Synthesis and unusual [2+2] cycloaddition reactions of haloacetylenes activated with the trifluoroacetyl group

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Halogenated trifluoroacetylacetylenes have been synthesized for the first time. It was shown that they undergo formally forbidden by the orbital-symmetry rules [2+2] cycloaddition reactions with nonactivated alkenes in the absence of light and catalyst. A possible mechanism for this transformation is suggested.

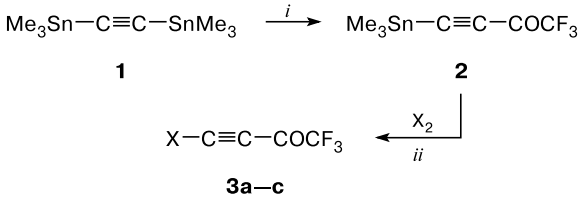
Key words: trifluoroacetylacetylenes, [2+2] cycloaddition reactions, ene reactions.

Cycloaddition reactions is one of the most simple and versatile methods for construction of various carbo- and heterocycles.[1] Though the thermal concerted [2+2] cycloaddition with participation of two alkene molecules or alkene and alkyne molecules is forbidden by the Woodward—Hoffmann orbital-symmetry rules, such processes take place under the UV light.[2] It is also known that polyfluorinated alkenes upon heating react with alkenes and acetylenes by the radical mechanism to form cyclobutanes and cyclobutenes,[3] in addition, in some cases the addition can be catalyzed by Lewis acids[4,5] or transition metal complexes.[6,7] When light and catalyst are absent, the process is possible only for the reactions of electron-withdrawing and electron-donating unsaturated compounds, when a high asymmetry of the transition state is present up to the formation of zwitterionic intermediates,[8] which is characteristic of the stepwise rather than concerted reactions.

Though trifluoroacetyl group belongs to the strongest mesomeric acceptors and is extremely prospective in further transformations of cycloadducts, so far in the literature there are described only separate examples of the Diels—Alder reactions involving trifluoroacetylacetylenes.[9—11] In the last years, we began to study the earlier unknown 1-trifluoroacetyl-2-haloacetylenes,[12,13] the presence of trifluoroacetyl group in which allowed us to suggest that they must exhibit properties of extremely active electrophiles. In the present work, we describe a general method for the synthesis of these compounds and their unusual [2+2] cycloaddition reactions to nonactivated alkenes.

In the first step of our research, it was found that easily available bis(trimethylstannyl)acetylene **1** exothermically reacts with trifluoroacetic anhydride to form 1,1,1-trifluoro-4-(trimethylstannyl)but-3-yn-2-one **2**, which is a stable and distillable *in vacuo* compound. Halogenation of the latter occurs rapidly under mild conditions and leads to the earlier unknown target acetylenes **3a—c** in high yields (Scheme 1), which have proved thermally stable compounds. For instance, chloride **3a** and bromide **3b** were distilled without decomposition even under atmospheric pressure.

Scheme 1



X = Cl (**a**), Br (**b**), I (**c**)

i. $(CF_3CO)_2O$, 20 °C, THF. *ii*. PhCOOEt or CS_2.

We used ^1H NMR method in the study of the reaction of bromide **3b** with isoprene, which leads to a complex mixture of products, and noticed that one of them was formed not by the Diels—Alder reaction. This allowed us to suggest that acetylene **3b** can react with simple alkene (Scheme 2).

Even first experiments not only confirmed this suggestion, but also led to striking results: it was found that compound **3b** forms with alkenes [2+2] cycloaddition products **5** in the absence of light and catalyst, with excess

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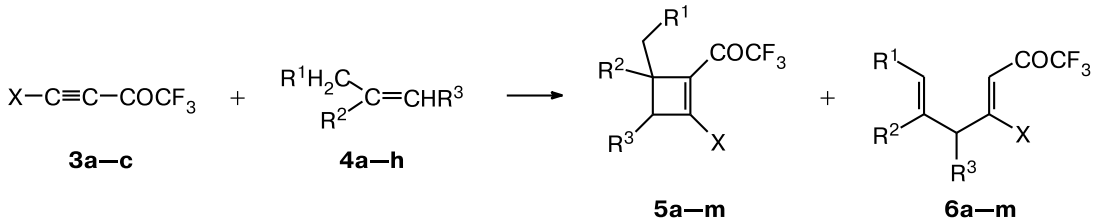
Scheme 2



X = Cl (**3a**), Br (**3b**), I (**3c**)

alkene serving as a solvent (Scheme 3). In the case of 1,1-disubstituted alkenes, the reaction rapidly takes place already at 20 °C, for addition of 1,2-disubstituted alkenes heating to 70—80 °C is required (Table 1). According to the ^{1}H NMR data, parallel formation of isomeric ene addition products **6** is observed, amount of which depends on the nature of alkene. Chloride **3a**, which has been so far studied by us only in the reactions with isobutylene, methylenecyclohexane, and methylenecyclopentane, in its activity is comparable with the bromide, however, it reacts with alkenes somewhat more selectively, exhibiting higher tendency to the formation of cyclobutenes. Iodide **3c**, which has been also studied only in the reactions with isobutylene and methylenecyclohexane, exhibits the lowest activity and has higher tendency to the ene addition.

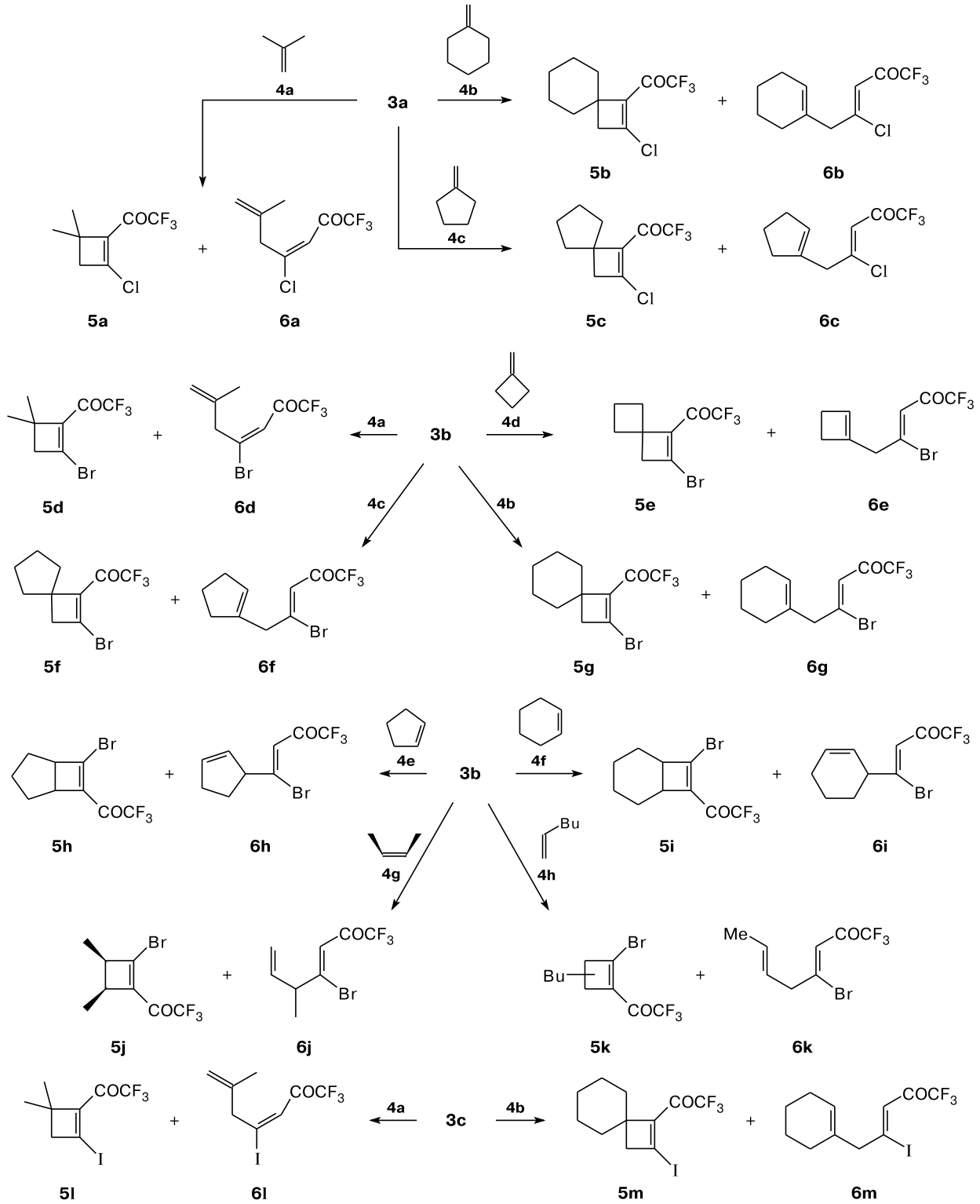
Table 1. Reactions of haloacetylenes **3a—c** with alkenes

Acetylene	Conditions		Products and their ratio	Total yield (%)	B.p./°C (*p*/Torr)
	T/°C	τ/h			
3a	20	120	**5a** : **6a** 4 : 1	92	42—60 (8)
3a	20	72	**5b** : **6b** 10 : 1	94	52—56 (1)
3a	20	72	**5c** : **6c** 1 : 2	83	38—50 (1)
3b	20	96	**5d** : **6d** 2 : 1	85	56—70 (7)
3b	20	72	**5e** : **6e** 3 : 1	90	45—50 (1)
3b	20	48	**5f** : **6f** 1 : 3	76	53—62 (1)
3b	20	96	**5g** : **6g** 7 : 1	90	66—68 (1)
3b	78	20	**5h** : **6h** 20 : 1	91	41—43 (1)
3b	78	40	**5i** : **6i** 20 : 1	88	54—56 (1)
3b	78	24	**5j** : **6j** 25 : 1	77	63—65 (10)
3b	78	40	**5k** : **6k** 10 : 1	68	52—62 (1)
3c	20	120	**5l** : **6l** 1 : 3	57	60—65 (1)
3c	20	96	**5m** : **6m** 3 : 2	64	85—90 (1)

In the most cases, we failed to completely separate the mixtures of isomers **5** and **6** neither by rectification nor by chromatography, and only ene adducts **6a**, **6c**, and **6f** were obtained with moderate yields by thorough fractional distillation of the mixtures. However, it was found that the ene adducts easily add bromine to the nonconjugated C=C-bond, whereas cyclobutenes **5** very slow react with it even at 20 °C. Thus, after distillation of the reaction mixture *in vacuo* and determination of isomeric ratio in it by ^{1}H NMR spectroscopy, it was treated with bromine in amount equivalent to that of the ene adduct and then redistilled. This method was successfully used for the isolation of pure cycloadducts **5** from isomeric mixtures in high yields, excluding compounds **5f**, **5l**, and **5m**, in the case of which decomposition of the reaction mixture occurs during the distillation process. In the case of **5c**, the chlorination of the reaction mixture was performed instead of bromination. Determination of isomeric ratios in the mixtures by ^{1}H NMR method does not cause any difficulties: for instance, in the spectra of all the ene adducts **6**, there is present characteristic singlet in the region 6.65—7.05 ppm (C=CH—$COCF_3$). In addition, the spectra of ene adducts **6a—g**, **6l**, **6m** formed with 1,1-disubstituted alkenes exhibit a singlet for the "twice allylic" protons (C=C—CH_2—C=C) in the region 3.25—3.50 ppm. The spectra of the corresponding cyclobutenes **5a—g**, **5l**, **5m** contain characteristic singlet in the region 2.60—2.80 ppm related to the protons on the third carbon atom of the cyclobutene fragment (CH_2—C=C—$COCF_3$); in the reactions with 1,2-disubstituted alkenes no more than 5% of ene adducts is formed.

To sum up, neither catalysts nor irradiation is required for these [2+2] cycloaddition reactions to occur. Addition of 2,6-di(*tert*-butyl)phenol to the reaction mixture as a radical trap shows no any effect on the process. It is known that polar solvents considerably increase the rates of dipolar additions, however, in the cases under study addition of acetonitrile had no any noticeable accelerating effect or any changes in the direction of the reaction. The formation of two regioisomers **5k** in the ratio 1 : 1 in the

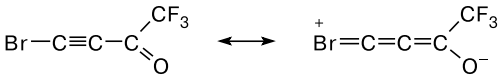
Scheme 3



reaction of acetylene **3b** with hex-1-ene, as well as an exclusive formation of *cis*-isomer **5j** in the reaction of **3b** with *cis*-but-2-ene contradict to both the polar and the radical mechanisms. These facts allow us to suggest that acetylenes **3a—c** add to alkenes according to the concerted mechanism, though this is forbidden by the orbital-

symmetry rules. To overcome this contradiction, we suggested that due to the powerful negative mesomeric effect of the trifluoroacetyl group in molecules **3a—c**, the double character of the bond between the terminal carbon atom and the halogen atom sharply increases (Scheme 4).

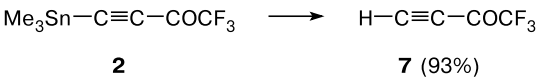
Scheme 4



The resonance formula describing such a redistribution of the electron density has a cumulene structure, which makes possible the supra-antarafacial concerted $[\pi 2_s + \pi 2_a]$ cycloaddition, well known for ketenes (Fig. 1).

To confirm this mechanism, we attempted to synthesize acetylene activated with trifluoroacetyl group, that makes it electron-withdrawing enough for the reactions with olefins, the second substituent of which, in contrast to the halogen atoms, does not possess a positive mesomeric effect, which makes impossible implementation of the ketene resonance structure. 1,1,1-Trifluoroobut-3-yn-2-one (**7**) was chosen as such a compound, which has been earlier synthesized in a mixture with isomeric trifluoropropiolaldehyde in low yield.[14] We found that the target compound **7** is formed in good yield upon treatment of acetylene **2** with trifluoroacetic acid in ethyl benzoate (Scheme 5).

Scheme 5



Reagents and conditions: CF_3COOH, 0—20 °C, PhCOOEt

It was found that acetylene **7** obtained exhibits lower reactivity in the reaction with alkenes as compared to compounds **3a,b**, however, it also slowly reacts with isobutylene and methylenecyclohexane already at 20 °C to exclusively give the ene addition products, whereas no [2+2] cycloadducts were found even in trace amounts (Scheme 6).

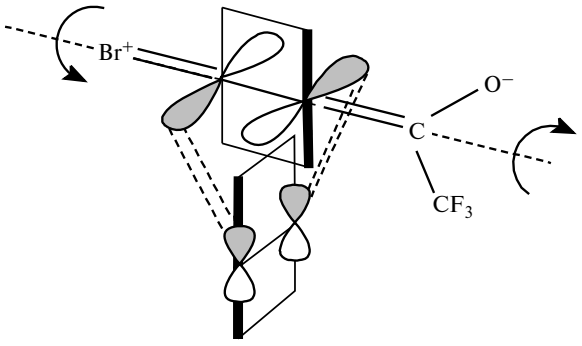
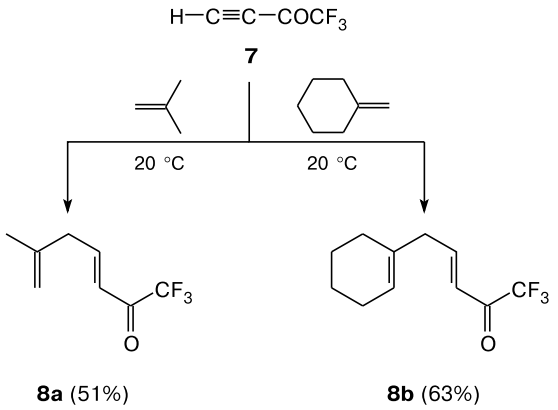


Fig. 1. Supra-antarafacial addition of acetylene **3b** to alkene.

Scheme 6



8a (51%) **8b** (63%)

It is obvious that these results confirm our suggestion on the necessity to implement a cumulene resonance structure for the [2+2] cycloaddition of acetylenes with alkenes to occur. Note that such electron-withdrawing acetylenes as acetylenedicarboxylic esters, hexafluorobut-2-yne, 1,1,1-trifluoropropyne, and propiolic esters, in the molecules of which there is no a mesomeric donor at the C≡C bond, react with alkenes under drastic conditions to exclusively form ene addition adducts.[15]

It is known[16] that α,β-unsaturated trifluoromethyl ketones, including those containing a leaving group at β-position, are extremely interesting and prospective compounds in various addition and heterocyclization processes. It should be noted that cycloadducts **5** are earlier unknown β-halo-α,β-unsaturated trifluoromethyl ketones of the cyclobutene series, which, probably, can serve as substrates for the synthesis of fluorine-containing heterocycles fused with substituted cyclobutene frameworks.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$. IR spectra were obtained on a Bruker IFS 25 spectrometer for neat samples. All manipulations with trimethylstannylacetylenes were performed under argon, though it is permissible for these substances to contact with air for several seconds. Acetylene was purified by bubbling through sulfuric acid and then through a trap cooled with dry ice. Trifluoroacetic anhydride was distilled over P_2O_5 just before use, collecting the fraction with b.p. 39—40 °C. Reactions of acetylenes **3a—c** with gaseous alkenes or if heating was necessary were performed in sealed tubes.

Bis(trimethylstannyl)acetylene (1). This compound was synthesized by the known procedure.[17]

1,1,1-Trifluoro-4-(trimethylstannyl)but-3-yn-2-one (2). Trifluoroacetic anhydride (63.0 g, 0.30 mol) was added in one portion to a stirred solution of acetylene **1** (100.0 g, 0.28 mol)

in anhydrous tetrahydrofuran (200 mL) and, after the exothermic reaction was over, the reaction mixture was kept for 2 h at 20 °C. The major amount of tetrahydrofuran was evaporated *in vacuo* using a water bath at 20 °C. The reflux condenser was exchanged for the distilling column with distilling condenser and, while keeping pressure at 10—15 Torr, the temperature of the water bath was gradually elevated up to 90—95 °C with intensive magnetic stirring until the product stopped to distill in the range of 45—65 °C. (The residue containing a growing amount of trimethylstannyl trifluoroacetate was rapidely solidified, making the stirring difficult, and was partially sublimed, however, the distillation was continued.) Additional amount of the substance was distilled from the reaction mixture *in vacuo* of an oil pump of 1—2 Torr after the receiving flask was changed. After the second distillation of the product contained an impurity of trimethylstannyl trifluoroacetate, pure acetylene **2** was obtained (72.7 g, 90%), b.p. 53—54 °C (9 Torr). Found (%): C, 29.49; H, 3.28; F, 20.03; Sn, 41.44. $C_7H_9F_3OSn$. Calculated (%): C, 29.52; H, 3.18; F, 20.01; Sn, 41.69. ^{1}H NMR, δ: 0.05 (s, $(CH_3)_3Sn$). ^{13}C NMR, δ: −7.9 (Me_3Sn); 100.7, 114.5 (C≡C); 115.1 (q, CF_3, $J_{C,F}$ = 288 Hz); 166.1 (q, C=O, $J_{C,F}$ = 42 Hz). IR (ν/cm^{-1}): 2140 (C≡C); 1705 (C=O).

4-Chloro-1,1,1-trifluorobut-3-yn-2-one (3a). A solution of chlorine (4.00 g, 0.056 mol) in ethyl benzoate (10 mL) precooled to −20 °C was added dropwise to a solution of acetylene **2** (15.00 g, 0.052 mol) in ethyl benzoate (10.0 mL) with stirring and cooling to −20 °C. The temperature of the reaction mixture was elevated to 20 °C over 0.5 h and then *in vacuo* of 15—20 Torr and gradual heating, the halogenation product was distilled using a short distilling column into a trap with a receiving flask cooled with dry ice. When the temperature in vapors reached 40—45 °C, the process was stopped, the distillate was redistilled at atmospheric pressure to obtain **3a** (6.90 g, 85%), b.p. 64—66 °C. Found (%): C, 30.45; F, 36.58. C_4ClF_3O. Calculated (%): C, 30.70; F, 36.42. ^{13}C NMR, δ: 64.3, 82.8 (C≡C); 115.0 (q, CF_3, $J_{C,F}$ = 286 Hz); 166.8 (q, C=O, $J_{C,F}$ = 43 Hz). IR (ν/cm^{-1}): 2225 (C≡C); 1740 (C=O).

4-Bromo-1,1,1-trifluorobut-3-yn-2-one (3b). This compound was obtained quite similarly to acetylene **3a** using equimolar amount of bromine instead of chlorine. The yield of **3b** was 9.20 g (87%), b.p. 89—90 °C. Found (%): C, 23.80; Br, 39.66; F, 28.53. C_4BrF_3O. Calculated (%): C, 23.91; Br, 39.80; F, 28.36. ^{13}C NMR, δ: 68.2, 75.0 (C≡C); 114.5 (q, CF_3, $J_{C,F}$ = 288 Hz); 165.1 (q, C=O, $J_{C,F}$ = 42 Hz). IR (ν/cm^{-1}): 2180 (C≡C); 1700 (C=O).

4-Iodo-1,1,1-trifluorobut-3-yn-2-one (3c). A solution of iodine (4.31 g) in carbon disulfide (30.0 mL) was added dropwise to a solution of acetylene **2** (4.84 g, 0.017 mol) in carbon disulfide (30.0 mL) with stirring and cooling to 5 °C at such a rate that to keep a weak color of iodine in solution (when the second half of the solution was being added, the discoloration occurred slower). The reaction mixture was stirred for another 0.5 h at 20 °C, then concentrated carefully *in vacuo* of 80—100 Torr at 20 °C, the residue was distilled collecting the fraction with b.p. 25—40 °C (7 Torr). The second distillation gave pure **3c** (3.40 g, 82%) b.p. 26—28 °C (7 Torr). Found (%): C, 19.28; F, 22.70. C_4F_3IO. Calculated (%): C, 19.38; F, 22.99. ^{13}C NMR, δ: 32.2 (I—C≡); 89.8 (≡C—CO); 114.6 (q, CF_3, $J_{C,F}$ = 285 Hz); 165.6 (q, C=O, $J_{C,F}$ = 40 Hz). IR (ν/cm^{-1}): 2180 (C≡C); 1720 (C=O).

Synthesis of cycloadducts 5 (general procedure). Acetylene **3a**, **3b**, or **3c** (0.01 mol) was mixed with alkene (0.04 mol) and the reaction mixture was kept for necessary time at a required temperature (Table 1). Excess alkene was evaporated *in vacuo*, the residue was distilled collecting the fraction in the temperature range indicated (see Table 1). Then it was dissolved in dichloromethane (5.0 mL), and a solution of bromine in dichloromethane (5.0 mL) in amount equivalent to the ene adduct was added dropwise to the solution with stirring and cooling to −20 °C (see Table 1). (In the case of adduct **5c**, an equimolar amount of chlorine in CCl_4 (5.0 mL) was used instead of bromine.) The reaction mixture was stirred for 10 min at 0 °C, the solvent was evaporated *in vacuo*, the residue was distilled. In the Table, the total yields of cycloadducts **5** after cycloaddition and purification by bromination steps are given.

1-(2-Chloro-4,4-dimethylcyclobut-1-en-1-yl)-2,2,2-trifluoroethanone (5a). The yield of **5a** was 1.44 g (68%), b.p. 41—42 °C (8 Torr). Found (%): C, 45.09; H, 3.90; F, 26.60. $C_8H_8ClF_3O$. Calculated (%): C, 45.20; H, 3.79; F, 26.81. ^{1}H NMR, δ: 1.36 (s, 6 H, $(CH_3)_2C$); 2.65 (s, 2 H, —CH_2—). ^{13}C NMR, δ: 23.9 ($(CH_3)_2$); 42.5 (C(4)); 50.9 (CH_2); 115.1 (q, CF_3, $J_{C,F}$ = 287 Hz); 141.0, 145.0 (C=C); 175.2 (q, C=O, $J_{C,F}$ =37 Hz). IR (ν/cm^{-1}): 1710 (C=O); 1610 (C=C).

1-(2-Chlorospiro[3.5]non-1-en-1-yl)-2,2,2-trifluoroethanone (5b). The yield of **5b** was 1.83 g (73%), b.p. 54—55 °C (1 Torr). Found (%): C, 52.19; H, 4.85; F, 22.40. $C_{11}H_{12}ClF_3O$. Calculated (%): C, 52.29; H, 4.79; F, 22.56. ^{1}H NMR, δ: 1.48—1.59, 1.63—1.81, 1.88—1.97 (all m, 10 H, —$(CH_2)_5$—); 2.62 (s, 2 H, —CH_2—). ^{13}C NMR, δ: 24.0, 25.2, 33.3 (—$(CH_2)_5$—); 47.4 (C(3)); 48.4 (C(4)); 116.1 (q, CF_3; $J_{C,F}$ = 290 Hz); 141.3, 145.8 (C=C); 173.1 (q, C=O, $J_{C,F}$ = 40 Hz). IR (ν/cm^{-1}): 1700 (C=O); 1608 (C=C).

1-(2-Chlorospiro[3.4]oct-1-en-1-yl)-2,2,2-trifluoroethanone (5c). The yield of **5c** was 0.50 g (21%), b.p. 48—50 °C (1 Torr). Found (%): C, 50.45; H, 4.19; F, 23.75. $C_{10}H_{10}ClF_3O$. Calculated (%): C, 50.33; H, 4.22; F, 23.88. ^{1}H NMR, δ: 1.55—1.70, 1.78—1.92 (all m, 8 H, —$(CH_2)_4$—); 2.70 (s, 2 H, —CH_2—). ^{13}C NMR, δ: 28.6, 31.9 (—$(CH_2)_4$—); 49.5 (C(3)); 50.8 (C(4)); 118.4 (q, CF_3, $J_{C,F}$ = 288 Hz); 144.2, 148.9 (C=C); 177.6 (q, C=O, $J_{C,F}$ = 38 Hz). IR (ν/cm^{-1}): 1705 (C=O); 1606 (C=C).

1-(2-Bromo-4,4-dimethylcyclobut-1-en-1-yl)-2,2,2-trifluoroethanone (5d). The yield of **4d** was 1.28 g (50%), b.p. 50—52 °C (9 Torr). Found (%): C, 37.11; H, 3.19; Br, 31.19; F, 22.03. $C_8H_8BrF_3O$. Calculated (%): C, 37.38; H, 3.14; Br, 31.08; F, 22.17. ^{1}H NMR, δ: 1.38 (s, 6 H, $(CH_3)_2C$); 2.74 (s, 2 H, —CH_2—). ^{13}C NMR, δ: 24.1 ($(CH_3)_2$); 45.8 (C(4)); 52.8 (CH_2); 116.6 (q, CF_3; $J_{C,F}$ = 290 Hz); 135.0, 146.9 (C=C); 172.2 (q, C=O, $J_{C,F}$ = 39 Hz). IR (ν/cm^{-1}): 1698 (C=O); 1602 (C=C).

1-(2-Bromospiro[3.3]hept-1-en-1-yl)-2,2,2-trifluoroethanone (5e). The yield of **5e** was 1.61 g (60%), b.p. 43—44 °C (1 Torr). Found (%): C, 40.08; H, 3.06; Br, 29.95; F, 21.18. $C_9H_8BrF_3O$. Calculated (%): C, 40.18; H, 3.00; Br, 29.70; F, 21.18. ^{1}H NMR, δ: 1.89—2.07, 2.12—2.22, 2.55—2.68 (all m, 6 H, —$(CH_2)_3$—); 2.82 (s, 2 H, —CH_2—). ^{13}C NMR, δ: 31.6, 39.9 ($(CH_2)_3$); 49.4 (C(3)); 53.1 (C(4)); 118.0 (q, CF_3, $J_{C,F}$ = 286 Hz); 137.8, 1482 (C=C); 178.4 (q, C=O, $J_{C,F}$ = 38 Hz). IR (ν/cm^{-1}): 1705 (C=O); 1600 (C=C).

1-(2-Bromospiro[3.4]oct-1-en-1-yl)-2,2,2-trifluoroethanone (5f) and 4-bromo-5-(cyclopent-1-en-1-yl)-1,1,1-trifluoropent-3-en-2-one (6f) (a mixture of isomers 1 : 3). We failed in selective bromination to the pure cycloadduct **5f**, hence, an isomeric mixture, obtained by fractional distillation after performing the reaction according to general procedure, was characterized. The

yield of the mixture **5f** and **6f** was 2.15 g (76%), b.p. 53—60 °C (1 Torr). Found (%): C, 42.19; H, 3.71; Br, 27.90; F, 20.35. $C_{10}H_{10}BrF_3O$. Calculated (%): C, 42.42; H, 3.57; Br, 28.22; F, 20.13. ^{1}H NMR, δ, **5f**: 1.49—1.67, 1.74—1.88 (both m, 8 H, $(CH_2)_4$); 2.72 (s, 2 H, $H_2C(3)$). ^{1}H NMR, δ, **6f**: 1.92, 2.36 (both m, 6 H, $—(CH_2)_3—$); 3.39 (s, 2 H, C=C—CH_2—C=C); 5.74 (t, 1 H, —CH=C, J = 1.5 Hz); 6.81 (s, 1 H, C=CH—CO). IR (ν/cm^{-1}): 1718 (C=O); 1645 (C=C); 1608 (C=C).

1-(2-Bromospiro[3.5]non-1-en-1-yl)-2,2,2-trifluoroethanone (5g). The yield of **5g** was 2.13 g (73%), b.p. 76—78 °C (1 Torr). Found (%): C, 44.23; H, 4.12; Br, 26.88; F, 19.03. $C_{11}H_{12}BrF_3O$. Calculated (%): C, 44.47; H, 4.07; Br, 26.89; F, 19.18. ^{1}H NMR, δ: 1.50—1.59, 1.62—1.68, 1.70—1.79, 1.87—1.98 (all m, 10 H, $—(CH_2)_5—$); 2.71 (s, 2 H, $—CH_2—$). ^{13}C NMR, δ: 23.9, 24.9, 33.2 ($—(CH_2)_5—$); 50.3 (C(3)); 50.8 (C(4)); 115.3 (q, CF_3, $J_{C,F}$ = 288 Hz); 136.2, 146.2 (C=C); 174.6 (q, C=O, $J_{C,F}$ = 40 Hz). IR (ν/cm^{-1}): 1708 (C=O); 1610 (C=C).

1-(7-Bromobicyclo[3.2.0]hept-6-en-6-yl)-2,2,2-trifluoroethanone (5h). The yield of **5h** was 2.20 g (82%), b.p. 44—45 °C (1 Torr). Found (%): C, 40.17; H, 2.89; Br, 29.81; F, 21.13. $C_9H_8BrF_3O$. Calculated (%): C, 40.18; H, 3.00; Br, 29.70; F, 21.18. ^{1}H NMR, δ: 1.31—1.44, 1.49—1.57, 1.75—1.90 (all m, 6 H, $—(CH_2)_3—$); 3.45 (dd, 1 H, H—C(4), J = 6.4 Hz, J = 3.4 Hz); 3.62 (dd, 1 H, HC(3), $J_{C,H}$ = 6.4 Hz, J = 3.4 Hz). ^{13}C NMR, δ: 22.4, 24.7, 25.8 ($—(CH_2)_3—$); 47.1 (C(3)); 54.7 (C(4)); 115.9 (q, CF_3, $J_{C,F}$ = 288 Hz); 138.0, 139.8 (C=C); 174.0 (q, C=O, $J_{C,F}$ = 38 Hz). IR (ν/cm^{-1}): 1706 (C=O); 1611 (C=C).

1-(7-Bromobicyclo[4.2.0]oct-7-en-7-yl)-2,2,2-trifluoroethanone (5i). The yield of **5i** was 2.12 g (75%), b.p. 53—54 °C (1 Torr). Found (%): C, 42.62; H, 3.59; Br, 28.68; F, 20.00. $C_{10}H_{10}BrF_3O$. Calculated (%): C, 42.43; H, 3.56; Br, 28.23; F, 20.13. ^{1}H NMR, δ: 1.40—1.59, 1.71—1.95 (both m, 4 H each, $—(CH_2)_4—$); 3.22 (dd, 1 H, J = 6.8 Hz, J = 4.2 Hz) C(4)H; 3.34 (dd, 1 H, HC(3), $J_{C,H}$ = 6.8 Hz, J = 4.2 Hz). ^{13}C NMR, δ: 13.6; 13.8; 18.4; 19.0 ($—(CH_2)_4—$); 36.8 (C(4)); 43.9 (C(3)); 111.8 (q, CF_3, $J_{C,F}$ = 288 Hz); 136.9; 138.3 (C=C); 169.7 (q, C=O, $J_{C,F}$ = 38 Hz). IR (ν/cm^{-1}): 1705 (C=O); 1605 (C=C).

1-(2-Bromo-3,4-dimethylcyclobut-1-en-1-yl)-2,2,2-trifluoroethanone (5j). The yield of **5j** was 1.72 g (67%), b.p. 66—67 °C (10 Torr). Found (%): C, 37.21; H, 3.08; F, 22.34. $C_8H_8BrF_3O$. Calculated (%): C, 37.38; H, 3.14; F, 22.17. ^{1}H NMR, δ: 1.13 (d, 3 H, $CH_3C(4)$, J = 7.0 Hz); 1.21 (d, 3 H, $CH_3—C(3)$, J = = 7.0 Hz); 3.23 (dq, 1 H, H—C(4), J = 7.0 Hz, J = 5.3 Hz); 3.38 (dq, 1 H, H—C(3), J =7.0 Hz, J = 5.3 Hz). ^{13}C NMR, δ: 11.1, 12.6 (2 CH_3); 40.1 (C(4)); 47.2 (C(3)); 115.3 (q, CF_3, $J_{C,F}$ = = 290 Hz); 140.9; 142.5 (C=C); 174.2 (q, C=O, $J_{C,F}$ = 38 Hz). IR (ν/cm^{-1}): 1702 (C=O); 1605 (C=C).

1-(2-Bromo-4-butylcyclobut-1-en-1-yl)- and 1-(2-bromo-3-butylcyclobut-1-en-1-yl)-2,2,2-trifluoroethanone (5k, a mixture of isomers 1 : 1). The yield of **5k** was 1.60 g (56%), b.p. 59—61 °C (1 Torr). Found (%): C, 42.03; H, 4.13; Br, 2809; F, 19.64. $C_{10}H_{12}BrF_3O$. Calculated (%): C, 42.13; H, 4.24; Br, 28.03; F, 19.19. ^{1}H NMR, δ: 0.91 (t, 6 H); 1.24—1.52 (m, 10 H); 1.78 (dt, 1 H, J = 12.0 Hz, J = 7.4 Hz); 1.92 (dt, 1 H, J = 12.0 Hz, J = 7.4 Hz); 2.62 (m, 2 H); 3.00—3.11 (m, 3 H); 3.21 (ddd, 1 H, J = 10.2 Hz, J = 7.4 Hz, J = 4.8 Hz). ^{13}C NMR, δ: 13.3; 13.9; 22.4; 22.5; 28.6; 28.9; 30.9; 31.5; 34.7; 42.9; 43.6; 49.2; 115.3; 115.7; 135.9; 136.2; 142.2; 142.3; 174.2; 175.0. IR (ν/cm^{-1}): 1715; 1605.

1-(2-Iodo-4,4-dimethylcyclobut-1-en-1-yl)-2,2,2-trifluoroethanone (5l) and 4-iodo-1,1,1-trifluoro-6-methylhepta-3,6-dien-2-one (6l, a mixture of isomers 1 : 3). We failed in selective bromination to the pure cycloadduct **4l**, hence, an isomeric mixture, obtained by fractional distillation after performing the reaction according to general procedure, was characterized. The yield of the mixture **5l** and **6l** was 1.73 g (57%), b.p. 60—65 °C (1 Torr). Found (%): C, 31.44; H, 2.61; I, 41.90; F, 18.58. $C_8H_8IF_3O$. Calculated (%): C, 31.60; H, 2.66; I, 41.73; F, 18.75. ^{1}H NMR, δ, **5l**: 1.36 (s, 6 H, $(CH_3)_2$); 2.77 (s, 2 H, CH_2). ^{1}H NMR, δ, **6l**: 1.73 (s, 3 H, CH_3—C=C); 3.48 (s, 2 H, $—CH_2—$); 4.90 (d, 1 H, H—C=C, J = 1.2 Hz); 5.16 (d, 1 H, H—C=C, J = 1.2 Hz); 7.02 (s, 1 H, CH—CO). ^{13}C NMR of the isomeric mixture, δ: 20.4; 24.9; 39.1; 42.6; 46.6; 113.5; 114.6; 115.9; 118.1; 120.7; 126.4; 141.0; 141.5; 173.8; 175.3. IR (ν/cm^{-1}): 1735; 1700; 1644; 1615; 1608.

1-(2-Iodospiro[3.5]non-1-en-1-yl)-2,2,2-trifluoroethanone (5m) and 5-(cyclohex-1-en-1-yl)-4-iodo-1,1,1-trifluoropent-3-en-2-one (6m) (a mixture of isomers 3 : 2). We failed in selective bromination to the pure cycloadduct **5m**, hence, an isomeric mixture, obtained by fractional distillation after performing the reaction according to general procedure, was characterized. The yield of the mixture **5m** and **6m** was 2.20 g (64%), b.p. 85—90 °C (1 Torr). Found (%): C, 38.11; H, 3.34; I, 37.05; F, 16.39. $C_{11}H_{12}IF_3O$. Calculated (%): C, 38.39; H, 3.52; I, 36.86; F, 16.56. ^{1}H NMR, δ, **5m**: 1.18—1.35 (m, 4 H, $(CH_2)_2$); 1.55—1.70 (m, 6 H, $(CH_2)_3$); 2.76 (s, 2 H, $H_2C(3)$). ^{1}H NMR, δ, **6m**: 1.79—1.92 (m, 4 H, $—(CH_2)_2—$); 1.95—2.10 (m, 4 H, CH_2—C=C—CH_2); 3.43 (s, 2 H, C=C—CH_2—C=C); 5.59 (t, 1 H, —CH=C, J = 0.8 Hz); 7.04 (s, 1 H, C=CH—CO). IR (ν/cm^{-1}): 1720; 1700; 1652; 1615; 1608.

4-Chloro-1,1,1-trifluoro-6-methylhepta-3,6-dien-2-one (6a). The isomeric mixture of **5a** and **6a** (4 : 1, 10.00 g; see Table 1), was thoroughly fractionally distilled *in vacuo* using a mirror distilling column. The yield of ene adduct **6a** was 0.80 g (32% on the rectification step), b.p. 59—60 °C (8 Torr). The product contains about 5% of isomer **5a**. Found (%): C, 45.13; H, 3.93; F, 26.88. $C_8H_8ClF_3O$. Calculated (%): C, 45.20; H, 3.79; F, 26.81. ^{1}H NMR, δ: 1.77 (s, 3 H, CH_3—C=C); 3.28 (s, 2 H, C=C—CH_2—C=C); 4.93 (d, 1 H, H—C=C, J = 1.2 Hz); 5.08 (d, 1 H, H—C=C, J = 1.2 Hz); 6.70 (s, 1 H, C=CH—CO). ^{13}C NMR, δ: 19.4 (CH_3); 38.9 (CH_2); 115.9, 122.7 (CH_2=C); 117.5 (q, CF_3, $J_{C,F}$ = 290 Hz); 144.0, 153.8 (C=C—Cl); 181.2 (q, C=O, $J_{C,F}$ = 40 Hz). IR (ν/cm^{-1}): 1716 (C=O); 1648 (C=C); 1610 (C=C).

5-(Cyclopent-1-en-1-yl)-4-chloro-1,1,1-trifluoropent-3-en-2-one (6c) was obtained similarly to compound **6a** by rectification of the isomeric mixture **5c** and **6c** (1 : 2, 9.00 g). The yield of product **6c** was 2.89 g (48% on the rectification step), b.p. 49—50 °C (1 Torr). Found (%): C, 50.40; H, 4.16; F, 23.73. $C_{10}H_{10}ClF_3O$. Calculated (%): C, 50.33; H, 4.22; F, 23.88. ^{1}H NMR, δ: 1.84, 2.40 (both m, 6 H, $—(CH_2)_3—$); 3.35 (s, 2 H, C=C—CH_2—C=C); 5.68 (t, 1 H, —CH=C, J = 1.6 Hz); 6.69 (s, 1 H, C=CH—CO). ^{13}C NMR, δ: 24.9, 34.0, 35.2 ($—(CH_2)_3—$); 44.6 ($—CH_2—$); 118.2 (q, CF_3, $J_{C,F}$ = 288 Hz); 120.4, 131.6 (C=C in ring); 146.8, 155.3 (C=C—Cl); 181.9 (q, C=O, $J_{C,F}$ = 39 Hz). IR (ν/cm^{-1}): 1722 (C=O); 1654 (C=C); 1602 (C=C).

1,1,1-Trifluorobut-3-yn-2-one (7). A solution of trifluoroacetic acid (6.00 g, 0.052 mol) in ethyl benzoate (5.0 mL) was added dropwise to a stirred with powerful magnetic stirrer solution of acetylene **2** (15.00 g, 0.052 mol) in ethyl benzoate (10 mL) at −10 °C, the reaction mixture was allowed to warm to 20 °C and additionally stirred for 0.5 h. (A dense precipitate of trime-

thylstannyl trifluoroacetate was formed interfering the stirring.) The reaction product was distilled off during gradual heating and stirring using a Wurtz adapter into a trap with a receiving flask cooled with dry ice. The second distillation gave acetylene **7** (5.91 g, 93%), b.p. 31 °C (Ref. 14: b.p. 30 °C). Found (%): C, 39.47; H, 0.81; F, 46.15. C_4HF_3O. Calculated (%): C, 39.36; H, 0.83; F, 46.70. ^{1}H NMR, δ: 3.70 (s, C≡C—H). ^{13}C NMR, δ: 75.7, 87.3 (C≡C); 114.2 (q, CF_3, $J_{C,F}$ = 286 Hz); 166.7 (q, C=O, $J_{C,F}$ = 42 Hz). IR (ν/cm^{-1}): 3320 (C—H); 2130 (C≡C); 1750 (C=O).

(3*E*)-1,1,1-Trifluoro-6-methylhepta-3,6-dien-2-one (8a). A mixture of acetylene **7** (1.22 g, 0.01 mol) and isobutylene (2.24 g, 0.04 mol) was kept in a sealed tube for 240 h at 20 °C, after the excess alkene was removed, the residue was distilled *in vacuo*. The yield of product **8a** was 0.91 g (51%), b.p. 42—42 °C (18 Torr). Found (%): C, 54.01; H, 5.16; F, 31.78. $C_8H_9F_3O$. Calculated (%): C, 53.94; H, 5.09; F, 31.99. ^{1}H NMR, δ: 1.81 (s, 3 H, CH_3); 3.06 (d, 2 H, —CH_2—, J = 7.3 Hz); 4.82 (d, 1 H, one of CH_2=C, J = 1.4 Hz); 4.94 (d, 1 H, one of CH_2=C, J = = 1.4 Hz); 6.48 (d, 1 H, C=CH—CO, J = 15.7 Hz); 7.36 (dt, 1 H, HC=C—CO, J = 15.7 Hz; J = 7.3 Hz). ^{13}C NMR, δ: 22.4 (CH_3); 41.2 (—CH_2—); 113.6, 122.4 (CH_2=C); 116.1 (q, CF_3, $J_{C,F}$ = 290 Hz); 140.8; 153.4 (—CH=CH—); 179.7 (q, C=O, $J_{C,F}$ = 36 Hz). IR (ν/cm^{-1}): 1705 (C=O); 1644 (C=C); 1608 (C=C).

(3*E*)-5-(Cyclohex-1-en-1-yl)-1,1,1-trifluoropent-3-en-2-one (8b) was obtained similarly to compound **8a** from acetylene **6** (1.22 g, 0.04 mol) and methylenecyclohexane (3.84 g, 0.04 mol). The yield was 1.37 g (63%), b.p. 77—78 °C (12 Torr). Found (%): C, 60.40; H, 5.78; F, 26.03. $C_{11}H_{13}F_3O$. Calculated (%): C, 60.55; H, 6.00; F, 26.12. ^{1}H NMR, δ: 1.46—1.73 (m, 4 H, —$(CH_2)_2$—); 1.85—2.04 (m, 4 H, —CH_2—C=C—CH_2—); 2.93 (d, 2 H, C=C—CH_2—C=C, J = 7.3 Hz); 5.50 (t, 1 H, —CH=C— in ring); 6.40 (d, 1 H, C=CH—CO, J = 15.7 Hz); 7.58 (dt, 1 H, HC=C—CO, J = 15.7 Hz, J = 7.3 Hz). ^{13}C NMR, δ: 22.4; 23.1; 29.6; 31.9 (—$(CH_2)_4$—); 42.6 (—CH_2—); 116.4 (q, CF_3, $J_{C,F}$ = 290 Hz); 123.6, 132.4 (C=C in ring); 140.8, 153.4 (C=C-conjug.); 183.2 (q, C=O, $J_{C,F}$ = 37 Hz). IR (ν/cm^{-1}): 1708 (C=O); 1650 (C=C); 1612 (C=C).

References

1. W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, Oxford, 1990.
2. T. Bach, *Synthesis*, 1998, **5**, 683.
3. J. D. Roberts, B. B. Kline, H. E. Simmons, *J. Am. Chem. Soc.*, 1953, **75**, 4765.
4. K. Takasu, M. Ueno, K. Inanaga, M. Ihara, *J. Org. Chem.*, 2004, **69**, 517.
5. M.B. Boxer, H. Yamamoto, *Org. Lett.*, 2005, **7**, 3127.
6. K. Villeneuve, R. W. Jordan, W. Tam, *Synlett.*, 2003, **13**, 2123.
7. T. Shibata, K. Takami, A. Kawachi, *Org. Lett.*, 2006, **8**, 1343.
8. M. Miesh, F. Wedling, *Eur. J. Org. Chem.*, 2000, 3381.
9. A. K. Zenova, V. V. Platonov, M. V. Proskurnina, N. S. Zefirov, *Zh. Org. Khim.*, 1996, **32**, 992 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1996, **32**].
10. A. B. Koldobskii, E. V. Solodova, V. N. Kalinin, *Dokl. Akad. Nauk*, 1999, **366**, 58 [*Dokl. Chem.* (*Engl. Transl.*), 1999].
11. D. Obrecht, C. Zumbrunn, K. Muller, *J. Org. Chem.*, 1999, **64**, 6182.
12. A. B. Koldobskii, O. S. Shilova, V. N. Kalinin, *Mendeleev Commun.*, 2001, 99.
13. N. P. Tsvetkov, A. B. Koldobskii, V. N. Kalinin, *Dokl. Akad. Nauk*, 2006, **404**, 201 [*Dokl. Chem.* (*Engl. Transl.*), 2006].
14. Y. Shen, W. Cen, Y. Huang, *Synthesis*, 1985, **2**, 159.
15. J. C. Sauer, G. N. Sausen, *J. Org. Chem.*, 1962, **27**, 2730.
16. S. V. Druzhinin, E. S. Balenkova, V. G. Nenaidenko, *Tetrahedron*, 2007, **63**, 7753.
17. A. B. Koldobskii, E. V. Solodova, I. A. Godovikov, V. N. Kalinin, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1537 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 1568].

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