DOI 10.1007/s10593-020-02778-2

Chemistry of Heterocyclic Compounds **2020**, *56*(8), 1092–1096

SHORT COMMUNICATIONS

Imidazolone-activated donor-acceptor cyclopropanes with a peripheral stereocenter. A study on stereoselectivity of cycloaddition with aldehydes

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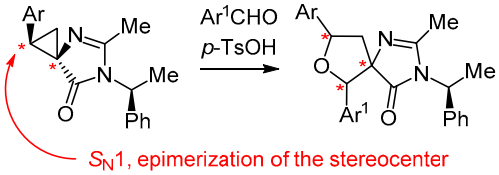
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2020, *56*(8), 1092–1096

Submitted July 3, 2020
Accepted after revision August 25, 2020



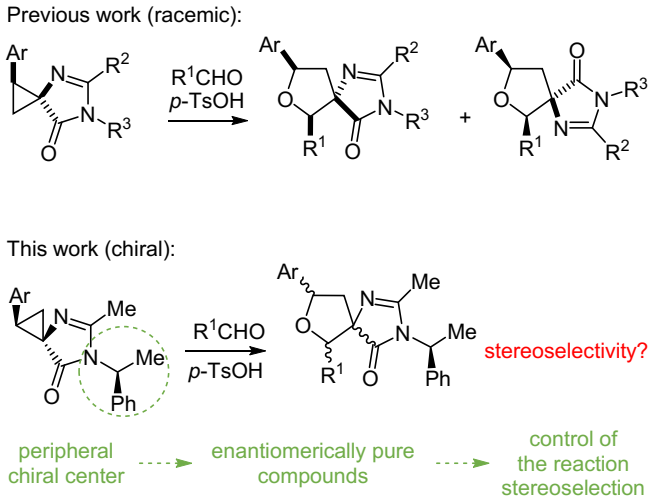
Nucleophilic cyclopropanation of arylideneimidazolones possessing a peripheral chiral center and the subsequent fractional crystallization of diastereomers allows access to the compounds with an enantiomerically uniform configuration of the spirocyclic donor-acceptor cyclopropane fragment. They were used to study the mechanism of the cycloaddition reaction with aldehydes; it was demonstrated that stereochemical information from the cyclopropane fragment is lost during the reaction.

Keywords: donor-acceptor cyclopropanes, imidazole, spirocyclic compounds, chirality, diastereoselectivity.

The strain energy embodied in small rings provides rich opportunities for a variety of chemical transformations.[1] Substitution of vicinal positions by both acceptor and donor substituents allows using this potential in cycloaddition and nucleophilic opening reactions.[2] The research on the so-called donor-acceptor cyclopropanes (DAC), in particular 1,1-cyclopropanedicarboxylates, has been advanced greatly.[2b] Such cyclopropanes can be used in (n+3) cycloaddition reactions for the synthesis of various heterocycles: pyrroles,[3] tetrahydrofurans,[4] pyrrolidines,[5] and many others.[6]

In our recent work, a new class of spirocyclic DACs containing a heterocyclic imidazolone fragment was proposed (Scheme 1, previous work).[7] We were able to show that, upon the promotion with protic acids, such as *p*-TsOH, their activation and participation in the cycloaddition reaction with aldehydes, resulting in the formation of a tetrahydrofuran ring, are possible. The reaction conditions were extended to a wide range of

Scheme 1. Cycloaddition reactions of spirocyclic DACs containing a heterocyclic imidazolone fragment



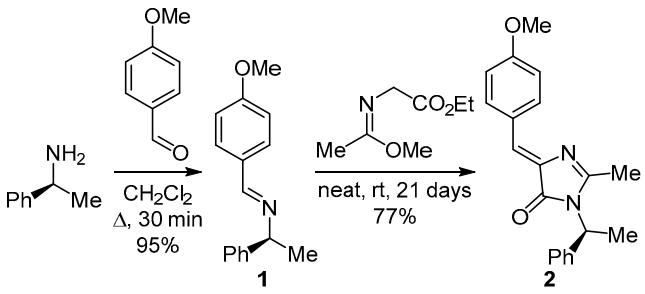
substrates and the major regularities were revealed, including those determining the stereoselectivity of the process for racemic substrates.

One of the unresolved issues is the stereoselectivity of the initial stages of this reaction. It is known that, for 1,1-cyclopropanedicarboxylates, the reaction with aldehydes proceeds with the inversion of the configuration of the stereocenter.[4b] In view of the fact that the spirocyclic DACs proposed by us have a fundamentally different activation mechanism, they require a separate investigation of this step, which is presented in this work.

For such a study it prompted to obtain enantiomerically pure imidazolone-substituted DACs (Scheme 1, this work). Since no enantioselective methods for the synthesis of such compounds are known at the moment,[4b,8] we synthesized compounds containing a chiral substituent at the peripheral position in the imidazole ring and separated the diastereomers formed after the cyclopropanation reaction. We have previously shown that the substitution of the imidazole ring has no noticeable effect on the course of the cycloaddition reaction with aldehydes.[7] However, the presence of an additional stereocenter would make it possible to reliably monitor the stereoselectivity of the reaction using NMR, and the enantiomeric purity of the chiral substituent would determine the configuration of the stereocenters formed and transformed during the reaction.

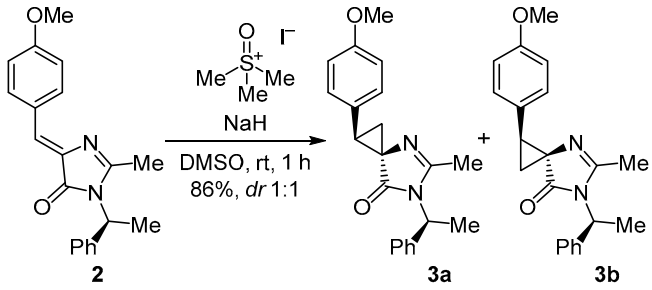
The commercially available (*S*)-α-phenylethylamine was chosen as the source of chirality (Scheme 2). At the first step, it was condensed with *p*-anisaldehyde to form Schiff base **1**.[9] The resulting imine was introduced into the cascade reaction of the formation of an imidazolone ring with ethyl *N*-(1-methoxyethylideneamino)acetate. Imidazolone **2** was obtained in 77% yield after 21 days.

Scheme 2. Synthesis of arylidenimidazolone **2**



At the next step, compound **2** was subjected to a reaction with dimethylsulfoxonium methylide in DMSO (Scheme 3). The reaction led to the formation of an equimolar mixture of diastereomers **3a** and **3b** in 86% yield. The nonselectivity of the transformation further confirms the absence of the influence of the introduced chiral substituent, and, consequently, the correct choice of the position for its introduction. The downside is the practically identical chromatographic characteristics of the diastereomers. In this regard, the separation of isomers was carried out using fractional crystallization. Double recrystallization from PhH yielded pure stereoisomer **3a**. Its structure was unambiguously established by X-ray

Scheme 3. Cyclopropanation of compound **2**



structural analysis (Fig. 1). The second diastereomer **3b** was obtained with a purity of 90% by recrystallization of the evaporated mother liquor from a hexane–EtOAc mixture.

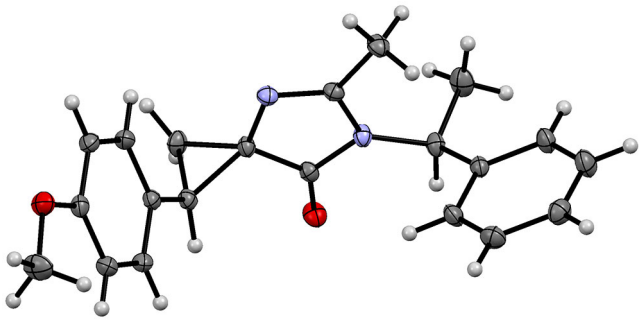
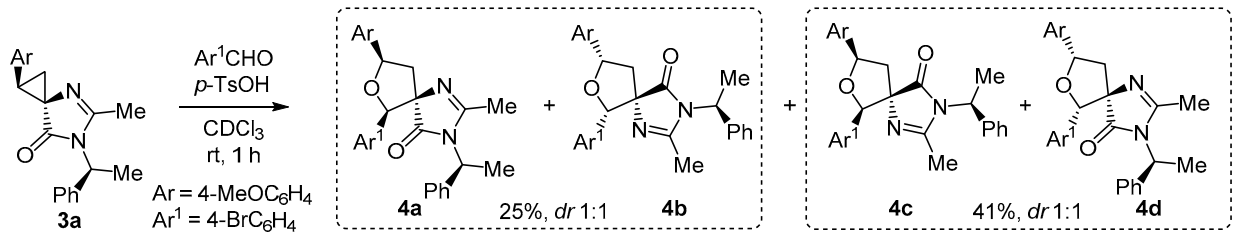


Figure 1. Molecular structure of compound **3a** with atoms represented as thermal vibration ellipsoids of 50% probability.

We found that the reaction of isomer **3a** (carried out in an NMR tube to guarantee the purity of the starting isomer) with 4-bromobenzaldehyde leads to the formation of a mixture of 4 isomers of spirocycles **4** in a ratio of 1.7:1.6:1:1. The products were separated into isomer pairs **4a**,**b** and **4c**,**d** using column chromatography (Scheme 4). Their structures were determined using a combination of COSY, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC 2D NMR spectra and correlation with previously obtained data.[7] The formation of two pairs of equimolar mixtures of stereoisomers indicates the loss of stereochemical information at the first stages of cycloaddition, and, consequently, the intermediate formation of a carbocation. Since stereochemical information is lost in the course of the reaction, the development of enantioselective approaches to the synthesis of chiral DACs containing an imidazolone fragment as well as the use of such compounds in cycloaddition reactions with aldehydes seem to be impractical, and chirality must be induced from the α-carbon atom of the aldehyde or using a chiral promoter.

Thus, in this study we have developed an approach to the preparation of chiral donor-acceptor cyclopropanes spiro-fused with an imidazolone fragment and also found the conditions for the separation of the resulting diastereomers using fractional recrystallization. The presence of a chiral fragment of (*S*)-phenylethylamine at the periphery of the molecule allows the obtained

Scheme 4. Utilization of compound **3a** in the reaction with 4-bromobenzaldehyde



compounds to be used as tools for studying the stereoselectivity of cycloaddition and nucleophilic opening reactions with no use of chiral chromatography. For the cycloaddition reaction of imidazolone-substituted cyclopropanes with aldehydes under the conditions of activation with a protic acid, it was shown that the stereochemical information of the cyclopropane part of the molecule is not preserved.

Experimental

^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance II 700 spectrometer (700 and 175 MHz, respectively) at 303 K. Residual signals of the solvent $CDCl_3$ were used as internal standard: 7.26 ppm for ^{1}H nuclei, 77.16 ppm for ^{13}C nuclei. High-resolution mass spectra were recorded on a Bruker micrOTOF-Q II mass spectrometer, electrospray ionization (ESI-TOF); ±5 ppm accuracy of given values. The angles of rotation were measured on a PerkinElmer 341 automatic polarimeter. Melting points were determined on a Kofler bench and are uncorrected. Thin-layer chromatography was performed on Merck 60 plates with the F_{254} fluorescent indicator. Column chromatography was performed on silica gel 60 (40–63 μm) as the stationary phase.

(5*Z*)-5-(4-Methoxybenzylidene)-2-methyl-3-((1*S*)-1-phenylethyl)-3,5-dihydro-4*H*-imidazol-4-one (2) was obtained analogously to a literature method.[7] Schiff base **1**[9] (0.90 g, 3.8 mmol, 1 equiv) was mixed with ethyl *N*-(1-methoxyethylideneamino)acetate[10] (0.60 g, 3.8 mmol, 1.0 equiv). The reaction mixture was kept for 21 days at room temperature, during which it became brown. Volatile reaction products were distilled off under reduced pressure, and the residue was purified by column chromatography on silica gel, eluent hexane–EtOAc, 3:1. Yield 0.92 g (2.9 mmol, 77%), yellow oil which crystallized upon standing, mp 59–60°C (hexane–EtOAc), R_f 0.26 (hexane–EtOAc, 3:1, visualization by UV light / vanillin reagent). $[\alpha]_D^{20}$ –30.1 (*c* 2.1, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.19 (2H, d, *J* = 8.8, H Ar); 7.42 (2H, t, *J* = 7.5, H Ar); 7.39–7.24 (3H, m, H Ar); 7.19 (1H, s, =CH); 7.01 (2H, d, *J* = 8.8, H Ar); 5.63 (1H, q, *J* = 7.2, NCH); 3.92 (3H, s, OCH_3); 2.16 (3H, s, CH_3); 1.90 (3H, d, *J* = 7.2, CH_3). ^{13}C NMR spectrum, δ, ppm: 171.0 (C=O); 161.4 (2C); 140.1 (C); 136.7 (C); 134.2 (2CH); 128.9 (2CH); 127.8 (CH); 127.7 (CH); 127.4 (C); 126.7 (2CH); 114.5 (2CH); 55.5 (OCH_3); 50.0 (CH); 18.4 (CH_3); 17.6 (CH_3). Found, *m*/*z*: 321.1600 $[M+H]^+$. $C_{20}H_{21}N_2O_2$. Calculated, *m*/*z*: 321.1598.

Cyclopropanation, preparation of compounds 3a,b.[7] NaH (60% dispersion in oil, 0.11 g, 2.8 mmol, 1.15 equiv) was added in one portion to a solution of trimethylsulfoxonium iodide (0.70 g, 3.2 mmol, 1.30 equiv) in anhydrous DMSO (5 ml) at room temperature under a flow of argon. The reaction mixture was stirred for 20 min until a clear solution formed and gas evolution ceased. Then, imidazolone **2** (0.79 g, 2.5 mmol, 1 equiv) was added in one portion. The resulting reaction mixture was stirred at room temperature for 1 h and then partitioned between EtOAc (30 ml) and H_2O (30 ml). The organic layer was separated, the aqueous layer was extracted with EtOAc (10 ml). The combined organic layers were washed with saturated aqueous NaCl (30 ml), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was applied to a silica gel column and chromatographed using hexane–EtOAc, 1:1 as eluent. Yield of an equimolar mixture of diastereomeric cyclopropanes **3a**,**b** 0.71 g (2.1 mmol, 86%), R_f 0.21 (hexane–EtOAc, 1:1). Pure diastereomers were obtained by fractional recrystallization.

(1*R*,3*R*)-1-(4-Methoxyphenyl)-5-methyl-6-((1*S*)-1-phenylethyl)-4,6-diazaspiro[2.4]hept-4-en-7-one (3a) was obtained by double recrystallization of the mixture of diastereomers **3a**,**b** from PhH (heating to reflux and cooling to room temperature; ~5 ml for the first crystallization and ~2 ml for the second). Yield of pure compound **3a** 123 mg, mp 171–172°C (PhH, single crystal). $[\alpha]_D^{20}$ +351.8 (*c* 1.3, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.34 (2H, t, *J* = 7.6, H Ar); 7.30–7.21 (5H, m, H Ar); 6.85 (2H, d, *J* = 8.7, H Ar); 5.45 (1H, q, *J* = 7.3, NCH); 3.77 (3H, s, OCH_3); 3.07 (1H, t, *J* = 9.1, CCH); 2.13 (1H, dd, *J* = 8.5, *J* = 4.8, CH_2); 2.08 (1H, dd, *J* = 9.7, *J* = 4.8, CH_2); 1.93 (3H, s, CH_3); 1.81 (3H, d, *J* = 7.3, CH_3). ^{13}C NMR spectrum, δ, ppm: 181.2 (C=O); 160.4 (C); 158.7 (C); 140.1 (C); 129.6 (2CH); 128.8 (2CH); 128.2 (C); 127.8 (CH); 126.6 (2CH); 113.8 (2CH); 56.3 (C); 55.3 (OCH_3); 50.5 (CH); 35.8 (CH); 23.9 (CH_2); 18.4 (CH_3); 17.7 (CH_3). Found, *m*/*z*: 335.1743 $[M+H]^+$. $C_{21}H_{23}N_2O_2$. Calculated, *m*/*z*: 335.1754.

(1*S*,3*S*)-1-(4-Methoxyphenyl)-5-methyl-6-((1*S*)-1-phenylethyl)-4,6-diazaspiro[2.4]hept-4-en-7-one (3b). The combined mother liquors from the crystallization of isomer **3a** were dissolved in PhH by heating under reflux. Crystallization in the refrigerator (~6°C) led to the precipitation of most of isomer **3a**. The resulting mother liquor was concentrated and the residue was recrystallized twice from a hexane–EtOAc mixture, 4:1. Yield of compound **3b** with purity of 90% 172 mg, mp 131–132°C

(hexane–EtOAc, single crystal). $[\alpha]_D^{20}$ +252.0 (*c* 0.4, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.36 (2H, t, *J* = 7.6, H Ar); 7.31–7.27 (3H, m, H Ar); 7.24 (2H, d, *J* = 8.5, H Ar); 6.85 (2H, d, *J* = 8.7, H Ar); 5.46 (1H, q, *J* = 7.2, NCH); 3.76 (3H, s, OCH_3); 3.04 (1H, t, *J* = 9.1, CCH); 2.15 (1H, dd, *J* = 8.4, *J* = 4.8, CH_2); 2.11 (1H, dd, *J* = 9.7, *J* = 4.8, CH_2); 1.93 (3H, s, CH_3); 1.80 (3H, d, *J* = 7.2, CH_3). ^{13}C NMR spectrum, δ, ppm: 181.2 (C=O); 160.5 (C); 158.8 (C); 140.2 (C); 129.6 (2CH); 128.9 (2CH); 128.3 (C); 127.8 (CH); 126.7 (2CH); 113.9 (2CH); 56.4 (C); 55.4 (OCH_3); 50.5 (CH); 35.9 (CH); 24.0 (CH_2); 18.4 (CH_3); 17.7 (CH_3). Found, *m*/*z*: 335.1750 $[M+H]^+$. $C_{21}H_{23}N_2O_2$. Calculated, *m*/*z*: 335.1754.

Reaction of cyclopropane 3a with 4-bromobenzaldehyde. Anhydrous *p*-TsOH (28 mg, 0.16 mmol, 1.1 equiv) was added to a solution of cyclopropane **3a** (49 mg, 0.15 mmol, 1 equiv) and 4-bromobenzaldehyde (81 mg, 0.44 mmol, 3.0 equiv) in anhydrous $CDCl_3$ (0.7 ml) in an NMR tube at room temperature. The tube was gently shaken several times until the content was homogeneous. The color of the solution instantly changed to a pale-yellow. The reaction mixture was kept for 1 h, after which *N*,*N*,*N*′,*N*′-tetramethylguanidine (28 μl, 25 mg, 0.22 mmol, 1.5 equiv) was added. The reaction mixture was homogenized and kept for 10 min. At this point, the NMR spectrum of the reaction mixture was recorded. Then, by means of column chromatography on silica gel (eluent hexane–EtOAc, 1:1), the products were separated into pairs of isomers (5*R*,6*R*,8*R*)/(5*S*,6*S*,8*S*)-**4a**,**b** (less polar, 18 mg, 35 μmol, 25%) and ((5*R*,6*S*,8*S*)/(5*S*,6*R*,8*R*)-**4c**,**d** (more polar, 31 mg, 60 μmol, 41%).

(5*R*,6*R*,8*R*)- and (5*S*,6*S*,8*S*)-6-(4-bromophenyl)-8-(4-methoxyphenyl)-2-methyl-3-((1*S*)-1-phenylethyl)-7-oxa-1,3-diazaspiro[4.4]non-1-en-4-ones 4a,b, mixture of isomers in 1:1 ratio. R_f 0.21 (hexane–EtOAc, 1:1, visualization by UV light / vanillin reagent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): one isomer: 7.55 (2H, d, *J* = 8.6, H Ar); 7.35–7.24 (5H, m, H Ar); 7.18 (2H, dd, *J* = 8.0, *J* = 1.5, H Ar); 7.09 (2H, d, *J* = 8.4, H Ar); 6.92 (2H, d, *J* = 8.6, H Ar); 5.31 (1H, q, *J* = 7.3, NCH); 5.27 (1H, t, *J* = 7.9, 8-CH); 5.07 (1H, s, 6-CH); 3.82 (3H, s, OCH_3); 2.94 (1H, dd, *J* = 13.2, *J* = 8.6, CH_2); 2.28 (1H, dd, *J* = 13.2, *J* = 7.2, CH_2); 1.70 (3H, s, CH_3); 1.66 (3H, d, *J* = 7.3, CH_3); other isomer: 7.57 (2H, d, *J* = 8.6, H Ar); 7.42 (2H, d, *J* = 8.4, H Ar); 7.27–7.22 (5H, m, H Ar); 6.92 (2H, d, *J* = 8.6, H Ar); 6.91–6.88 (2H, m, H Ar); 5.26 (1H, q, *J* = 7.3, NCH); 5.28 (1H, t, *J* = 7.7, 8-CH); 5.11 (1H, s, 6-CH); 3.82 (3H, s, OCH_3); 2.94 (1H, dd, *J* = 13.2, *J* = 8.7, CH_2); 2.26 (1H, dd, *J* = 13.2, *J* = 6.8, CH_2); 1.69 (3H, d, *J* = 7.3, CH_3); 1.65 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm (both isomers): 182.8 and 182.5 (C=O); 159.8 (2C); 159.6 (C(4)–O Ar); 139.5 and 139.5 (C); 134.8 and 134.4 (C); 133.6 and 133.5 (C); 130.9 (4CH); 128.9 and 128.8 (2CH); 128.6 (2CH); 128.5 (2CH); 127.9 (4-CH Ph); 126.6 and 126.3 (2CH); 122.3 and 121.8 (C); 114.1 (2CH); 88.7 and 88.5 (OCH); 80.7 and 80.6 (OCH); 78.7 and 78.6 (C); 55.5 (OCH_3); 50.6 and 50.0 (NCH); 45.1 (CH_2); 18.6 (CH_3); 17.9 (CH_3); 17.3 (CH_3); 16.9 (CH_3). Found, *m*/*z*: 521.1267 $[M+H]^+$. $C_{28}H_{28}{}^{81}BrN_2O_3$. Calculated, *m*/*z*: 521.1262.

(5*R*,6*S*,8*S*)- and (5*S*,6*R*,8*R*)-6-(4-bromophenyl)-8-(4-methoxyphenyl)-2-methyl-3-((1*S*)-1-phenylethyl)-7-oxa-1,3-diazaspiro[4.4]non-1-en-4-ones 4c,d, mixture of isomers in 1:1 ratio. R_f 0.05 (hexane–EtOAc, 1:1, visualization by UV light / vanillin reagent). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): one isomer: 7.65 (2H, d, *J* = 8.6, H Ar); 7.49 (2H, d, *J* = 8.4, H Ar); 7.32 (2H, d, *J* = 8.4, H Ar), 7.27–7.22 (3H, m, H Ar), 6.96 (2H, d, *J* = 8.6, H Ar); 6.54 (2H, dd, *J* = 6.5, *J* = 1.8, H Ar), 5.25 (1H, t, *J* = 8.1, 8-CH); 5.10 (1H, s, 6-CH); 5.06 (1H, q, *J* = 7.3, NCH); 3.83 (3H, s, OCH_3); 2.75 (1H, dd, *J* = 13.2, *J* = 7.7, CH_2); 2.48 (1H, dd, *J* = 13.3, *J* = 8.4, CH_2); 1.84 (3H, s, CH_3); 1.48 (3H, d, *J* = 7.3, CH_3); other isomer: 7.63 (2H, d, *J* = 8.6, H Ar); 7.39 (2H, d, *J* = 8.4, H Ar); 7.27–7.22 (5H, m, H Ar); 6.96 (2H, d, *J* = 8.6, H Ar); 6.94 (2H, dd, *J* = 7.2, *J* = 1.9, H Ar); 5.25 (1H, t, *J* = 8.1, 8-CH); 5.09 (1H, s, 6-CH); 4.97 (1H, q, *J* = 7.2, NCH); 3.83 (3H, s, OCH_3); 2.72 (1H, dd, *J* = 13.2, *J* = 7.4, CH_2); 2.50 (1H, dd, *J* = 13.2, *J* = 8.8, CH_2); 1.92 (3H, s, CH_3); 1.30 (3H, d, *J* = 7.2, CH_3). ^{13}C NMR spectrum, δ, ppm (both isomers): 182.4 (2C=O); 162.4 and 162.3 (C); 159.8 (2C(4)–O Ar); 139.5 and 139.0 (C); 134.9 and 134.7 (C); 132.9 and 132.7 (C); 131.4 and 131.2 (2CH); 128.9 (C); 128.8 (CH); 128.7 (CH); 128.6 (CH); 128.1 (2CH); 127.8 (2 4-CH Ph); 126.5 and 126.3 (2CH); 122.4 and 122.3 (C); 114.1 (2CH); 85.9 and 85.8 (OCH); 80.81 (2OCH); 79.2 (2C); 55.5 (OCH_3); 50.4 and 49.2 (NCH); 44.8 and 44.6 (CH_2); 17.7 ($2CH_3$); 17.5 (CH_3); 17.3 (CH_3). Found, *m*/*z*: 521.1249 $[M+H]^+$. $C_{28}H_{28}{}^{81}BrN_2O_3$. Calculated, *m*/*z*: 521.1262.

X-ray structural analysis of compound 3a was performed on an APEX DUO diffractometer (MoKα radiation, graphite monochromator, ω-scanning). Crystals suitable for X-ray structural analysis were grown by slow cooling of a saturated solution in PhH. The structure was solved using the dual-space algorithm and refined against F^2_{hkl} by the least-squares technique in the full-matrix anisotropic approximation using the Bruker SHELXTL program set. Hydrogen atom positions were refined geometrically. All calculations were performed using the SHELXT, SHELXL, and OLEX2 software packages.[11–13] The full set of X-ray structural data for compound **3a** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 2012447).

Supplementary information file containing details of the assignment of stereoisomers, ^{1}H and ^{13}C NMR spectra for all synthesized compounds, COSY, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC spectra of mixtures of compounds **4a**,**b** and **4c**,**d**, as well as the main crystallographic data and parameters of the X-ray structural analysis of compound **3a**, is available at the journal website at http://link.springer.com/journal/10593.

This work was supported by the Russian Science Foundation (grant 19-73-00319).

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