodium bicarbonate solution while maintaining a reaction temperature below -20°C to prevent the product decomposition in the acidic environment. The rate of addition must also be controlled to avoid excessive foaming and ensure that the aqueous layer remains slightly basic.

The chromatographic purification is necessary to purify the target pyranones in both diene cases.

Conclusion

The comparative analysis of Danishefsky's and Rawal's dienes in hetero-Diels-Alder reactions with aldehydes underscores their distinct reactivity profiles and practical implications in synthetic applications. Despite DD's historical prominence and extensive literature coverage, RD demonstrates clear advantages in reactivity, operational simplicity, and scalability. The RD's ability to engage aldehyde dienophiles under thermal conditions without Lewis acid catalysts makes it particularly suitable for acid-sensitive substrates and the large-scale synthesis. However, DD remains valuable for reactions requiring selective activation of specific dienophiles, as evidenced by its exclusive reactivity with acrolein. The results also highlight critical experimental factors, such as the temperature control and catalyst selection, that impact the reaction efficiency and the product isolation. This study not only refines our understanding of these two pivotal dienes, but also provides a framework for their strategic application in synthetic methodologies, particularly in pharmaceutical and materials chemistry. In future, additional functionalized dienophiles should be studied to further expand the scope and efficiency of Diels-Alder transformations.

Experimental part

This section contains protocols for the preparation of the compounds described in the paper. Unless otherwise stated, all starting compounds were obtained from commercial sources and used without additional purification. All solvents were purified according to the standard procedures. All compounds known from the literature are given appropriate references; experimental data comply with the referenced papers.

^{1}H NMR spectra were recorded on a Varian Unity Plus 400 (400 MHz) or a Bruker 170 AVANCE 500 (500 MHz) instrument; ^{13}C NMR spectra were recorded on a Bruker 170 AVANCE 500 (126 MHz) or an Agilent ProPulse 600 (151 MHz) spectrometer. The NMR chemical shifts are referenced using the solvent signals at 7.26 and 77.1 ppm for ^{1}H and ^{13}C nuclei, respectively, in $CDCl_3$. GCMS analyses were performed using an Agilent 5890 Series II 5972 GCMS instrument [electron impact (EI) ionization (70 eV)]. Results for the elemental analysis were obtained at the Analytical Laboratory of the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine.

The general procedure for the reaction of Danishefsky's diene with aldehydes

To a solution of Danishefsky's diene (1.0 equiv.) in diethyl ether (25 mL for 1 mmol of the diene)

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under argon at -78°C an aldehyde (1.1 equiv.) was added followed by the dropwise addition of boron trifluoride etherate (1.0 equiv.). In 1 hour at a temperature of -78°C the mixture was carefully added to the saturated solution of $NaHCO_3$ (~10 mL for 1 mmol of the diene). The organic phase was separated, the water fraction was additionally extracted with two more portions of diethyl ether. Combined organic fractions were dried over $MgSO_4$ and evaporated. The crude product obtained was purified by the flash-chromatography (hexane/methyl *tert*-butyl ether, 100:0→80:20→50:50). The presence of pyranones in the eluted fractions was controlled by TLC, hexane/methyl *tert*-butyl ether 4:1, the staining reagent was $KMnO_4$.

The general procedure for the reaction of Rawal's diene with aldehydes

An aldehyde (4.0 equiv. for **1a–d** and 2.0 equiv. for **1e–h**) was dissolved in toluene (550 mL for 1 mol of the aldehyde) under the argon atmosphere, followed by the Rawal's diene (1.0 equiv.) added dropwise at room temperature (water bath). The reaction mixture was allowed to stir overnight, then the volatiles were removed on a rotary evaporator under reduced pressure. The residue was dissolved in methyl *tert*-butyl ether (550 mL for 1 mol of the aldehyde), and the solution was cooled to -78°C under argon. Acetyl chloride (2.0 equiv.) was added to the solution slowly, keeping the temperature at -78°C. Then, the cooling bath was removed, and the mixture was allowed to cool to 0°C and poured into the saturated solution of $NaHCO_3$ (the resulting pH must be > 7). The organic layer was separated, and the water fraction was extracted with methyl *tert*-butyl ether again. The combined organic fraction was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product obtained was purified by the flash-chromatography (hexane/methyl *tert*-butyl ether, 100:0→80:20→50:50). The first eluted fraction (100:0) contained non-identified components, in the second fraction (80:20) there were TBS-containing by-products (^{1}H NMR), the target product was obtained with the most polar eluent (50:50). The presence of pyranones in the eluted fractions was controlled by TLC, hexane/methyl *tert*-butyl ether 4:1, the staining reagent was $KMnO_4$.

2-Methyl-2,3-dihydro-4*H*-pyran-4-one (**2a**) [19]

A light-brown oil. Yield: RD – 57% (52 g), DD – 45% (5.9 g). Anal. Calcd for $C_6H_8O_2$, %: C 64.27, H 7.19. Found, %: C 64.35, H 7.13. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 1.40–1.50 (3H, m), 2.38–2.57 (2H, m), 4.54 (1H, dp, *J* = 12.2, 6.0 Hz), 5.35–5.44 (1H, m), 7.30–7.39 (1H, m). ^{13}C NMR (151 MHz, Chloroform-*d*), *δ*, ppm: 20.31, 43.45, 75.96, 106.85, 163.25, 192.58. GCMS (EI), m/z: 112.1 $[M]^{+\cdot}$.

2-Ethyl-2,3-dihydro-4*H*-pyran-4-one (**2b**) [19]

A colorless oil. Yield: RD – 63% (22 g), DD – 68% (4.8 g). Anal. Calcd for $C_7H_{10}O_2$, %: C 66.65, H 7.99. Found, %: C 66.77, H 7.91. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 1.00 (3H, t, *J* = 7.5 Hz), 1.66–1.87 (2H, m), 2.41 (1H, ddd, *J* = 16.7, 3.7, 1.2 Hz), 2.50 (1H, dd, *J* = 16.8, 13.5 Hz), 4.32 (1H, dddd, *J* = 13.2, 7.3, 5.4, 3.7 Hz), 5.38 (1H, dd, *J* = 6.0, 1.2 Hz), 7.35 (1H, d, *J* = 6.0 Hz). ^{13}C NMR (151 MHz, Chloroform-*d*), *δ*, ppm: 9.12, 27.42, 41.38, 80.68, 106.89, 163.30, 192.75. GCMS (EI), m/z: 126.0 $[M]^{+\cdot}$.

2-Isopropyl-2,3-dihydro-4*H*-pyran-4-one (**2c**) [19]

A yellow oil. Yield: RD – 64% (17 g), DD – 68% (3.2 g). Anal. Calcd for $C_8H_{12}O_2$, %: C 68.55, H 8.63. Found, %: C 68.67, H 8.51. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 0.98 (3H, d, *J* = 6.9 Hz), 1.00 (3H, d, *J* = 6.8 Hz), 1.92–2.06 (1H, m, *J* = 7.2, 6.7 Hz), 2.37 (1H, ddd, *J* = 16.5, 3.4, 1.2 Hz), 2.52 (1H, dd, *J* = 16.7, 14.6 Hz), 4.14 (1H, ddd, *J* = 14.6, 5.9, 3.3 Hz), 5.38 (1H, dd, *J* = 6.0, 1.2 Hz), 7.37 (1H, d, *J* = 5.9 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*), *δ*, ppm: 17.04, 17.26, 31.24, 38.44, 83.60, 106.30, 162.95, 192.51. GCMS (EI), m/z: 140.1 $[M]^{+\cdot}$.

2-*tert*-Butyl-2,3-dihydro-4*H*-pyran-4-one (**2d**) [19]

A light-yellow oil. Yield: RD – 74% (11 g), DD – 52% (1.1 g). Anal. Calcd for $C_9H_{14}O_2$, %: C 70.10, H 9.15. Found, %: C 69.97, H 9.24. ^{1}H NMR (400 MHz, Chloroform-*d*), *δ*, ppm: 1.01 (9H, s), 2.41 (1H, ddd, *J* = 16.6, 3.3, 1.3 Hz), 2.54 (1H, dd, *J* = 16.6, 15.1 Hz), 4.04 (1H, dd, *J* = 15.1, 3.3 Hz), 5.41 (1H, dd, *J* = 5.9, 1.3 Hz), 7.42 (1H, dd, *J* = 5.9, 0.8 Hz). ^{13}C NMR (151 MHz, $CDCl_3$), *δ*, ppm: 25.37, 33.78, 37.17, 86.89, 106.60, 163.89, 193.70. GCMS (EI), m/z: 154.1 $[M]^{+\cdot}$.

2-Vinyl-2,3-dihydro-4*H*-pyran-4-one (**2e**) [21]

A yellow liquid. Yield: DD – 37% (19.2 g). Anal. Calcd for $C_7H_8O_2$, %: C 67.73, H 6.50. Found, %: C 67.88, H 6.42. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 2.49–2.68 (2H, m), 4.90 (1H, dt, *J* = 12.8, 5.0 Hz), 5.33 (1H, dd, *J* = 10.7, 3.5 Hz), 5.37–5.45 (2H, m), 5.97 (1H, ddd, *J* = 16.9, 10.6, 5.7 Hz), 7.36 (1H, d, *J* = 5.9 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*), *δ*, ppm: 41.47,

79.49, 107.26, 118.39, 134.33, 162.80, 191.81. GCMS (EI), m/z: 124.1 $[M]^{+\cdot}$.

2-Cyclopropyl-2,3-dihydro-4*H*-pyran-4-one (2f)

A yellow liquid. Yield: RD – 72% (0.7 g), DD – 66% (1.2 g). Anal. Calcd for $C_8H_{10}O_2$, %: C 69.55, H 7.30. Found, %: C 69.40, H 7.39. ^{1}H NMR (500 MHz, Chloroform-*d*), δ, pm: 0.29 (1H, dq, *J* = 10.3, 4.7 Hz), 0.47 (1H, dq, *J* = 8.8, 4.8 Hz), 0.57–0.70 (2H, m), 1.11–1.21 (1H, m), 2.53 (1H, ddd, *J* = 16.8, 3.7, 1.3 Hz), 2.65 (1H, dd, *J* = 16.8, 13.3 Hz), 3.67 (1H, ddd, *J* = 12.7, 8.6, 3.6 Hz), 5.37 (1H, dd, *J* = 6.0, 1.2 Hz), 7.34 (1H, d, *J* = 6.0 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*), *δ*, ppm: 2.09, 3.37, 14.55, 41.90, 84.15, 106.94, 163.38, 192.73. GCMS (EI), m/z: 138.1 $[M]^{+\cdot}$.

2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (2g) [22]

A brown oil. Yield: RD – 80% (0.8 g), DD – 64% (1.2 g). Anal. Calcd for $C_{11}H_{10}O_2$, %: C 75.84, H 5.79. Found, %: C 75.99, H 5.83. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 2.66 (1H, dd, *J* = 16.8, 3.6 Hz), 2.91 (1H, dd, *J* = 16.9, 14.4 Hz), 5.43 (1H, dd, *J* = 14.5, 3.5 Hz), 5.53 (1H, d, *J* = 6.0 Hz), 7.36–7.45 (5H, m), 7.48 (1H, d, *J* = 6.0 Hz). ^{13}C NMR (126 MHz, Chloroform-*d*), *δ*, ppm: 42.85, 80.58, 106.86, 125.58, 128.33, 128.41, 137.35, 162.63, 191.59. GCMS (EI), m/z: 174.0 $[M]^{+\cdot}$.

2-((Benzyloxy)methyl)-2,3-dihydro-4*H*-pyran-4-one (2h) [20]

A yellow oil. Yield: RD – 15% (0.4 g). Anal. Calcd for $C_{13}H_{14}O_3$, %: C 71.54, H 6.47. Found, %: C 71.71, H 6.38. ^{1}H NMR (500 MHz, Chloroform-*d*), *δ*, ppm: 2.40 (1H, dd, *J* = 16.8, 3.5 Hz), 2.74 (1H, dd, *J* = 16.9, 14.2 Hz), 3.64–3.76 (2H, m), 4.53–4.68 (3H, m), 5.41 (1H, d, *J* = 5.9 Hz), 7.28–7.43 (6H, m). ^{13}C NMR (126 MHz, Chloroform-*d*), *δ*, ppm: 38.34, 70.58, 73.58, 78.29, 107.11, 127.75, 127.98, 128.55, 137.40, 162.90, 192.01. GCMS (EI), m/z: 218.1 $[M]^{+\cdot}$.

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Information about the authors:
Oleksii I. Shamrai (*corresponding author*), Ph.D. Student, Institute of Organic Chemistry of the National Academy of Sciences of Ukraine; Laboratory Head, Enamine Ltd.; e-mail for correspondence: shilo2890@gmail.com.
Evgenij V. Zarudnitskii, Ph.D. in Chemistry, Senior Researcher of the Medicinal Chemistry Department, Institute of Organic Chemistry of the National Academy of Sciences of Ukraine; Associate professor of the Department of Organic Chemistry and Technology of Organic Compounds, Faculty of Chemistry and Technology, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute». https://orcid.org/0000-0003-2038-4243.