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New insights into the competitive copper-catalyzed reactions of 1-benzylidene-2-phenylhydrazines with CCL$_4$

Ulviyya Askerova [a], Alakbar Huseynzada [b,c], Abel Maharramov [a], Namiq Shikhaliyev [d,*], Gulnar Atakishiyeva [a], Afsun Sujayev [e]

[a] Baku State University, Z. Khalilov 33, Baku, AZ 1148, Azerbaijan
[b] ICRL, Baku State University, Z. Khalilov 33, Baku, AZ 1148, Azerbaijan
[c] ICESCO Biomedical Materials Chair, Baku State University, Z. Khalilov 33, Baku, AZ 1148, Azerbaijan
[d] Department of Chemical Engineering, Baku Engineering University, Hasan Aliyev 120, Absheron, AZ0101, Azerbaijan
[e] Laboratory of Fine Organic Chemistry, Institute of Chemistry of Additives, 1029, Baku, Azerbaijan

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ABSTRACT

In our previously published articles, we presented for the first time the results of quantum mechanical calculations of the reaction profile for a new reaction involving N-substituted hydrazones with CCl$_4$ in the presence of a catalytic complex based on CuCl and TMEDA, leading to the formation of halogenated vinyldiazenyl systems containing geminal chlorine atoms at the terminal vinyl position. The DFT calculations of the electronic structure of the molecules demonstrated that the introduction of electron-donating and electron-withdrawing substituents into the aromatic fragments of the molecules significantly affects their properties by altering electronic parameters and reactivity descriptors. Based on these findings and experimental data, it was of interest to perform calculations and analyze the energetic profile of the reactions under conditions of qualitative changes in the substrate composition. The study showed that in the case of hydrazones with complementary electron density shifts (i.e., donor substituents in the aldehyde moiety and acceptor substituents in the hydrazine moiety of the molecule), in addition to the expected formation of dichlorinated vinyldiazenes (dichlorodiazadienes), new competitive reactions occur. The products of these reactions are pseudo-dimers (bis-hydrazone derivatives), formed by the coupling of two molecules of the initial hydrazone. Energetic calculations were carried out for both reactions, viz the formation of dichlorovinyldiazenes and bis-hydrazone derivatives. Based on these studies, the mechanisms for the formation of bis-hydrazone derivatives were proposed for the first time.

1. Introduction

Currently, most reactions, within the framework of which research work is carried out, have a history of more than a century. However, a new chemical transformation reaction was discovered in 1999, viz a copper salt-catalyzed reaction of hydrazones of carbonyl compounds and polyhaloalkanes, leading to the formation of alkenes. The reaction in which the hydrazone is transformed into an olefin is a catalytic olefination reaction [1]. The history of the reaction using N-substituted phenylhydrazones under the conditions of the catalytic olefination reaction has an even shorter history and begins in 2016 [2–4]. All these years, our research groups, along with collecting statistical material using modern analysis methods, have been engaged in analytical studies aimed at identifying the specifics of the reaction mechanism, the structure of the synthesized compounds and their supramolecular features.

Nowadays, along with practical research, computer-aided research has become widely popular, in particular computer modelling using quantum chemistry and molecular dynamics methods. Quantum chemical methods with high accuracy allow not only to calculate the properties of individual molecular systems but also to identify and substantiate existing process patterns and describe reaction mechanisms, identify the chemical potential of synthesized systems and conduct correlations.

In the last 20–25 years, quantum chemistry has undergone a revolution thanks to density functional theory (DFT), which is based on the well-known Hohenberg and Kohn theorems. Conceptual DFT has recently provided a framework for interpreting and forecasting

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* Corresponding author. Department of Chemical Engineering, Baku Engineering University, Azerbaijan.
E-mail address: umumi_shobe@aki.science.az (N. Shikhaliyev).

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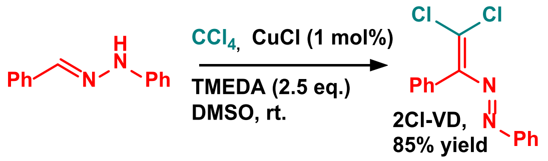


Scheme 1. The considered reaction in the quantum chemical calculations.

theoretical and experimental reactivity data based on a sequence of reaction functions to changes in the electron count and/or external potential. This method has made it possible to precisely define and calculate a number of well-known but occasionally ambiguously defined chemical concepts. DFT is now a computational workhorse that is used not only by quantum chemists but also by experimental chemists working in inorganic, organic, material, biological, and pharmaceutical chemistry to provide guidance for the interpretation and/or planning of their experiments because of the development of ν_{xc} potentials of ever-increasing performance over the last 10–15 years (although occasionally heavy parameterization shows up) [5–7].

At present, there are a sufficient number of computing complexes and software products that implement quantum chemical methods. Such platforms as Gaussian, Gamess, ChemCraft, and Castep are often used.

Earlier, at first time, based on the Gaussian 16 program [8], a computer study of the reaction mechanism of the synthesis of (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene was carried out - a matrix model, i.e. a system that does not contain any substituents in aromatic systems (Scheme 1).

Our study has made some adjustments to the order of formation of intermediates compared to the proposed mechanism. However, the main focus was on the study of the reaction mechanism of both ligand-free (LF) and ligand-containing (L) pathways for the conversion of 1-benzylidene-2-phenylhydrazine with CCl_4 to (E)-1-(2,2-dichloro-1-phenylvinyl) catalyzed by copper chloride. Importantly, the studies show that the total potential energy surface is thermodynamically favourable and the turnover frequency (TOF) is significantly higher in the case of the Cu(I)-TMEDA complex-catalyzed pathway (L).

At the next stage of our research, quantum chemical calculations were performed for a number of dichlorovinyldiazenes using computer modelling methods. The analysis of NBO, electronic parameters and reactivity descriptors revealed that correlations of the qualitative composition of molecules (the presence of electron-donating and electron-withdrawing substituents) introduce significant changes both in the nature of the molecules themselves and in the nature of their supramolecular relationships. For example, the value of μ (dipole moment) for (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene (matrix model) is 1.9051 D, while in (E)-4-({2,2-dichloro-1-[4-(dimethyl amino)phenyl]-ethenyl}diazenyl)benzonitrile this value increases to 7.7017 D [9–11].

Following this line of reasoning, from our point of view, it would be interesting to conduct a computer study of the reaction profile under conditions of changing the composition of the substrate (introduction of electron-donating and electron-accepting groups) and compare them with practical results.

2. Materials and methods

2.1. Computational details

To calculate the Gibbs free energy for a reaction involving reactants, intermediates, and products, Density Functional Theory (DFT) was employed within the Materials Studio environment, combining results from various modules. The overall workflow integrates electronic energy calculations, vibrational analysis, and thermodynamic property estimation to determine the Gibbs free energy of the entire reaction. The total electronic energy of each species (reactants, intermediates, and products) was computed using the CASTEP module. CASTEP performs DFT calculations based on plane-wave pseudopotentials, providing highly accurate electronic structures. Additionally, phonon calculations were conducted using CASTEP to estimate the vibrational contributions to the free energy, particularly relevant at finite temperatures [12].

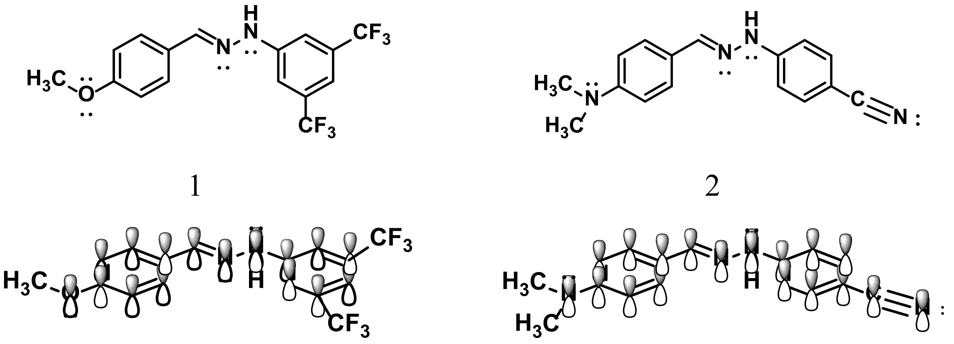
Vibrational analysis was performed using either Forcite or $DMol^3$ modules to calculate the vibrational frequencies of all species involved. These frequencies were then used to compute the zero-point energy (ZPE), as well as the thermal contributions to the Gibbs free energy, including enthalpy and entropy at various temperatures. $DMol^3$, which employs a numerical basis set, was particularly useful for precise vibrational frequency calculations and thermodynamic properties [13].

3. Results and discussion

Two phenylhydrazones were chosen as models: (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-ethoxybenzylidene)hydrazine and (E)-4-(2-(4(dimethylaminobenzylidene)hydrazinyl)-benzonitrile (Fig. 1):

X-ray structural analysis of (E)-4-(2-(4(dimethylaminobenzylidene)-hydrazinyl) benzonitrile has established that the molecule has a planar structure, which is the result of complete conjugation of the p-electron system in the molecule, with a complementary shift of the electron density from the aldehyde component of the molecule (contains an electron-donor –$N(CH_3)_2$ group) to the hydrazine component of the molecule (contains an electron-acceptor –CN group) [14]. As studies show [11], dichlorovinyldiazenes, derivatives of this type of hydrazones, are distinguished by an increased value of the dipole moment.

We would like to draw attention to the fact that the hydrazine component of hydrazone molecules, in addition to the quality of the electron acceptor, also differs in their position.



1

2

Fig. 1. Structures of (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxybenzylidene)hydrazine and (E)-4-(2-(4-(dimethylamino)benzylidene)hydrazineyl) benzonitrile.

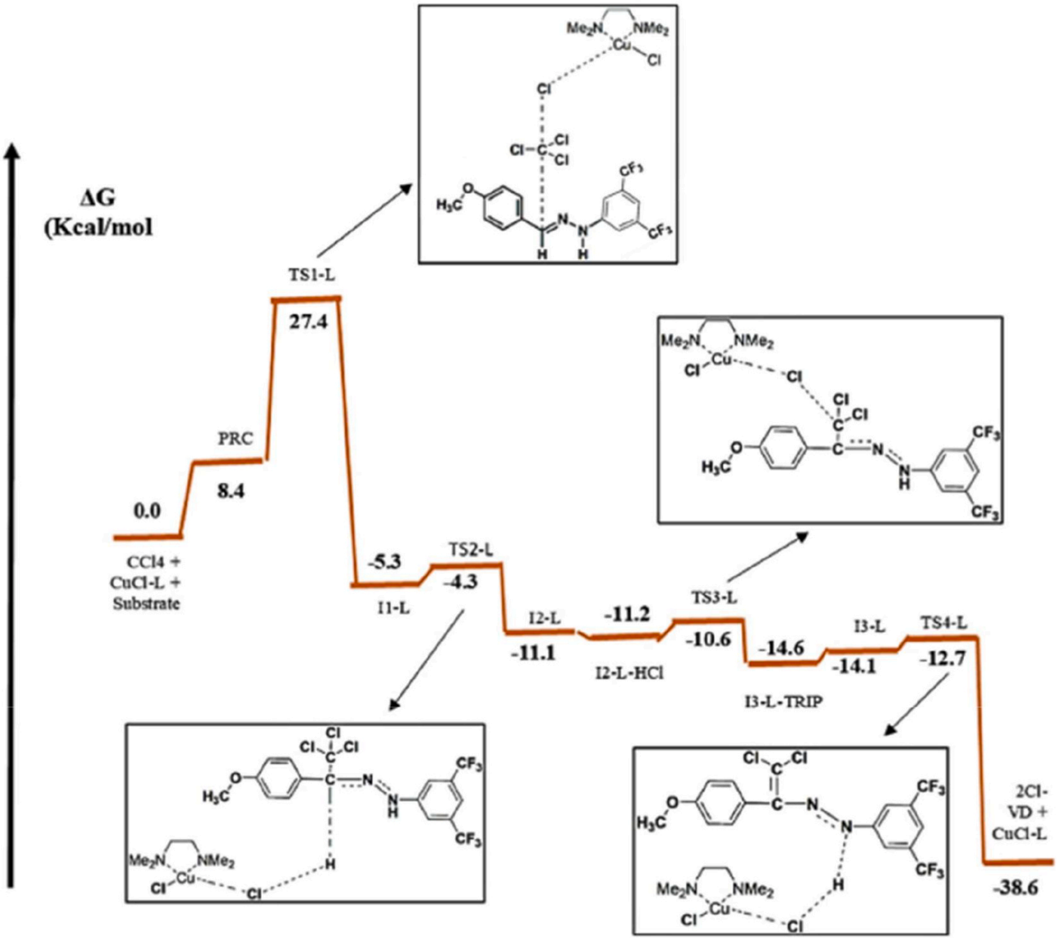


Fig. 2. Gibbs free energy profile for the first reaction.

3.1. *First reaction discussion*

In the first reaction, the trans configuration is used with a starting mixture of (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxybenzylidene)hydrazine in the presence of TMEDA (Fig. 2):

The initial interaction between the substrate, CuCl-L and CCl_4 forms a pre-reaction complex (PRC) with a relative energy of 8.4 kcal/mol. The coordination of TMEDA to CuCl stabilizes this complex slightly but introduces some steric hindrance, which is reflected in the positive energy. The first significant transition state involves the migration of a chlorine atom from CCl_4 to CuCl-L, coupled with the attack of the $\cdot CCl_3$ radical on the substrate. The energy of TS1-L is calculated to be 27.4 kcal/mol, indicating a significant energy barrier due to the presence of bulky groups and the coordination with TMEDA. This step is crucial as it dictates the reaction rate, with TMEDA likely contributing to the increased activation energy by stabilizing the CuCl complex. Following the high-energy transition state, the reaction stabilizes into the first intermediate (I1-L) with an energy of −5.3 kcal/mol. It should be noted that this value of the Gibbs energy is higher than the energy value calculated for the matrix model (−8,6 kcal/mol). The formation of I1-L is exergonic, suggesting a strong stabilization after the chlorine migration and radical addition. The TMEDA ligand helps stabilize the copper center, reducing the overall energy of the intermediate.

The next step involves deprotonation of I1-L, leading to the formation of the second intermediate (I2-L). The transition state for this step, TS2-L, has an energy of −4.26 kcal/mol, indicating that the energy barrier is relatively low. The resulting intermediate, I2-L, is further stabilized with an energy of −11.1 kcal/mol, reflecting the exothermic nature of the deprotonation step.

A minor transition occurs here, forming I2-L-HCl with a slightly lower energy of −11.2 kcal/mol. This suggests that the removal of HCl from I2-L is nearly thermoneutral.

The removal of the second chlorine atom from I2-L-HCl proceeds through TS3-L, with an energy of −10.6 kcal/mol. This relatively small energy barrier suggests that the removal of the chlorine atom is facilitated by the structure's trans configuration.

The next intermediate, I3-L, is formed with an energy of −14.1 kcal/mol. A triplet state version of this intermediate (I3-L-TRIP) is also possible, with an energy of −14.6 kcal/mol. The slight energy difference indicates that the triplet state is slightly more stable, possibly due to the spin state of the copper center being influenced by TMEDA coordination.

The reaction concludes with the formation of the 2Cl-VD derivative product and the regeneration of CuCl-L, with a significant release of energy (−38.6 kcal/mol). This highly exergonic step underscores the thermodynamic favorability of the product formation in the trans configuration.

In conclusion, the inclusion of TMEDA in the reaction mechanism influences the energy landscape significantly. The presence of TMEDA increases the activation energy in the early stages (notably TS1-L) but stabilizes the intermediates and transition states, especially in the trans configuration. This stabilization is crucial in guiding the reaction towards the formation of the *trans*-configured product, 2Cl-VD. The final step, which releases a substantial amount of energy, ensures that the reaction is both thermodynamically and kinetically favourable, despite the initial energy barriers imposed by TMEDA and the bulky substituents on the hydrazone substrate.

The mechanism of the investigated process is presented above.

Cartesian Coordinates of the Reported Structures for Ligand-

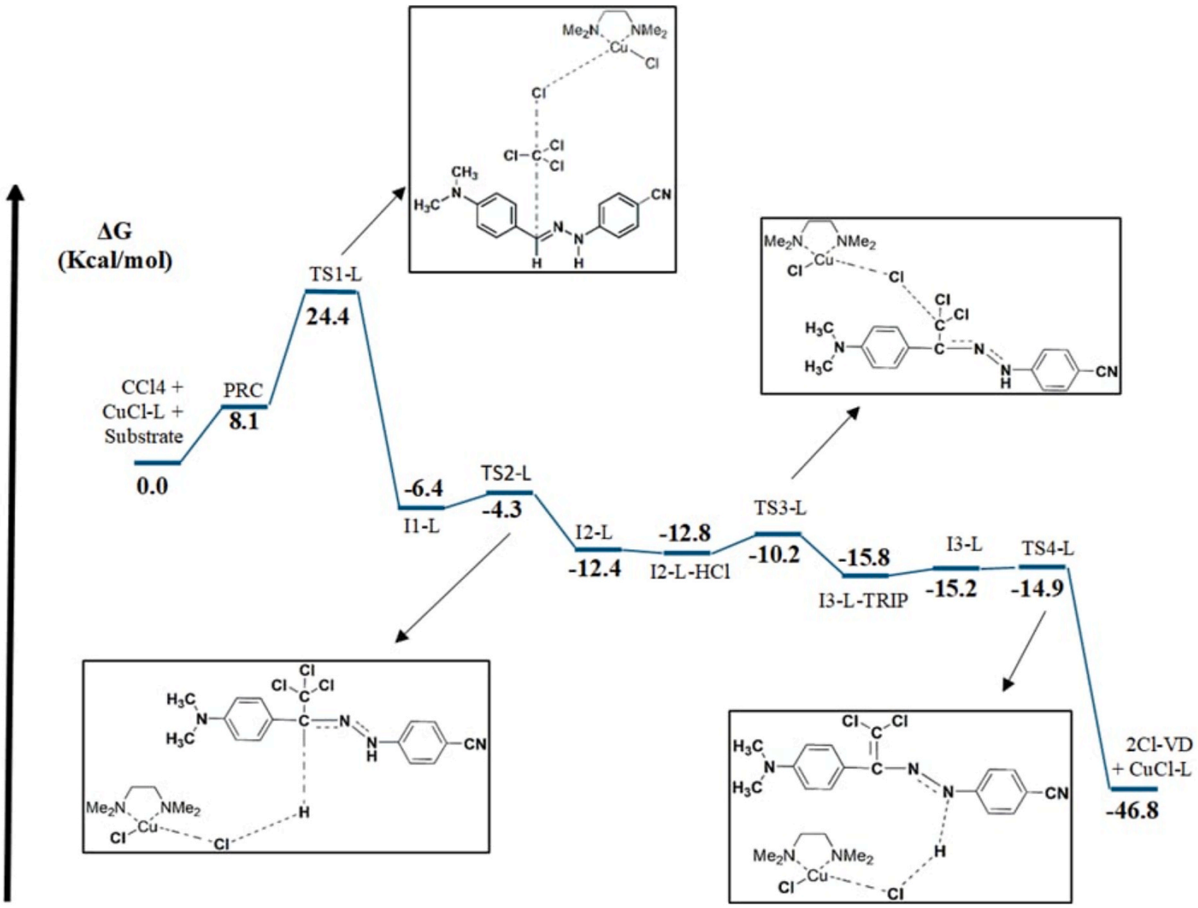


Fig. 3. Gibbs free energy profile for the second reaction.

Inclusive (L) for the first reaction are presented in Appendix 1 (See Supplementary Material).

3.2. Second reaction discussion

In the second reaction, the substrate is (E)-4-(2-(4-(dimethylamino) benzylidene)hydrazineyl) benzonitrile combined with CCl_4, CuCl-L and TMEDA to produce a 2Cl-VD derivative (Fig. 3):

The initial interaction forms a pre-reaction complex (PRC) with a relative energy of 8.1 kcal/mol. The slightly lower energy compared to the previous substrate (8.4 kcal/mol) suggests that the interaction is marginally more favourable, likely due to the electron-donating dimethylamino group enhancing the coordination of the substrate with CuCl-L.

The presence of TMEDA continues to play a role in stabilizing the copper complex, although the steric effects from the ligand slightly elevate the energy.

The transition state TS1-L, which involves the migration of a chlorine atom from CCl_4 to CuCl-L and the subsequent radical attack on the substrate, has an energy of 24.4 kcal/mol. The reduced energy barrier can be attributed to the electron-donating effect of the dimethylamino group, which increases the reactivity of the C=N bond in the substrate, facilitating the radical addition. The first intermediate, I1-L, is formed with an energy of −6.4 kcal/mol, indicating that the reaction stabilizes significantly after the initial transition state. This Gibbs energy value is higher than the stabilization energy value calculated for the matrix model (−8.6 kcal/mol), but lower than that of a similar intermediate in the first reaction. The more negative energy reflects the enhanced stabilization provided by the electron-donating dimethylamino group and the electron-withdrawing cyano group on the substrate. The TMEDA-ligated copper center continues to stabilize this intermediate effectively, further reducing the energy.

The deprotonation step occurs via TS2-L with an energy of −4.26 kcal/mol, similar to the previous reaction, indicating that the energy barrier for this step remains low.

The resulting intermediate, I2-L, has an energy of −12.4 kcal/mol, which is more negative than the previous −11.1 kcal/mol, again reflecting the stabilizing effects of the cyano group.

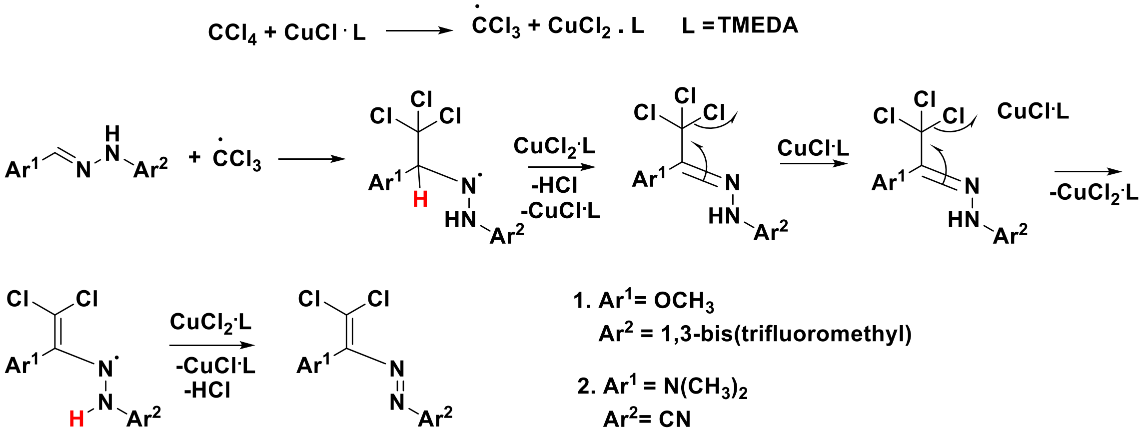
The formation of I2-L-HCl, with an energy of −12.8 kcal/mol, shows that the removal of HCl is slightly more exergonic compared to the previous substrate, likely due to the favourable electronic environment created by the substituents.

The energy barrier for the removal of the second chlorine atom, represented by TS3-L, is −10.2 kcal/mol. This energy is slightly higher than the previous −10.6 kcal/mol, potentially due to some steric interactions between the dimethylamino group and the reaction center, despite the favourable electronic environment.

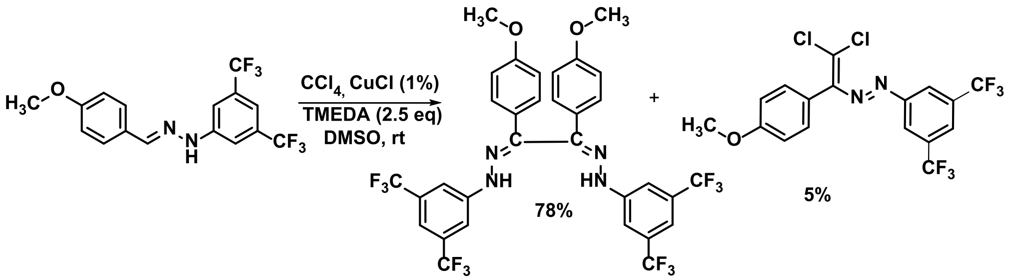
The I3-L intermediate is formed with an energy of −15.2 kcal/mol, and its triplet state (I3-L-TRIP) is even more stable at −15.8 kcal/mol. These values indicate that the new substrate's electronic effects significantly stabilize the intermediates. The triplet state stabilization suggests that the spin state of the copper complex is favourably influenced by the substrate's electronic environment.

The final transition state, TS4-L, has an energy of −14.9 kcal/mol, which suggests that the final step of the reaction, leading to the formation of the 2Cl-VD derivative, is more energetically favourable due to the combined effects of the dimethylamino and cyano groups on the substrate.

The reaction concludes with the formation of the 2Cl-VD derivative and the regeneration of CuCl-L with a significant release of energy



Scheme 2. The mechanism of considered reactions in the quantum chemical calculations.



Scheme 3. General scheme of the reaction involving (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxybenzylidene)hydrazine.

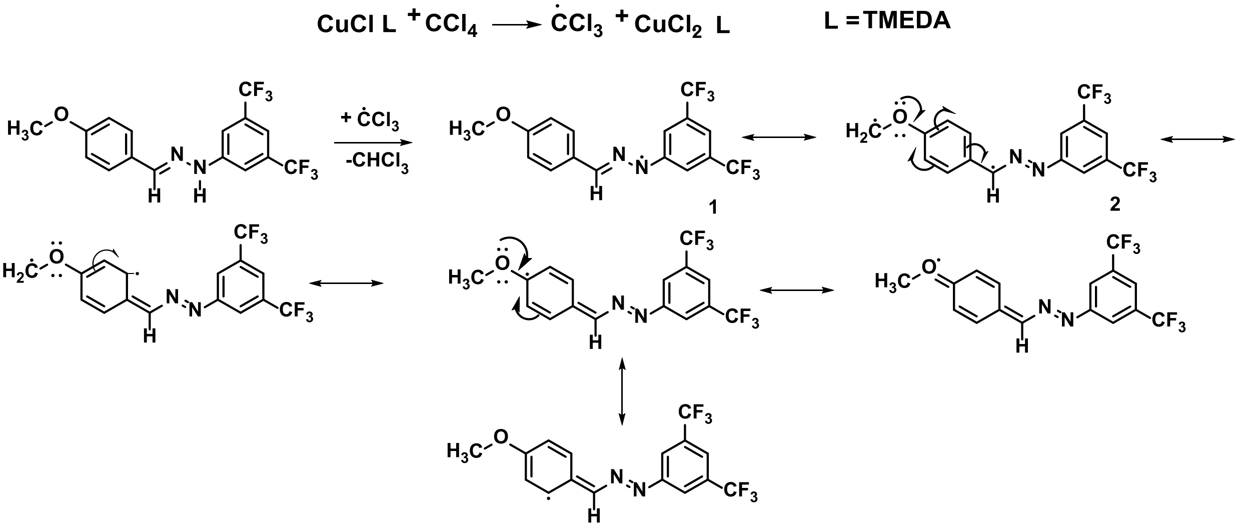
(−46.8 kcal/mol). This is considerably more exergonic indicating that the overall process is highly favourable with the new substrate.

This reaction pathway is both kinetically and thermodynamically more favourable compared to the previous substrate. The electron-donating dimethylamino group and the electron-withdrawing cyano group work together to lower the activation energies for key transition states and stabilize the intermediates, leading to a highly exergonic overall reaction.

The final product, a 2Cl-VD derivative, is formed with a substantial release of energy, suggesting that this reaction pathway is not only feasible but also highly efficient. The TMEDA ligand, while slightly increasing the steric hindrance, contributes to the stabilization of the copper complex throughout the reaction, further ensuring a smooth and favourable transformation.

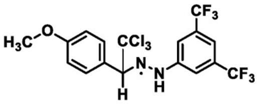
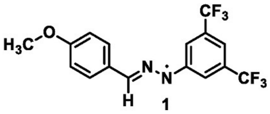
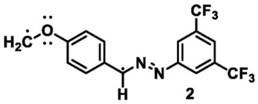
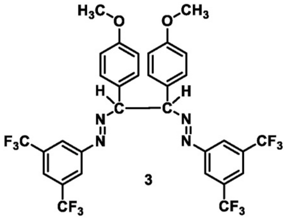
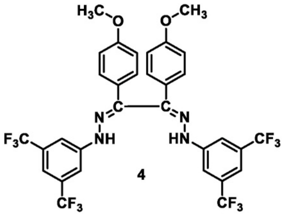
Cartesian Coordinates of the Reported Structures for Ligand-Inclusive (L) for the second reaction are presented in Appendix 2 (See Supplementary Material).

Thus, reaction 1 can end with the formation of the derivative 2Cl-VD - (E)-1-(3,5-bis (trifluoromethyl) phenyl)-2-(2,2-dichloro-1-(4-methoxyphenyl) ethyl) diazene with a significant release of energy (−38.6 kcal/mol). Similarly, reaction 2 can also end with the formation of the derivative 2Cl-VD - is (E)-4-(2-(4-(dimethylamino) benzylidene) hydrazineyl) benzonitrile and with a significantly higher release of energy (−46.8 kcal/mol). This is significantly more exergonic, indicating



Scheme 4. Stage of formation of intermediates 1 and 2.

Table 1
Calculated Gibbs energies for the formation of ((1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazinylidene)-1,2-bis(4-methoxyphenyl)ethane.

Structures	ΔG, kcal/mol
	−5.3
 1	−8,6
 2	8,4
	−38.8
	−41.6

that the overall process is more favourable for the new substrate. Based on the above, the following mechanism can be imagined for the reactions (Scheme 2):

However, practical studies have shown that under the proposed reaction conditions with (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxybenzylidene)hydrazine and with ((E)-4-(2-(4-(dimethylamino)benzylidene)hydrazinyl)benzonitrile along with the expected vinyl disenes (5–10 %), the formation of a predominantly new type of products was observed - 1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazinylidene)-1,2-bis(4-methoxyphenyl)ethane (first model) and (Z)-N, N-bis(4-cyanophenyl)-4-(dimethylamino)-N-(4-(dimethylamino)benzyl)-benzohydrazine hydrazide (second model) with a product yield of 70–78 %, respectively [11–13]. In fact, we are talking about reactions competitive with the production of dichlorovinyldiazenes.

Thus, the reaction occurring on the basis of (E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-(4-methoxybenzylidene)hydrazine can be described by the following scheme (Scheme 3):

Static analysis of the substrate electron system showed that in the hydrazone molecule, the hydrogen atom of the –NH– group is in a more mobile position (more acidic) due to conjugation with an aromatic system containing electron-withdrawing substituents. The flat structure of this type of hydrazone molecules indicates that –NH– is in the sp^2-hybrid state [14,15]. Thus, the absence of hydrogen at the nitrogen atom does not destroy the unity of the conjugated system of at least 16 p-orbitals. Moreover, the conjugation of the –NH– unshared pair of electrons with the electron-deficient aromatic ring increases the acidic nature of the hydrogen atom, so, it can easily split off with $\cdot CCl_3$, which can explain the probability of obtaining radical 1 (Scheme 4). The Gibbs energy (ΔG) calculated for this radical is −8.6 kcal/mol, which is significantly lower than that of the intermediate I1-L formed in a parallel reaction during the formation of vinyldiazene (−5.3 kcal/mol) (Table 1). Further, radical 1 transforms into radical 2, which has a direct conjugation with *para*-methoxybenzyl and the Gibbs energy value of which is −8.4 kcal/mol.

According to calculations, the Gibbs free energy of the intermediate 1,2-bis((E)-(3,5-bis(trifluoromethyl)phenyl)diazenyl)-1,2-bis(4-methoxyphenyl)ethane **(3)** is −38.8 kcal/mol, while that of its final tautomer (1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazineylidene)-1,2-bis(4-methoxephenyl)ethane **(4) is** −41.6 kcal/mol. The difference in Gibbs free energy between tautomers 3 and 4 is 2.8 kcal/mol, indicating the thermodynamic stability of the reaction adduct.

$$\Delta G = \Delta G(4) - \Delta G(3) = 3,3 \text{ kcal/mol})$$

It should be noted that trifluoromethyl groups are strong acceptors (the aromatic ring as a whole is electron-deficient), but are located in the meta position and, accordingly, there is no direct conjugation.

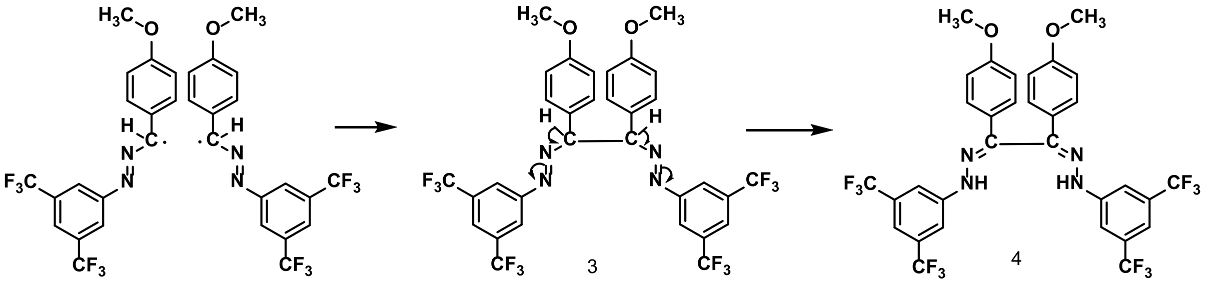
Thus, based on the Gibbs energies values presented in Table 1, the following scheme of the formation mechanism of ((1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazinylidene)-1,2-bis(4-methoxyphenyl)ethane can be presented.

As a result of the attack of the $\cdot CCl_3$ radical, intermediate 1 is formed, which can then transform into the resonance-stabilized intermediate 2 (Scheme 2).

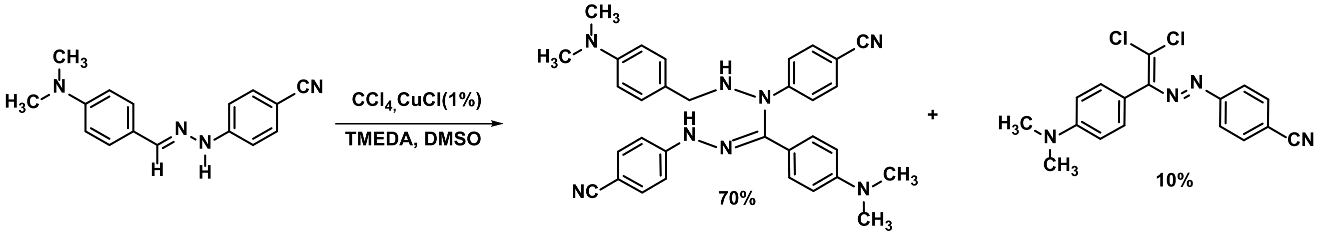
Further "crosslinking" of two radicals of 2 leads to the formation of intermediate 3 (ΔG = −38.8 kcal/mol), the tautomer of which is the "pseudo-dimer" we obtained 4 - ((1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazinylidene)-1,2-bis(4-methoxyphenyl) ethane (ΔG = −41.6 kcal/mol) (Scheme 5):

In the case of the reaction with ((E)-4-(2-(4-(dimethylamino)benzylidene)hydrazinyl) benzonitrile, ((Z)-N,N″-bis(4-cyanophenyl)-4-(dimethylamino)-N'-(4-(dimethylamino)benzyl)-benzoylhydrazinohydrazide was identified as the main product during the reaction [16] (see Scheme 6).

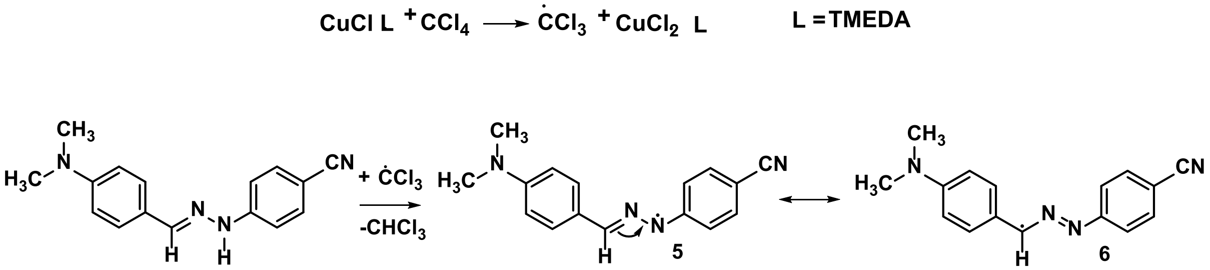
Thus, in this case, the crosslinking of the hydrazone occurs with the formation of C–N, and not C–C as shown earlier. Calculations showed that in the case of ((E)-4-(2-(4(dimethylaminobenzylidene)-hydrazinyl) benzonitrile, two resonance-stabilized radicals 5 and 6 are formed (Scheme 7). The Gibbs energy (ΔG) for radical 5 is −8.6 kcal/mol and −8.1 kcal/mol for radical 6, which is an order of magnitude less than that for the formation of the initial radical in the reaction to obtain the corresponding dichlorovinyldiazene (−6.4 kcal/mol) (Table 2).



Scheme 5. The final stage of formation of ((1Z,2Z)-1,2-bis(2-(3,5-bis(trifluoromethyl)phenyl)hydrazinylidene)-1,2-bis(4-methoxyphenyl)ethane.

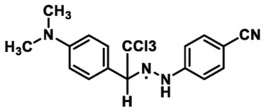
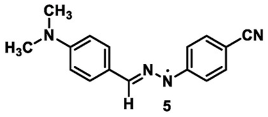
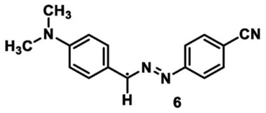
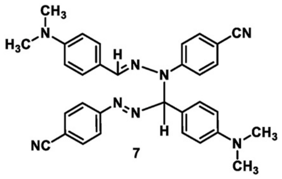
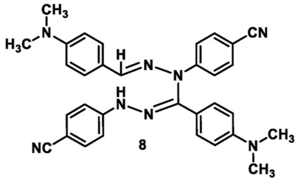
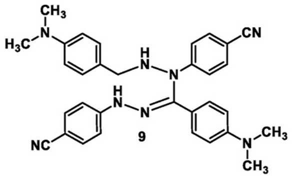


Scheme 6. General scheme of the reaction involving ((E)-4-(2-(4-(dimethylamino)benzylidene)hydrazinyl) benzonitrile.



Scheme 7. Stage of formation of radicals 3 and 4.

Table 2
Calculated Gibbs energies for the formation of ((Z)-N,N″-bis(4-cyanophenyl)-4-(dimethylamino)-N'-(4-(dimethylamino)benzyl)-benzoylhydrazinohydrazide.

Structures	ΔG, kcal/mol
	−6,4
	−8,6
	−8,1
	−46.8
	−49.9
	−54.8

Further, as a result of the crosslinking of two radicals 5 and 6, an intermediate compound 7 is formed with ΔG = −46.8 kcal/mol. The resulting intermediate is transformed into a more stable tautomer 8 ΔG = −49.9 kcal/mol. A feature of the obtained compound 8 is the presence of a methylene group instead of the expected NH system. Taking into account the activated position of the latter – the presence of an electron-donor group on one side and acceptor groups on the other, it is possible to assume hydrogenation of the latter due to hydrogen radicals formed in a parallel reaction. The hydrogenation energy of the final product (9) – (Z)-N,N″-bis(4-cyanophenyl)-4-(dimethylamino)-N'-(4-(dimethylamino) benzyl)benzohydrazonohydrazide is −54.8 kcal/mol.

The slight decrease in the energy value for this molecule is due to the large electron-donating nature of the dimethylamine group as well as the "complementary shift of the electron density towards the –CN group and its favourable location in the para position (there is a direct conjugation).

In the case of radical 5, there is direct conjugation with the benzonitrile system (Scheme 8):

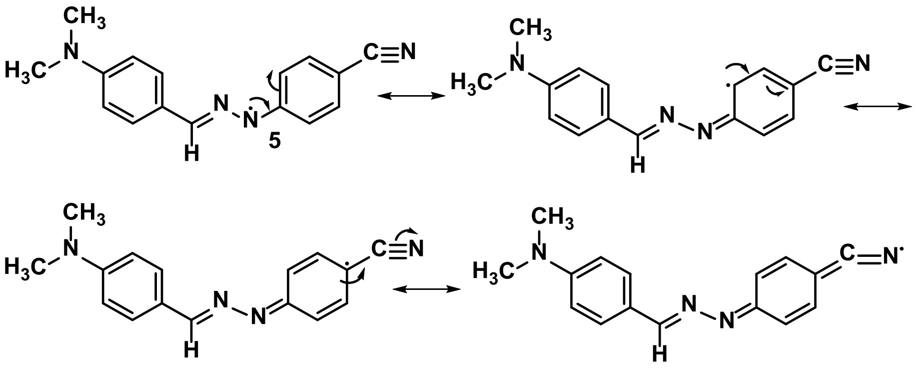
In the case of radical 6 there is also direct conjugation with the dimethylaminobenzyl system (Scheme 9):

Further, as a result of the crosslinking of two radicals 5 and 6, an intermediate compound 7 is formed with ΔG = −46,8 kcal/mol. The resulting intermediate is transformed into a more stable tautomer 8 with ΔG = −49.9 kcal/mol (Scheme 10).

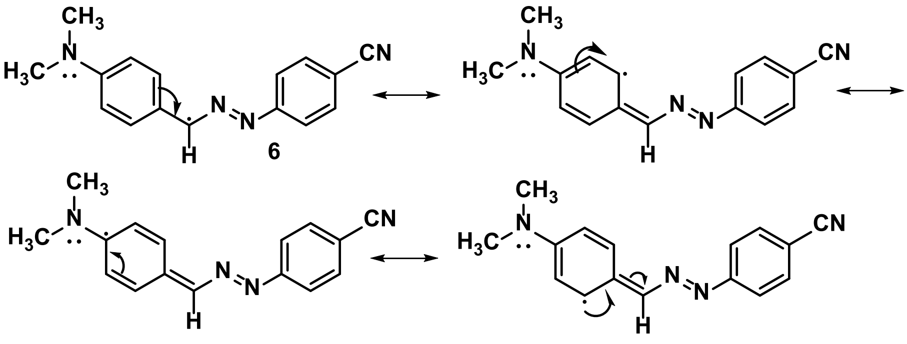
A feature of the obtained compound 8 is the presence of a methylene group instead of the expected NH system. Taking into account the activated position of the latter, the presence of an electron-donor group on one side and acceptor groups on the other, it is possible to assume hydrogenation of the latter due to hydrogen radicals formed in a parallel reaction (Scheme 11):

4. Conclusions

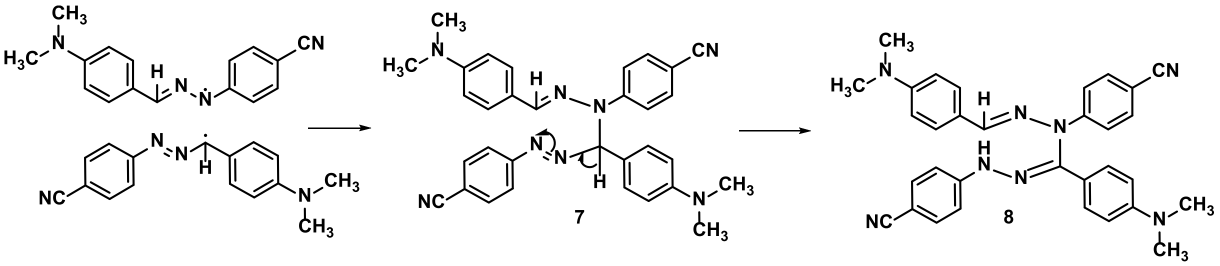
The reaction of N-substituted hydrazones with haloalkanes represents a novel and insufficiently explored area of organic synthesis. Until recently, it was believed that the primary adducts of this type of reaction were dichlorovinyl diazenes. However, for the first time, it has been shown that the introduction of electron-donating and electron-withdrawing substituents into the aromatic rings alters the electronic nature of the initial N-substituted hydrazones and, consequently, affects the course of the subsequent reactions. In addition to the formation of



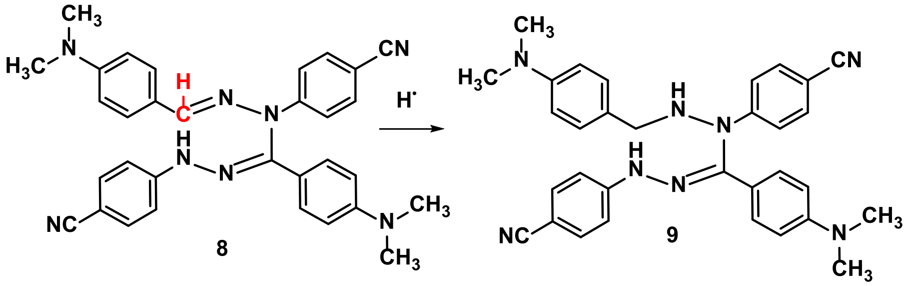
Scheme 8. Resonance structures for radical 5.



Scheme 9. Resonance structures for radical 4.



Scheme 10. Formation of intermediate 7 and 8.



Scheme 11. Hydrogenation of 8–9.

dichlorovinyl diazenes, which were previously considered as the main products of reactions of N-substituted hydrazone with CCl_4, competing reactions were observed while using (E)-1-(3,5-bis(trifluoromethyl) phenyl)-2-(4-methoxybenzylidene)hydrazine and (E)-4-(2-(4-(dimethylamino)benzylidene)hydrazineyl) benzonitrile as substrates. These competing pathways lead to "coupling" products of two hydrazone molecules, yielding pseudodimers (bis-derivatives). Utilizing the capabilities of DFT (Density Functional Theory), transition states, intermediate species, and final products energies were calculated for both reactions, viz the formation of dichlorovinyldiazenes and the newly discovered competitive pathway leading to pseudodimers. In the specific variation of substituents featuring complementary electron density distribution (electron-donating groups in the aldehyde and electron-withdrawing groups in the hydrazine part), a detailed analysis was performed using the energy span model. Analysis of the results showed that the change in the direction of the reaction is primarily associated with a change in the location of the primary attack of CCl_3 and the formation of thermodynamically more stable intermediates 1 and 5. The second factor determining the direction of the reactions, in our opinion, is also a decrease in the number of stages in obtaining bis-derivatives of hydrazones. It should be noted that the purpose of this article is to record and perform primary analysis of reactions for obtaining bis-derivatives of hydrazones, competing with reactions for obtaining dichlorovinyldiazenes. As practical material accumulates, we plan to conduct more extensive studies related to both the kinetics and thermodynamics of processes. Overall, the present study demonstrates that reactions of N-substituted hydrazones with halogen alkanes under catalytic olefination reaction conditions are a promising platform for the development of new synthetic strategies.

CRediT authorship contribution statement

Ulviyya Askerova: Writing – original draft, Methodology, Investigation, Data curation. **Alakbar Huseynzada:** Investigation, Formal analysis, Data curation. **Abel Maharramov:** Supervision, Conceptualization. **Namiq Shikhaliyev:** Writing – review & editing, Conceptualization. **Gulnar Atakishiyeva:** Resources, Investigation. **Afsun Sujayev:** Writing – review & editing, Resources, Investigation.

Conflict of interest statement

The authors declare that there are no conflicts of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jics.2025.101827.

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