ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 10, pp. 1758–1763. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Zhurnal Organicheskoi Khimii, 2020, Vol. 56, No. 10, pp. 1590–1597.

Three-Component Reaction of Dimethyl Malonate with α,β-Acetylenic Aldehydes and Amines. Synthesis of Push–Pull Buta-1,3-dienes

S. A. Sokov[a,b], I. S. Odin[b], S. S. Zlotskii[a], and A. A. Golovanov[b,*]

[a] *Ufa State Petroleum Technological University, Ufa, 450062 Russia*

[b] *Togliatti State University, Togliatti, 445020 Russia*

**e-mail: aleksandgolovanov@yandex.ru*

Received July 10, 2020; revised July 21, 2020; accepted July 25, 2020

Abstract—Three-component reaction of dimethyl malonate with α,β-acetylenic aldehydes and cyclic secondary amines (pyrrolidine, piperidine, morpholine, and piperazine) under mild conditions afforded dimethyl 2-(3-aminoprop-2-en-1-ylidene)malonates in 50–91% yields. The products were formed preferentially as *E* isomers, and the described reaction provides a convenient method for the synthesis of push–pull buta-1,3-dienes that are interesting as fluorescent, solvatochromic, and nonlinear optical materials and starting compounds in the synthesis of carbo- and heterocycles. A plausible reaction mechanism involves Knoevenage condensation of dimethyl malonate with α,β-acetylenic aldehyde to give dimethyl 2-(prop-2-yn-1-ylidene)malonate and subsequent nucleophilic addition of cyclic amine to the latter.

Keywords: multicomponent reactions, prop-2-ynals, cyclic amines, dimethyl malonate, stereoselectivity, Knoevenagel condensation, nucleophilic addition, buta-1,3-dienes

DOI: 10.1134/S1070428020100140

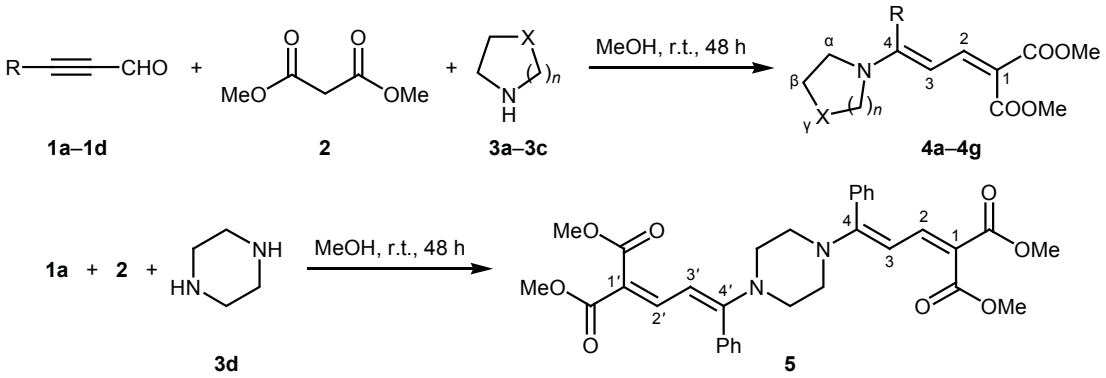
Di- and polyenes containing electron-donating and electron-withdrawing functional groups at the opposite ends of a conjugated bond chain (push–pull di- and polyenes) possess a combination of valuable physical and chemical properties. Due to strong polarization of the π-electron system, such compounds exhibit fluorescence [1, 2] and solvatochromic properties [3, 4] and are promising as dyes [5, 6] and nonlinear optical materials [7, 8]. Push–pull dienes are used in organic synthesis, in particular for the preparation of carbo- and heterocycles [9–11] and polyunsaturated carbonyl compounds [12]. Development of simple and efficient procedures for the synthesis of push–pull di- and polyenes from accessible starting materials is of great importance for the design of modern smart materials and organic synthesis.

We previously synthesized 5-amino- and 5-sulfanylpenta-2,4-dien-1-ones by nucleophilic addition of the corresponding amines and thiols to activated enynes [13–15] which were prepared in turn by condensation of prop-2-ynals with carbonyl compounds containing an active methylene group [13, 16]. It seemed reasonable to combine the stages of preparation of activated enyne and nucleophilic addition into a single three-component synthetic procedure. Therefore, the present work was aimed at developing a one-pot procedure for the synthesis of push–pull buta-1,3-dienes by three-component condensation of dimethyl malonate, α,β-acetylenic aldehyde, and cyclic amine.

As expected, 3-phenylprop-2-ynal (**1a**) reacted with dimethyl malonate (**2**) and pyrrolidine (**3a**) in methanol to give the target product, dimethyl 2-[3-(pyrrolidin-1-yl)-3-phenylprop-2-en-1-ylidene]malonate (**4a**). In the optimal case, an equimolar amount of amine **3a** was added to a solution of ester **2** and aldehyde **1a**. The addition of **3a** was accompanied by strong evolution of heat, so that cooling of the reaction mixture in the initial period was necessary. Under these conditions, the maximum yield of **4a** (91%) was achieved in 48 h. Likewise, the reactions of aldehydes **1a**–**1d** with dimethyl malonate (**2**) and amines **3a**–**3c** afforded 50–82% of **4a**–**4g** (Scheme 1).

In the reaction of aldehyde **1a** with ester **2** and piperazine (**3d**) (molar reactant ratio 1:1:0.5) we isolated tetraester **5** but with a lower yield (42%). It should

Scheme 1.



1, R^1 = Ph (**a**), 4-MeC_6H_4 (**b**), Me (**c**), 5-bromofuran-2-yl (**d**); **3**, X = CH_2, *n* = 1 (**a**); X = CH_2, *n* = 2 (**b**); X = O, *n* = 2 (**c**); X = NH, *n* = 2 (**d**); **4**, R = Ph, X = CH_2, *n* = 1 (**a**); R = Ph, X = CH_2, *n* = 2 (**b**); R = Ph, X = O, *n* = 2 (**c**); R = 4-MeC_6H_4, X = CH_2, *n* = 2 (**d**); R = 4-MeC_6H_4, X = O, *n* = 2 (**e**); R = Me, X = CH_2, *n* = 2 (**f**); R = 5-bromofuran-2-yl, X = CH_2, *n* = 2 (**g**).

be noted that we failed to isolate the corresponding monoadduct like **4** even when excess amine (1–1.5 equiv) was used. Similar results were obtained previously in the reactions of piperazine with 1,5-diarylpent-2-en-4-yn-1-ones [17].

According to the ^{1}H NMR and TLC data, compounds **4a**–**4g** and **5** were isolated as almost pure stereoisomers. The double C^3=C^4 bond was reliably assigned *E* configuration on the basis of the two-dimensional ^{1}H–^{1}H NOESY spectrum which showed a correlation between the H_α and 3-H protons (Fig. 1a). According to the ^{1}H–^{13}C HMQC and HMBC spectra, the 2-H and 3-H protons of the diene fragment resonated at δ 7.3–8.1 and 6.2–7.0 ppm, respectively ($^3J_{HH}$ = 12.5–13.1 Hz). The C^1 ($C^{1'}$), C^2 ($C^{2'}$), C^3 ($C^{3'}$), and C^4 ($C^{4'}$) signals were located at δ_C 104–112, 150–153, 98–101, and 152–166 ppm, respectively, in the ^{13}C NMR spectra; their positions demonstrated charge alternation typical of conjugated π-systems. The ester groups are magnetically nonequivalent, and their signals appeared separately in both proton and carbon spectra.

The fraction of the corresponding *Z* isomers did not exceed 5%. We succeeded in partially characterizing by ^{1}H NMR data minor isomers (*Z*)-**4c** and (*Z*)-**g** (see Experimental) whose concentration in the reaction mixture was the largest among to the other derivatives.

A probable mechanism of the three-component condensation is shown in Scheme 2. We believe that the reaction begins with 1,2-addition of amine **3** to aldehyde **1** [18] with the formation of adduct **A** which then reacts with anion **B** generated from ester **2** by the action of base **3**. The subsequent protonation and dehydration lead to dimethyl 2-(1-aminoprop-2-yn-1-yl)malonate **6**, and elimination of secondary amine from the latter yields conjugated enyne **7**. It should be noted that the formations of intermediate products **A**, **6**, and **7** are, in fact, the main stages of the Knoevenagel condensation. Final products (*E*)-**4** and (*Z*)-**4** are formed as a result of nucleophilic addition of amine **3** to the triple bond of enyne **7**.

We succeeded in confirming intermediacy of compounds **6** and **7** and their role in the overall mechanism. For this purpose, the reaction of aldehyde **1a** with dimethyl malonate (**2**) and morpholine (**3c**) was carried out on cooling. After 1 h, compound **6a** separated as a colorless powder (yield 56%). When a solution of **6a** in ethanol was kept at room temperature for 48 h, it

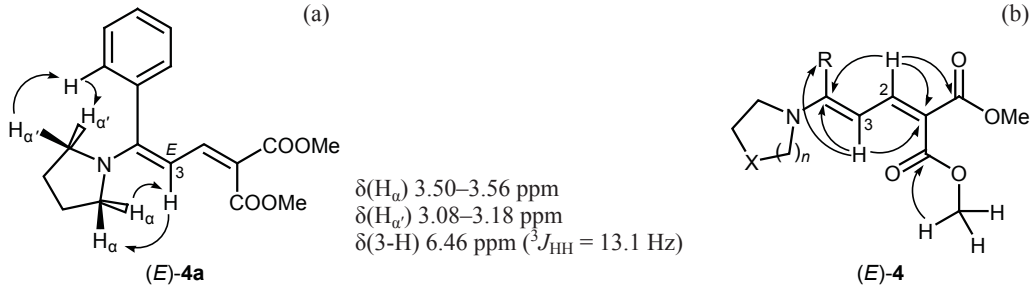
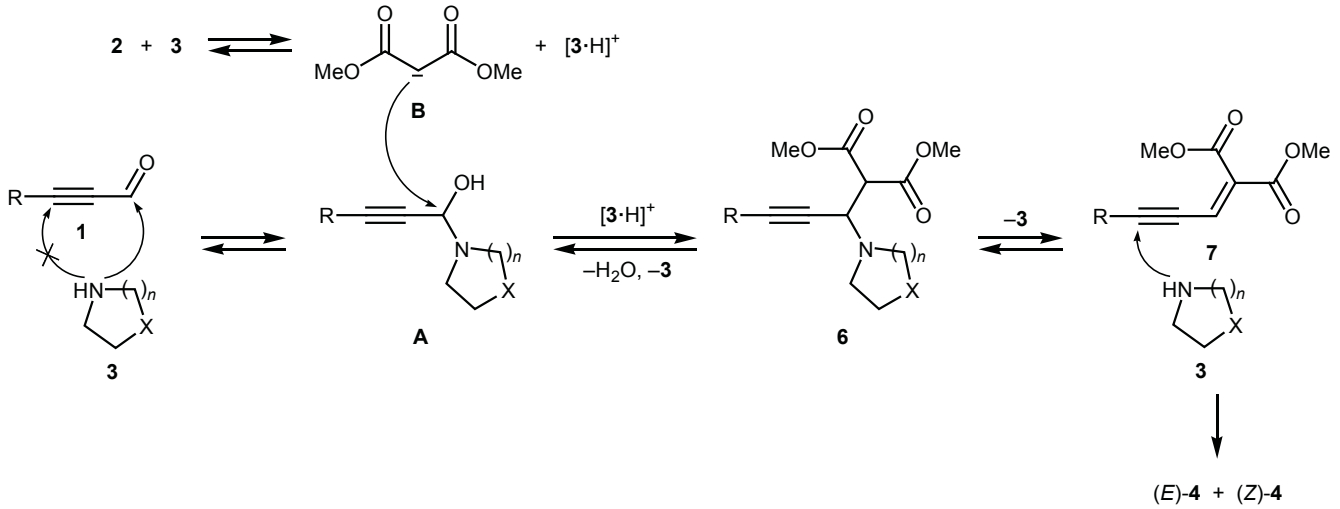


Fig. 1. Principal correlations in the (a) NOESY and (b) HMQC and HMBC spectra of compound (*E*)-**4a**.

Scheme 2.



was completely converted to push–pull buta-1,3-diene (*E*)-**4c** with an impurity of isomer (*Z*)-**4c** (Scheme 3).

Dimethyl 2-(3-phenylprop-2-yn-1-ylidene)malonate (**7a**) was synthesized independently by heating aldehyde **1a** with ester **2** in acetic anhydride [19]. Conjugated enyne **7** reacted with piperidine (**3b**) under the same conditions as for the three-component reaction to afford 65% of (*E*)-**4b** with an impurity of its *Z* isomer.

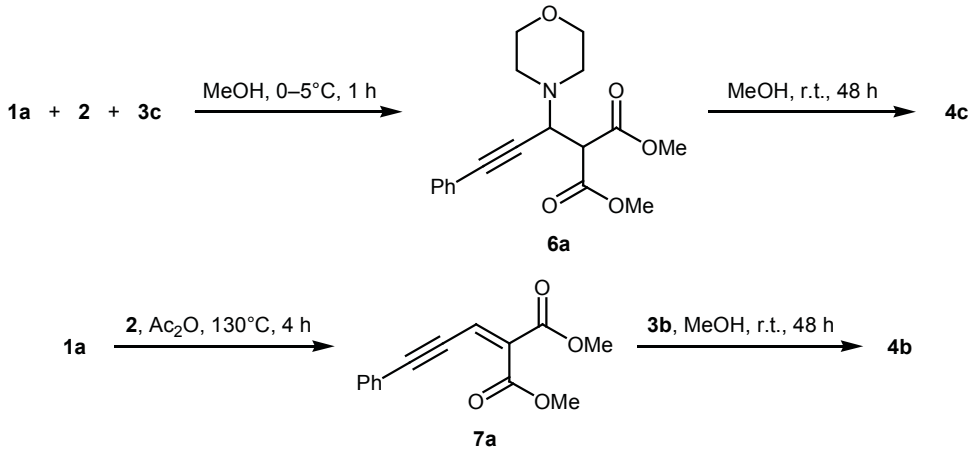
Thus, we have developed a one-pot procedure for the stereoselective synthesis of push–pull buta-1,3-dienes by three-component condensation of preparatively accessible [20] α,β-acetylenic aldehydes, dimethyl malonate, and cyclic secondary amines. The reaction involves initial formation of the corresponding Knoevenagel condensation product [dimethyl 2-(prop-2-yn-1-ylidene)malonate], followed by nucleophilic addition of cyclic amine to the triple bond of intermediate conjugated enyne.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded at 25°C on a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ (or C_6D_6 for **6a**) as solvent and reference. The IR spectra were recorded in KBr on an FSM-1201 spectrometer with Fourier transform. Elemental analyses for carbon, hydrogen, and bromine were carried out by express gravimetry using standard equipment [21]. The reaction mixtures were analyzed, and the purity of the isolated products was checked, by TLC on Sorbfil plates using ethyl acetate–petroleum ether (1:5) as eluent; spots were visualized by treatment with iodine vapor. The melting points were measured in open capillaries and are uncorrected.

Initial cyclic amines and dimethyl malonate were commercial products. α,β-Acetylenic aldehydes were synthesized as described in [20].

Scheme 3.



Dimethyl 2-(3-aminoprop-2-en-1-ylidene)malonates 4a–4g (*general procedure*). A solution of 3 mmol of aldehyde **1a**–**1d** and 3 mmol of dimethyl malonate (**2**) in 1.5 mL of methanol was cooled with ice, and 3 mmol of amine **3a**–**3c** or a solution of 129 mg (1.5 mmol) of piperazine (**3d**) in 0.5 mL of methanol was added dropwise with stirring. The mixture was stirred for 48 h at room temperature and cooled with an ice–salt mixture, and the precipitate was rapidly filtered off, washed on a filter with a minimum amount of ice-cold methanol, and dried in air.

Dimethyl (*E*)-2-[3-phenyl-3-(pyrrolidin-1-yl)-prop-2-en-1-ylidene]malonate [(*E*)-4a]. Yield 861 mg (91%), yellow prisms, mp 97–98°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1694, 1674. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.82–1.90 m (2H, β-H), 2.01–2.06 m (2H, β-H), 3.08–3.13 m (2H, α-H), 3.50–3.56 m (2H, α-H), 3.60 s (3H, OMe), 3.82 s (3H, OMe), 6.46 d (1H, 3-H, $^3J_{HH}$ = 13.1 Hz), 7.23–7.26 m (2H, H_{arom}), 7.39 d (1H, 2-H, $^3J_{HH}$ = 13.1 Hz), 7.45–7.48 m (3H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.0 (C^{β}), 25.3 (C^{β}), 48.7 (C^{α}), 51.2 (OMe), 51.3 (OMe), 99.2 (C^3), 105.0 (C^1), 128.6 (C_{arom}), 128.7 (C_{arom}), 129.3 (C_{arom}), 134.9 (C_{arom}), 152.7 (C^2), 163.2 (C^4), 167.7 (C=O), 168.0 (C=O). Found, %: C 68.61; H 6.79. $C_{18}H_{21}NO_4$. Calculated, %: C 68.55; H 6.71.

Dimethyl (*E*)-2-[3-phenyl-3-(piperidin-1-yl)prop-2-en-1-ylidene]malonate [(*E*)-4b]. Yield 692 mg (70%), yellow needles, mp 82–83°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1694, 1674. ^1H NMR spectrum, δ, ppm: 1.64–1.71 m (6H, β-H, γ-H), 3.31–3.42 m (4H, α-H), 3.61 s (3H, OMe), 3.83 s (3H, OMe), 6.62 d (1H, 3-H, $^3J_{HH}$ = 12.8 Hz), 7.25–7.28 m (2H, H_{arom}), 7.34 d (1H, 2-H, $^3J_{HH}$ = 12.8 Hz), 7.46–7.51 m (3H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 24.3 (C^{γ}), 26.0 (C^{β}), 49.9 (C^{α}), 51.3 (OMe), 51.4 (OMe), 99.4 (C^3), 106.9 (C^1), 128.7 (C_{arom}), 129.4 (C_{arom}), 129.6 (C_{arom}), 134.9 (C_{arom}), 153.1 (C^2), 165.3 (C^4), 167.4 (C=O), 167.8 (C=O). Found, %: C 69.44; H 7.12. $C_{19}H_{23}NO_4$. Calculated, %: C 69.28; H 7.04.

Dimethyl (*E*)-2-[3-(morpholin-4-yl)-3-phenyl-prop-2-en-1-ylidene]malonate [(*E*)-4c]. Yield 815 mg (82%), yellow prisms, mp 97–98°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1685, 1674. ^1H NMR spectrum, δ, ppm: 3.25–3.27 m (4H, β-H), 3.64 s (3H, OMe), 3.73–3.76 m (4H, α-H), 3.84 s (3H, OMe), 6.47 d (1H, 3-H, $^3J_{HH}$ = 12.8 Hz), 7.26–7.30 m (2H, H_{arom}), 7.34 d (1H, 2-H, $^3J_{HH}$ = 12.5 Hz), 7.46–7.50 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 48.8 (C^{α}), 51.57 (OMe), 51.58 (OMe), 66.5 (C^{β}), 100.0 (C^3), 110.7 (C^1), 128.8 (C_{arom}), 129.7 (C_{arom}), 129.9 (C_{arom}), 134.2 (C_{arom}), 151.0 (C^2), 164.3 (C^4), 167.0 (C=O), 167.5 (C=O). Found, %: C 65.64; H 6.61. $C_{18}H_{21}NO_5$. Calculated, %: C 65.24; H 6.39.

Dimethyl (*Z*)-2-[3-(morpholin-4-yl)-3-phenyl-prop-2-en-1-ylidene]malonate [(*Z*)-4c] was characterized as a minor impurity in the reaction mixture. ^1H NMR spectrum: δ 6.88 ppm, d (1H, $^3J_{HH}$ = 8.9 Hz); no other signals were identified.

Dimethyl (*E*)-2-[3-(4-methylphenyl)-3-(piperidin-1-yl)prop-2-en-1-ylidene]malonate [(*E*)-4d]. Yield 670 mg (65%), yellow needles, mp 119–120°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1703, 1683. ^1H NMR spectrum, δ, ppm: 1.59–1.74 m (6H, β-H, γ-H), 2.42 s (3H, **Me**C_6H_4), 3.24–3.42 m (4H, α-H), 3.61 s (3H, OMe), 3.82 s (3H, OMe), 6.95 d (1H, 3-H, $^3J_{HH}$ = 12.8 Hz), 7.13–7.16 m (2H, H_{arom}), 7.24–7.31 m (2H, H_{arom}), 7.38 d (1H, 2-H, $^3J_{HH}$ = 12.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.4 (**Me**C_6H_4), 24.3 (C^{γ}), 26.0 (C^{β}), 50.0 (C^{α}), 51.2 (OMe), 51.3 (OMe), 99.5 (C^3), 106.4 (C^1), 129.4 (2C, C_{arom}), 131.8 (C_{arom}), 139.7 (C_{arom}), 153.4 (C^2), 165.7 (C^4), 167.5 (C=O), 167.9 (C=O). Found, %: C 69.77; H 7.50. $C_{20}H_{25}NO_4$. Calculated, %: C 69.95; H 7.34.

Dimethyl (*E*)-2-[3-(4-methylphenyl)-3-(morpholin-4-yl)prop-2-en-1-ylidene]malonate [(*E*)-4e]. Yield 518 mg (50%), yellow needles, mp 118–119°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1702, 1685. ^1H NMR spectrum, δ, ppm: 2.42 s (3H, **Me**C_6H_4), 3.24–3.27 m (4H, β-H), 3.64 s (3H, OMe), 3.69–3.76 m (4H, α-H), 3.83 s (3H, OMe), 6.43 d (1H, 3-H, $^3J_{HH}$ = 12.5 Hz), 7.15 d (2H, H_{arom}, $^3J_{HH}$ = 7.9 Hz), 7.25–7.30 m (2H, H_{arom}), 7.38 d (1H, 2-H, $^3J_{HH}$ = 12.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.4 (**Me**C_6H_4), 48.8 (C^{α}), 51.5 (OMe), 51.6 (OMe), 66.6 (C^{β}), 99.9 (C^3), 110.3 (C^1), 129.5 (C_{arom}), 129.7 (C_{arom}), 131.1 (C_{arom}), 140.0 (C_{arom}), 151.3 (C^2), 164.7 (C^4), 167.1 (C=O), 167.5 (C=O). Found, %: C 66.37; H 6.82. $C_{19}H_{23}NO_5$. Calculated, %: C 66.07; H 6.71.

Dimethyl (*E*)-2-[3-(piperidin-1-yl)but-2-en-1-ylidene]malonate [(*E*)-4f]. Yield 615 mg (80%), orange needles, mp 91–92°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1687, 1680. ^1H NMR spectrum, δ, ppm: 1.61–1.69 m (6H, β-H, γ-H), 2.18 s (3H, Me), 3.48–3.50 m (4H, α-H), 3.74 s (3H, OMe), 3.79 s (3H, OMe), 6.54 d (1H, 3-H, $^3J_{HH}$ = 13.1 Hz), 8.11 d (1H, 2-H, $^3J_{HH}$ = 12.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.3 (Me), 24.3 (C^{γ}), 25.9 (C^{β}), 48.8 (C^{α}), 51.2 (OMe), 51.4 (OMe), 97.7 (C^3), 104.2 (C^1), 151.0 (C^2), 160.9 (C^4), 167.9 (C=O), 168.1 (C=O). Found, %: C 63.07; H 7.83. $C_{14}H_{21}NO_4$. Calculated, %: C 62.90; H 7.92.

Dimethyl (*E*)-2-[3-(5-bromofuran-2-yl)-3-(piperidin-1-yl)prop-2-en-2-ylidene]malonate [(*E*)-4g]. Yield 645 mg (54%), yellow needles, mp 92–93°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1701, 1681. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.65–1.71 m (6H, β-H, γ-H), 3.22–3.25 m (4H, α-H), 3.72 s (3H, OMe), 3.83 s (3H, OMe), 6.43 d (1H, 3-H, $^3J_{HH}$ = 12.5 Hz), 6.47 d and 6.58 d (1H each, 3′-H, 4′-H, $^3J_{HH}$ = 3.4 Hz), 7.74 d (1H, 2-H, $^3J_{HH}$ = 12.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.3 (C^{γ}), 25.7 (C^{β}), 50.4 (C^{α}), 51.5 (OMe), 51.7 (OMe), 101.4 (C^3), 110.2 (C^1), 113.3 and 118.9 ($C^{3'}$, $C^{4'}$), 124.8 and 148.5 ($C^{2'}$, $C^{5'}$), 149.9 (C^2), 151.8 (C^4), 167.1 (C=O), 167.4 (C=O). Found, %: C 51.52; H 5.27; Br 19.60. $C_{17}H_{20}BrNO_5$. Calculated, %: C 51.27; H 5.06; Br 20.06.

Dimethyl (*Z*)-2-[3-(5-bromofuran-2-yl)-3-(piperidin-1-yl)prop-2-en-1-ylidene]malonate [(*Z*)-4g] was characterized as a minor impurity in the reaction mixture. ^1H NMR spectrum, δ, ppm: 6.33 d (1H, H_{Fu}, $^3J_{HH}$ = 3.4 Hz), 6.62 d (1H, H_{Fu}, $^3J_{HH}$ = 3.4 Hz); no other signals were identified.

Tetramethyl 2,2′-[(2*E*,2′*E*)-piperazine-1,4-diylbis(3-phenylprop-2-en-3-yl-1-ylidene)]dimalonate [(*E*)-5]. Yield 724 mg (42%), yellow powder, mp 224–225°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 1721, 1699. ^1H NMR spectrum, δ, ppm: 3.29–3.37 m (8H, α-H, β-H), 3.63 s (6H, OMe), 3.82 s (6H, OMe), 6.41 d (2H, 3-H, $^3J_{HH}$ = 12.5 Hz), 7.25–7.29 m (4H, H_{arom}), 7.30 d (2H, 2-H, $^3J_{HH}$ = 12.5 Hz), 7.44–7.50 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 47.8 (C^{α}, C^{β}), 51.60 (OMe), 51.61 (OMe), 100.3 (C^3), 111.6 (C^1), 128.9 (C_{arom}), 129.6 (C_{arom}), 130.0 (C_{arom}), 134.0 (C_{arom}), 150.3 (C^2), 163.3 (C^4), 166.8 (C=O), 167.3 (C=O). Found, %: C 66.65; H 6.13. $C_{32}H_{34}N_2O_8$. Calculated, %: C 66.89; H 5.96.

Dimethyl 2-[1-(morpholin-4-yl)-3-phenylprop-2-yn-1-yl]malonate (6a). The amounts of the reactants were the same as in the synthesis of **4c**, but the reaction mixture was stirred for 1 h at 0–5°C, and the precipitate of **6a** was rapidly filtered off, washed on a filter with a minimum amount of ice-cold methanol, and dried for 1 h under reduced pressure. Yield 553 mg (56%), colorless powder, mp 89–90°C (from petroleum ether). IR spectrum: ν 1740 cm^{-1}. ^1H NMR spectrum, δ, ppm: 2.55–2.62 m and 3.10–3.14 m (4H, α-H), 3.33 s (3H, OMe), 3.36 s (3H, OMe), 3.44–3.57 m (4H, β-H), 3.99 d (1H, 1-H, $^3J_{HH}$ = 11.3 Hz), 4.59 d (1H, 2-H, $^3J_{HH}$ = 11.3 Hz), 7.35–7.42 m (2H, H_{arom}), 6.94–7.00 m (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 50.9 (C^{α}), 51.6 (OMe), 51.8 (OMe), 55.9 (CH), 57.5 (CH), 65.9 (C^{α}), 66.8 (C^{β}), 83.7 and 87.8 (C≡C), 128.2 (C_{arom}), 128.4 (C_{arom}), 129.6 (C_{arom}), 131.9 (C_{arom}), 166.5 (C=O), 166.6 (C=O). Found, %: C 65.43; H 6.47. $C_{18}H_{21}NO_5$. Calculated, %: C 65.24; H 6.39.

Isomerization of compound 6a to 1,3-diene 4c. A solution of 331 mg of compound **6a** in 1.5 mL of methanol was kept at room temperature until the conversion was complete (48 h, TLC). The solvent was removed under reduced pressure, and the residue was rerecrystallized from petroleum ether to obtain 249 mg (75%) of (*E*)-**4c**.

Dimethyl 2-(3-phenylprop-2-yn-1-ylidene)malonate (7a) [19]**.** A mixture of 2.56 g (19.7 mmol) of aldehyde **1a**, 6.99 g (52.9 mmol) of dimethyl malonate **2**, and 3 mL of acetic anhydride was stirred for 4 h at 130°C. The product was isolated by vacuum distillation in a nitrogen atmosphere. Yield 3.61 mg (75%), light yellow liquid which crystallized to form colorless needles on storage, bp 190–191°C (3 mm Hg), mp 46–46.5°C (from petroleum ether). IR spectrum, ν, cm^{-1}: 2199, 1734, 1703, 1688. ^1H NMR spectrum, δ, ppm: 3.86 s (3H, OMe), 3.94 s (3H, OMe), 7.16 s (1H, ≡CCH), 7.33–7.48 m (3H, H_{arom}), 7.48–7.54 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 52.5 (OMe), 52.7 (OMe), 84.7 and 105.4 (C≡C), 121.8, 125.9, 128.6, 130.0, 132.3, 134.3, 163.7 (C=O), 164.6 (C=O). Found, %: C 68.59; H 4.74. $C_{14}H_{12}O_4$. Calculated, %: C 68.85; H 4.95.

Nucleophilic addition of morpholine (3c) to enyne 7a. A solution of 244 mg (1 mmol) of enyne **7a** and 96 mg (1.1 mmol) of morpholine (**3c**) in 1.5 mL of methanol was kept at room temperature for 48 h. The mixture was cooled to 0°C, and the precipitate of (*E*)-**4c** was filtered off, washed with a minimum amount of ice-cold methanol, and dried in air. Yield 255 mg (77%).

ACKNOWLEDGMENTS

The authors thank K.V. Gordon for performing elemental analyses.

FUNDING

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 20-33-80004/20).

CONFLICT OF INTEREST

The authors declare the absence of conflict of interest.

REFERENCES

1. Kopchuk, D.S., Chepchugov, N.V., Taniya, O.S., Khasanov, A.F., Giri, K., Kovalev, I.S., Santra, S., Zyryanov, G.V., Majee, A., Rusinov, V.L., and Chupakhin, O.N., *Tetrahedron Lett*., 2016, vol. 57, p. 5639. https://doi.org/10.1016/j.tetlet.2016.11.008
2. Fayed, T.A., Etaiw, S.E.D.H., and Saleh, N.Z., *J. Lumin*., 2006, vol. 121, p. 431. https://doi.org/10.1016/j.jlumin.2005.11.006
3. Metelina, A.V., Lokshin, V., Micheau, J.C., Samat, A., Guglielmetti, R., and Minkin, V.I., *Phys. Chem. Chem. Phys*., 2002, vol. 4, p. 4340. https://doi.org/10.1039/B204603B
4. Lanke, S.K. and Sekar, N., *J. Fluoresc*., 2016, vol. 26, p. 949. https://doi.org/10.1007/s10895-016-1783-6
5. Gabbutt, C.D., Hepworth, J.D., Heron, B.M., Partington, S.M., and Thomas, D.A., *Dyes Pigm*., 2001, vol. 49, p. 65. https://doi.org/10.1016/S0143-7208(01)00005-5
6. Nakatsuji, Sh.-i., Yahiro, T., Nakashima, K., Akiyama, Sh., and Nakazumi, H., *Bull. Chem. Soc. Jpn*., 1991, vol. 64, p. 1641. https://doi.org/10.1246/bcsj.64.1641
7. Williams, D.J., *Angew. Chem., Int. Ed. Engl*., 1984, vol. 23, p. 690. https://doi.org/10.1002/anie.198406901
8. Laage, D., Thompson, W.H., Balanchard-Desce, M., and Hynes, J.T., *J. Phys. Chem. A*, 2003, vol. 107, p. 6032. https://doi.org/10.1021/jp0276597
9. Branchadell, V., Sodupe, M., Ortuno, R.M., Oliva, A., Gomez-Pardo, D., Guingant, A., and D'Andelo, J., *J. Org. Chem*., 1991, vol. 56, p. 4135. https://doi.org/10.1021/jo00013a012
10. Gillard, M., T'Kint, C., Sonveaux, E., and Ghosez, L., *J. Am. Chem. Soc*., 1979, vol. 101, p. 5837. https://doi.org/10.1021/ja00513a069
11. Yoshimatsu, M., Hibino, M., Ishida, M., Tanabe, G., and Muraoka, O., *Chem. Pharm. Bull*., 2002, vol. 50, p. 1520. https://doi.org/10.1248/cpb.50.1520
12. Orlewska, C., Shaker, R.M., Dees, M., and Otto, H.-H., *Monatsh. Chem*., 2000, vol. 131, p. 889. https://doi.org/10.1007/s007060070066
13. Sokov, S.A., Odin, I.S., Gusev, D.M., Kunavin, Yu.A., Vologzhanina, A.V., Voronova, E.D., and Golovanov, A.A., *Russ. Chem. Bull., Int. Ed*., 2020, vol. 69, p. 305. https://doi.org/10.1007/s11172-020-2761-3
14. Golovanov, A.A., Odin, I.S., Vologzhanina, A.V., Bekin, V.V., and Nebritova, A.E., *Russ. J. Org. Chem*., 2014, vol. 50, p. 943. https://doi.org/10.1134/S1070428014070045
15. Golovanov, A.A., Gusev, D.M., Vologzhanina, A.V., Bekin, V.V., and Pisareva, V.S., *Russ. J. Org. Chem*., 2014, vol. 50, p. 13. https://doi.org/10.1134/S1070428014010035
16. Golovanov, A.A., Latypova, D.R., Bekin, V.V., Pisareva, V.S., Vologzhanina, A.V., and Dokichev, V.A., *Russ. J. Org. Chem*., 2013, vol. 49, p. 1264. https://doi.org/10.1134/S1070428013090030
17. Golovanov, A.A., Bekin, V.V., Odin, I.S., Chertov, A.Yu., Grigor'eva, O.B., and Pisareva, V.S., *Russ. J. Org. Chem*., 2015, vol. 51, p. 1688. https://doi.org/10.1134/S1070428015120039
18. Medvedeva, A.S., Mareev, A.V., and Demina, M.M., *Russ. Chem. Bull., Int. Ed*., 2008, vol. 57, p. 929. https://doi.org/10.1007/s11172-008-0128-2
19. Belil, C., Pascual, J., and Serratosa, F., *Tetrahedron*, 1964, vol. 20, p. 2701. https://doi.org/10.1016/S0040-4020(01)90851-8
20. Gusev, D.M., Bormotin, A.A., Rakshin, S.O., Mel'nikov, P.A., Raskil'dina, G.Z., and Chanyshev, R.R., *Bashk. Khim. Zh*., 2018, vol. 25, p. 90. https://doi.org/10.17122/bcj-2018-1-90-95
21. Klimova, V.A., *Osnovnye mikrometody analiza organicheskikh soedinenii* (Main Methods for Micro Analysis of Organic Compounds), Moscow: Khimiya, 1975.