JOC The Journal of Organic Chemistry

Article

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Donor–Acceptor Cyclopropanes as 1,2-Dipoles in $GaCl_3$-Mediated [4 + 2]-Annulation with Alkenes: Easy Access to the Tetralin Skeleton

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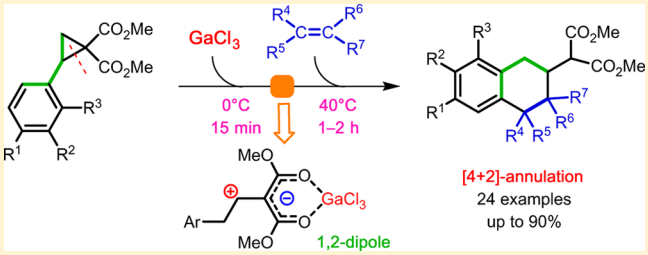
Supporting Information

ABSTRACT: A new process for (4 + 2)-annulation of donor–acceptor cyclopropanes (DACs) with unsaturated compounds in the presence of anhydrous $GaCl_3$ has been developed. In this process, DACs act as sources of formal 1,2- and 1,4-dipoles to give polysubstituted tetralins in high yields and with high regio- and diastereoselectivity. Alkenes with both aryl and alkyl substituents at the double bond undergo this reaction equally readily. A most likely mechanism of the reaction has been proposed. It involves preliminary generation of a key 1,2-dipolar gallium complex and its subsequent participation in annulation with an alkene.



INTRODUCTION

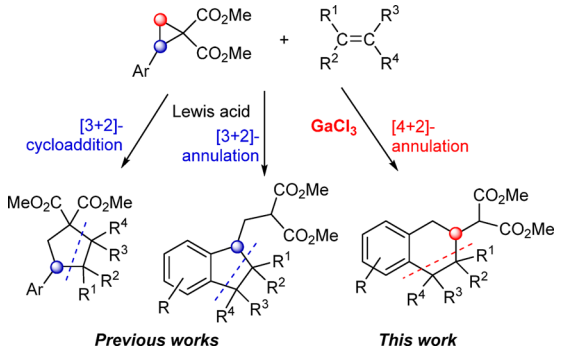
Donor–acceptor cyclopropanes (DACs) are widely used in contemporary organic synthesis as carbon-based building blocks for the construction of various carbo- and heterocyclic compounds, including enantioselective reactions and full syntheses of natural compounds.[1,2] They can act as synthetic equivalents of 1,3-dipoles and undergo cycloaddition and annulation with diverse substrates under acid catalysis conditions. Owing to this feature, they are currently very popular among chemists who deal with organic synthesis all over the world. However, though the scope of reactions involving DACs is very broad and diverse, their reactivity known to date is limited to use as 1,3-dipoles only.[1]

We have recently discovered a new type of DAC reactivity, where they can act as sources of formal 1,2- and 1,4-dipoles in the presence of anhydrous $GaCl_3$ due to positive charge migration from the benzyl center.[3,4] This type of reactivity was demonstrated for dimerization of 2-arylcyclopropane-1,1-dicarboxylates,[3] which considerably limited its applicability to the use of these substrates. In this study, we expanded the use of DACs as formal 1,2- and 1,4-dipoles to their reactions with various unsaturated substrates.

In general, reactions of DACs with alkenes in the presence of Lewis acids have been known for a long time. They are widely used today in organic synthesis to build five-membered carbocycles.[1a,h,5] These reactions are known to follow two pathways, namely, (3 + 2)-cycloaddition to give substituted cyclopentanes[5a−e] and (3 + 2)-annulation to an aromatic substituent in DACs to give substituted indanes[5f] (Scheme 1). Both variants involve initial generation of a highly reactive 1,3-dipole. In this study, we have developed a new pathway of DAC reactions with alkenes, namely, (4 + 2)-annulation, where DACs, specifically 2-arylcyclopropane-1,1-dicarboxylates, act as formal 1,4-dipoles that react with alkenes to give substituted tetralins. This change in reactivity is achieved by using anhydrous $GaCl_3$ and a specially developed approach for selective generation of 1,2-dipoles.[3b]

The (4 + 2)-annulation of DACs developed by us is a synthetically valuable process that allows one-stage syntheses of polysubstituted tetralins with high regio- and diastereoselectivity from simple and readily available 2-arylcyclopropanedicar-

Scheme 1. Reactions of DACs with Alkenes in the Presence of a Lewis Acid



Received: June 8, 2015
Published: July 18, 2015

DOI: 10.1021/acs.joc.5b01179
J. Org. Chem. 2015, 80, 8225−8235

boxylates and unsaturated compounds. The latter may be of interest as synthons in organic synthesis and as compounds possessing biological activity. In fact, aryltetralin moieties are found in the structures of a number of compounds that were isolated from various natural sources and that manifest a broad spectrum of biological activity,[6] including antitumor activity[6f] (Figure 1).

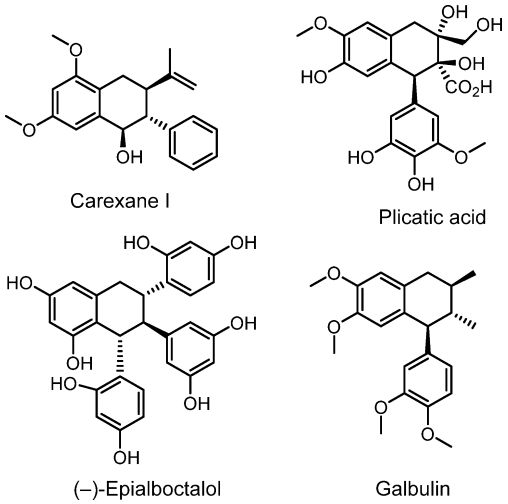


Figure 1. Tetralin skeleton in nature.

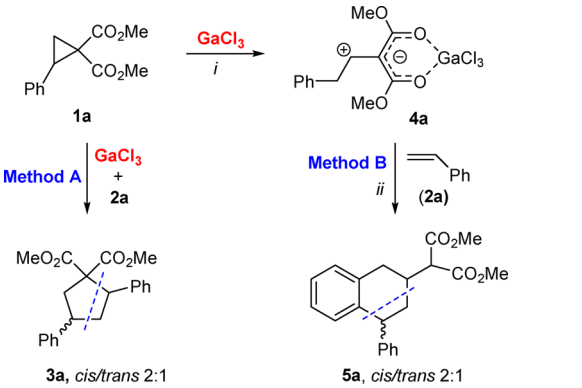
RESULTS AND DISCUSSION

To implement the reactions of DACs with alkenes by the selective (4 + 2)-annulation pathway, we had to perform a detailed and thorough adjustment of the process conditions. As a result, the nature of the reaction intermediates changed. We studied the reaction of dimethyl 2-phenylcyclopropanedicarboxylate (**1a**) with styrene (**2a**) as a model reaction for optimization (Table 1).

It was found that if one just mixes cyclopropane **1a** with styrene in the presence of $GaCl_3$, then cyclopentane **3a**, a (3 + 2)-cycloaddition product, is mainly formed (method A). However, if one prepares relatively stable 1,2-dipolar gallium complex **4a** and then performs its reaction with the alkene, then tetralin derivative **5a** is formed as the main reaction product (Scheme 2). Thus, the most important condition for the reaction to follow the (4 + 2)-annulation pathway is the preliminary generation of 1,2-dipole **4a** (Table 1, method B), which changes the direction of the reaction. We have shown previously[3b] that the optimum conditions for generation of this intermediate include the use of equimolar amounts of a DAC and anhydrous $GaCl_3$ in dichloromethane at 0−5 °C. In this case, intermediate **4a** was detected by NMR spectroscopy and was shown to exist in rather narrow temperature and time ranges.

Furthermore, we studied a series of 2-arylcyclopropane-1,1-dicarboxylates and various unsaturated compounds that react by (4 + 2)-annulation (Scheme 2). It has been found that reactions in the presence of $GaCl_3$ to give polysubstituted tetralins **5** are of general scope and apply to alkenes with both aryl and alkyl substituents at the double bond, as well as arylcyclopropanedicarboxylates with various substituents at the aromatic ring. In this case, the process conditions depend on the substrate type quite insignificantly.

Table 1. Optimization of the Reaction Conditions for the Model (4 + 2)-Annulation between Cyclopropane 1a and Styrene (2a) in the Presence of $GaCl_3$



entry	$[GaCl_3]$, mol %	amt of **2a**, equiv	T_i, °C	t_i, min	T_{ii}, °C	t_{ii}, h	yield[a] % **3a**	yield[a] % **5a**
1[c]	120	3	20		40	1	95	0
2	120	3	0	0.5	40	2	87	6
3	100	3	0	15	40	2	5[b]	70[b]
4	110	3	5	8	40	2	0	76[b]
5	150	3	0	10	40	2	0	53[b,d]
6	105	1	0	10	40	2	5[b]	40[b,d]
7	110	5	0	10	40	2	0	85
8	100	3	0	10	20	2.5	41[b]	33[b]
9[e]	105	3	0	10	40	2	80[b]	10[b]

[a]Product yields strongly depend on the quality of $GaCl_3$ used and the traces of moisture. [b]NMR yields. [c]Method A was used. [d]The dimers of starting cyclopropane **1a** are formed in a large quantity (see refs 3b and 4e). [e]Water traces were used in the reaction mixture after the first step by the short contact with air.

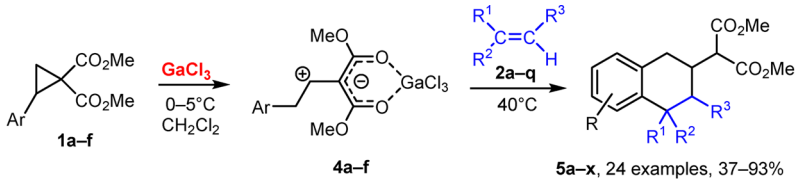
In fact, styrenes with substituents at the aromatic ring (**2b−e**) underwent this process rather well; however, the yields of the corresponding tetralins **5b−e** turned out to be noticeably smaller than in the case of nonsubstituted styrene, probably due to easier polymerization of substituted styrenes in the presence of $GaCl_3$. All disubstituted tetralins **5a−e** were formed as mixtures of *cis*- and *trans*-isomers in a (2−7):1 ratio, with the *cis*-isomer predominating. The reaction with **1a** also occurs with methoxy-substituted styrenes **2d,e**. This is particularly valuable despite the moderate yields of the resulting tetralins **5d,e**, since tetralins with alkoxy substituents at the aromatic rings are widespread in nature and have a broad spectrum of biological activity.[6]

(4 + 2)-Annulation of **1a** readily occurs with α- and β-alkyl- or aryl-substituted styrenes **2g,h,j,k**, as well as with monosubstituted and *gem*-disubstituted alkenes (hex-1-ene and 2-methylpropene). In the latter two cases, the yields of products **5f** and **5i** reached 93% and 86%, respectively. Tetralin **5f** unexpectedly formed to favor the *trans*-isomer in contrast to tetralins **5a−e**. The reactions with cycloalkenes gave fused tetralins **5l−o** in 40−53% yields. In this case, the reactions of **1a** with *trans*-stilbene, 1-phenylcyclohexene, cyclohexene, and dihydronaphthalene gave the respective tetralins **5j,l,m,o**, each as a single diastereomer.

Reaction of (4 + 2)-annulation can also be carried out with more complex unsaturated substrates. In fact, styrylmalonates **2p,q** react fairly well with 1,2-dipoles that are formed from 2-phenyl- and 2-(4-fluorophenyl)cyclopropanedicarboxylates **1a,b**

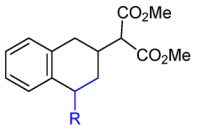
DOI: 10.1021/acs.joc.5b01179
J. Org. Chem. 2015, 80, 8225−8235

Scheme 2. Scope of (4 + 2)-Annulation of Cyclopropanes 1 to Alkenes 2[a]

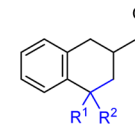


1a: Ar = Ph
1b: Ar = 4-FC_6H_4
1c: Ar = 4-ClC_6H_4
1d: Ar = 3-ClC_6H_4
1e: Ar = 2-ClC_6H_4
1f: Ar = 2-naphthyl

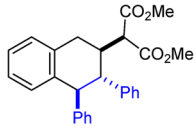
2a: styrene
2b: 4-methylstyrene
2c: 4-(*t*-butyl)styrene
2d: 4-methoxystyrene
2e: 2-methoxystyrene
2f: 1-hexene
2g: 1,1-diphenylethylene
2h: α-methylstyrene
2i: *iso*-butylene
2j: *trans*-stilbene
2k: β-methylstyrene
2l: 1-phenylcyclohexene
2m: cyclohexene
2n: indene
2o: dihydronaphthalene
2p: (*E*)-dimethyl 2-styrylmalonate
2q: (*E*)-dimethyl 2-(4-fluorostyryl)malonate



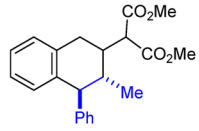
5a, R = Ph, 85%, *cis/trans* 2:1
5b, R = 4-MeC_6H_4, 40%, *cis/trans* 4.5:1
5c, R = 4-t-BuC_6H_4, 48%, *cis/trans* 2.5:1
5d, R = 4-$MeOC_6H_4$, 37%, *cis/trans* 3.5:1
5e, R = 2-$MeOC_6H_4$, 42%, *cis/trans* 7:1
5f, R = n-Bu, 93%, *cis/trans* 1:1.6



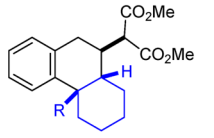
5g, $R^1 = R^2$ = Ph, 61%
5h, R^1, R^2 = Ph, Me, 45%, *Z/E* 1.5:1
5i, $R^1 = R^2$ = Me, 86%



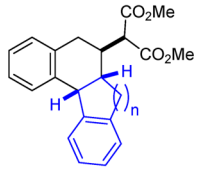
5j, 81%, single diast.



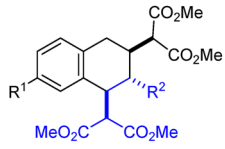
5k, 89%, *EE/ZE* 1.2:1



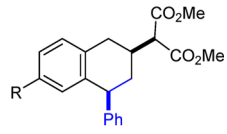
5l, R = Ph, 53%, single diast.
5m, R = H, 42%, single diast.



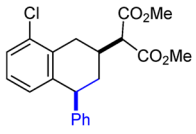
5n, n = 1, 40%, dr 2.5:1
5o, n = 2, 44%, single diast.



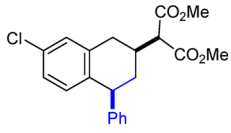
5p, R^1 = H, R^2 = Ph, 83%, single diast.
5q, R^1 = H, R^2 = 4-FC_6H_4, 79%, single diast.
5r, R^1 = F, R^2 = Ph, 52%, single diast.



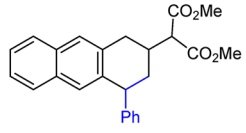
5s, R = F, 82%, *cis/trans* 8:1
5t, R = Cl, 70%, *cis/trans* 9:1



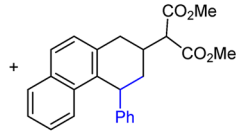
5u, 40%, *cis/trans* 7:1



5v, 59%, *cis/trans* 6:1



5w, 25%, *cis/trans* 1.9:1



5x, 37%, *cis/trans* 1:2.3

[a]Reaction conditions: (i) 0–5 °C, $GaCl_3$ (1.0–1.1 equiv for **1a–d,f**, 1.2–1.5 equiv for **1e**), time 8–15 min for **1a–c,f**, 20–30 min for **1d**, and 30–60 min for **1e**; (ii) 40 °C, 1–3 h. Excess of alkenes: 1–1.2 equiv for tetralins **5i,p–r**, 2 equiv for tetralin **5f**, 3–5 equiv for tetralins **5a–e,g,h,j–l,o**, and 5–8 equiv for tetralins **5m,n,s–x**.

in the presence of $GaCl_3$ to give polysubstituted tetralins **5p–r** as single diastereomers, which in essence are formal homodimers and cross-dimers of the starting cyclopropanes.[3b] It should be noted that, in the case of nonsymmetric alkenes, all the reactions of 1,2-dipole addition studied occur with exclusively high regioselectivity, in agreement with the more efficient stabilization of the carbocationic center in the intermediate, which allows the synthesis of substituted tetralins to be performed on a sufficiently preparative scale.

Besides unsaturated compounds, the substituents in the starting cyclopropane **1** in (4 + 2)-annulation can also be varied. In fact, 4-fluoro- and 4-chloro-substituted cyclopropanes **1b,c** readily react with styrene, though in this case one has to use an even greater excess of styrene due to easier dimerization of the starting cyclopropanes. Arylcyclopropanes with a chlorine atom at the *meta* and *ortho* positions of the phenyl substituent (**1d,e**) can also be used in this reaction. However, due to their lower reactivity in comparison with that of unsubstituted phenylcyclopropane **1a**, especially in the case of the *o*-chlorophenyl substituent, the time for generation of 1,2-dipoles **4d,e** has to be increased considerably. As a result, the efficiency of generation decreases, and side processes occur during this long time; hence, the yields of the target tetralins decrease. However, as such, the new approach to the synthesis of substituted tetralins is rather successful. It is interesting to note that the structurally identical moiety in *m*-chlorophenyl-substituted cyclopropane **1d** gives only regioisomer **5v** in the same reaction with styrene; i.e., annulation occurs only at the less sterically hindered position.

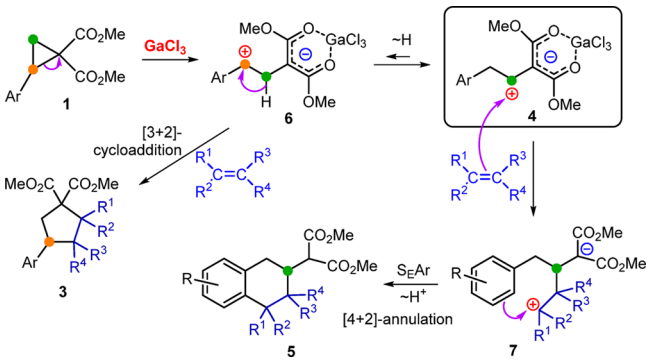
The reaction of dimethyl 2-naphthylcyclopropanedicarboxylate (**1f**) with styrene in the presence of $GaCl_3$ has to be noted separately. In this case, (4 + 2)-annulation is also the predominating process; however, since electrophilic attack on the naphthyl ring can occur at two different adjacent positions, the reaction gives two different regioisomers, **5w** and **5x**, in a 1:1.5 ratio.

The composition of all the target products was established by means of elementary analyses or HRMS. The structure and stereochemistry of the compounds obtained were determined by ^1H, ^{19}F, and ^{13}C NMR spectroscopy using 1D and 2D DEPT, COSY, TOCSY, NOESY, HMQC/HSQC, and HMBC (for details, see the Supporting Information).

DOI: 10.1021/acs.joc.5b01179
J. Org. Chem. 2015, 80, 8225–8235

On the basis of previous experimental data[3a,b] and the data obtained in this study, it is obvious that (4 + 2)-annulation of DACs with alkenes occurs via the key 1,2-dipolar gallium complex **4** formed by DAC opening to give a classic 1,3-dipole, **6**, followed by positive charge migration from the benzyl position in the presence of $GaCl_3$. In this case, 1,2-dipole **4** exists in equilibrium with 1,3-dipole **6**. This equilibrium is strongly shifted toward the 1,2-dipole[3a,b] (Scheme 3).

Scheme 3. Proposed Mechanism of the [4 + 2]-Annulation of DACs with Alkenes



The two dipoles have different reactivities. In particular, this fact allows the existence of a 1,2-dipolar gallium intermediate to be observed experimentally for a few hours, unlike in the case of the 1,3-dipole. As a consequence, full generation of the 1,2-dipole and its subsequent reaction with an unsaturated compound are the key stages for the synthesis of tetralins substituted in a certain way.

After the formation of the 1,2-dipole and addition of an unsaturated compound, intermediate **7** is formed at an elevated temperature. In this case, addition of the carbocationic center in the 1,2-dipole to the double bond in the alkene occurs in such a way that the positive charge is located at the benzyl position in the case of styrenes or at the most substituted carbon atom in the case of alkenes, which explains the exceptional regioselectivity of the reaction. After that, intermediate **7** undergoes intramolecular electrophilic substitution at the aromatic ring to give the final tetralin **5**, which is also facilitated by an increase in temperature. At reduced temperatures, tetralins **5** are not formed at all or are formed in minor amounts. Instead of (4 + 2)-annulation, the resulting 1,2-dipole **4** gradually regenerates 1,3-dipole **6**, which instantly reacts with dipole **4** and an alkene available in the system to give (3 + 2)-cycloaddition products.

CONCLUSION

We have discovered a new regio- and diastereoselective (4 + 2)-annulation of aryl-substituted DACs with alkenes to give polysubstituted tetralins and developed the corresponding preparative technique. The process occurs only in the presence of anhydrous gallium trichloride and involves preliminary generation of a 1,2-dipolar gallium complex. The reaction is of general scope and applies to diverse unsaturated compounds, with both aryl and alkyl substituents at the double bond, as well as DACs with substituents at various aromatic ring positions. This process is a unique example where DACs are used as sources of formal even-numbered 1,2- and 1,4-dipoles in reactions with unsaturated substrates.

EXPERIMENTAL SECTION

General Experimental Details. All reagents and solvents used were commercial grade chemicals without additional purification. All operations with $GaCl_3$ were carried out under a dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040−0.063 mm) was used. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on 400 MHz (400.1 and 100.6 MHz, respectively) and 300 MHz (300.1 and 75.5 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Determinations of the structures and stereochemistry of the obtained compounds and assignments of the ^1H and ^{13}C signals were made with the aid of 1D and 2D DEPT, JMOD, COSY, TOCSY, NOESY, XHCORR, HSQC, and HMBC spectra. ^{19}F NMR spectra were recorded on a 300 MHz spectrometer (282.4 MHz; standard $CFCl_3$). Determinations of the structures and assignments of the ^{19}F signals were made with the aid of 2D $^1H,^{19}F$ HMQC, and HMBC spectra. Monitoring of the reactions in an NMR tube was done in a CD_2Cl_2 solution containing 0.05% Me_4Si as the internal standart. IR spectra were obtained on an FT-IR spectrometer in $CHCl_3$ solution (1%). Mass spectra were recorded using electron impact ionization (EI; 70 eV, direct inlet probe). High-resolution mass spectra (HRMS TOF) were obtained using simultaneous electospray ionization (ESI). The elemental compositions were determined on a CHN analysis instrument.

General Procedure for the Synthesis of Cyclopropanes 1a−f and Alkenes 2p,q. Starting cyclopropanes **1a−f** were synthesized from the corresponding aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey−Chaykovsky reactions.[3b,4c] (*E*)-Dimethyl 2-styrylmalonate (**2p**) and (*E*)-dimethyl 2-(4-fluorostyryl)malonate (**2q**) were synthesized from the corresponding DACs **1a,b** through (TMS)OTf-mediated isomerization.[7]

General Procedure for the Synthesis of Tetralins 5a−y. Solid $GaCl_3$ (1−1.5 equiv) in one portion was added at 0 °C to a solution of cyclopropane **1** (0.5−1.0 mmol) in dry CH_2Cl_2 (3−5 mL), and the mixture was stirred at the same temperature until completion of the generation of 1,2-dipole **4** (optimal conditions: 1 equiv of $GaCl_3$, 10−15 min, for cyclopropanes **1a−c,f**; 1.1−1.2 equiv of $GaCl_3$, 20−30 min, for cyclopropane **1d**; 1.2−1.5 equiv of $GaCl_3$, 40−60 min, for cyclopropane **1e**). Then a solution of alkene **2** (1−8 equiv) in dry CH_2Cl_2 (1−2 mL) was added, and the reaction mixture was immediately heated to 40 °C and refluxed for 1−3 h until reaction completion. After that, an aqueous solution of HCl (5%) was added at room temperature until pH 3 was achieved, and the reaction mixture was extracted with CH_2Cl_2 (3 × 10−15 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (benzene−EtOAc, 50:1 to 10:1) to afford the title tetralin **5** as a thick colorless oil. If necessary, the resulting compound **5** may be additionally purified on a Silufol chromatographic plate (20 × 20 cm), eluting with hexane−acetone (5:1) or benzene−EtOAc (10:1) to give a pure product.

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenyl-1,2,3,4-tetrahydronaphthalene (5a).** The title compound was prepared according to the general procedure as a mixture of diastereomers (*cis*:*trans* = 2:1) from cyclopropane **1a** (234 mg, 1.0 mmol), styrene (**2a**) (520 mg, 5 mmol), and $GaCl_3$ (194 mg, 1.1 mmol) in 287 mg yield (85%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3020, 2955, 2927, 1732 br (O═CO), 1601, 1582, 1516, 1493, 1451, 1437 cm^{-1}. MS (*m*/*z* (rel intens, %))): 338 (6, M^+), 307 (10, $M^+ - OCH_3$), 275 (3), 206 (100), 191 (22), 178 (30), 165 (15), 128 (27), 115 (16), 91 (32), 59 (31). HRMS: calcd for $C_{21}H_{22}O_4$ M + H 339.1591, M + Na 361.1410, found *m*/*z* 339.1590, 361.1409.

The following are data for compound *cis*-**5a** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.67 (ddd, 1H, *syn*-H(3), ^2J = 12.6 Hz, ^3J = 12.3 and 12.1 Hz), 2.17 (dddd, 1H, *anti*-H(3), ^2J = 12.6 Hz, ^3J = 5.4 and 2.6 Hz, ^4J = 2.2 Hz), 2.68−2.76 (m, 1H, H(2)), 2.82 (dd, 1H, *anti*-H(1), ^2J = 15.5 Hz, ^3J = 11.7 Hz), 2.93 (ddd, 1H, *syn*-H(1), ^2J = 15.5 Hz, ^3J = 4.2 Hz, ^4J = 2.2 Hz), 3.38 (d, 1H, CH, ^3J = 8.4 Hz), 3.72 and 3.77 (both s, 2 × 3H, 2 OMe), 4.12 (dd, 1H, H(4), ^3J = 12.1 and

DOI: 10.1021/acs.joc.5b01179
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5.4 Hz), 6.75 (br d, 1H, H(5), ^3J = 7.6 Hz), 7.00 (m, 1H, H(6)), 7.07 (m, 1H, H(7)), 7.08 (m, 1H, H(8)), 7.16 (m, 2H, 2 *o*-H), 7.24 (m, 1H, *p*-H), 7.29 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.3 ($CH_2(1)$), 35.1 (CH(2)), 38.4 ($CH_2(3)$), 46.9 (CH(4)), 52.51 and 52.54 (2OMe), 57.4 (CH(2′)), 126.1 (2C, CH(6) and CH(8)), 126.5 (*p*-CH), 128.6 (2 *m*-CH), 128.86 (2 *o*-CH), 128.90 (CH(7)), 129.5 (CH(5)), 135.7 (C(8a)), 139.3 (C(4a)), 146.4 (*i*-C), 168.7 and 168.8 (2COO).

The following are data for compound *trans*-**5a** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.96−2.05 (m, 2H, $CH_2(3)$), 2.60−2.67 (m, 1H, H(2), ^3J = 9.8, 8.4, 4.6 Hz), 2.72 (dd, 1H, *syn*-H(1), ^2J = 16.2 Hz, ^3J = 9.8 Hz), 3.03 (dd, 1H, *anti*-H(1), ^2J = 16.2 Hz, ^3J = 4.6 Hz), 3.36 (d, 1H, CH, ^3J = 8.4 Hz), 3.65 and 3.69 (both s, 2 × 3H, 2 OMe), 4.29 (dd, 1H, H(4), ^3J = 5.3 and 5.1 Hz), 6.94 (br d, 1H, H(5), ^3J = 7.6 Hz), 7.00 (m, 2H, 2 *o*-H), 7.11 (m, 1H, H(6)), 7.14 (m, 1H, H(8)), 7.15 (m, 1H, H(7)), 7.17 (m, 1H, *p*-H), 7.25 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 30.2 (CH(2)), 32.3 ($CH_2(1)$), 36.0 ($CH_2(3)$), 43.6 (CH(4)), 52.35 and 52.38 (2OMe), 56.3 (CH(2′)),126.1 (CH(6)), 126.2 (*p*-CH), 126.4 (CH(8)), 128.2 (2 *m*-CH), 128.7 (2 *o*-CH), 129.2 (CH(7)), 130.4 (CH(5)), 136.0 (C(8a)), 137.6 (C(4a)), 146.6 (*i*-C), 168.7 and 168.9 (2COO).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-methylphenyl)-1,2,3,4-tetrahydronaphthalene (5b).** The title compound was prepared according to the general procedure from cyclopropane **1a** (150 mg, 0.64 mmol), 4-methylstyrene (**2b**) (378 mg, 3.20 mmol), and $GaCl_3$ (118 mg, 0.67 mmol) as a mixture of diastereomers (*cis*:*trans* = 4.5:1) in 88 mg yield (39%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3011, 2955, 2926, 1733 (O═CO), 1514, 1493, 1450, 1436 cm^{-1}. MS (*m*/*z* (rel intens, %)): 352 (4, M^+), 321 (2, $M^+ - OCH_3$), 220 (100), 205 (30), 178 (14), 128 (23), 105 (38), 91(11), 59 (15). HRMS: calcd for $C_{22}H_{24}O_4$ M + H 353.1747, M + Na 375.1567, 391.1306, found *m*/*z* 353.1749, 375.1562.

The following are data for compound *cis*-**5b** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.59 (ddd, 1H, *syn*-H(3), ^2J = 12.5 Hz, ^3J = 12.3, 12.1 Hz), 2.08 (dddd, 1H, *anti*-H(3), ^2J = 12.5 Hz, ^3J = 5.4 and 2.9 Hz, ^4J = 2.3 Hz), 2.26 (s, 3H, Me), 2.61−2.69 (m, 1H, H(2)), 2.74 (dd, 1H, *anti*-H(1), ^2J = 15.4 Hz, ^3J = 11.7 Hz), 2.85 (ddd, 1H, *syn*-H(1), ^2J = 15.4 Hz, ^3J = 4.3 Hz, ^4J = 2.3 Hz), 3.29 (d, 1H, CH, ^3J = 8.4 Hz), 3.65 and 3.70 (both s, 2 × 3H, 2 OMe), 4.02 (dd, 1H, H(4), ^3J = 12.1 and 5.4 Hz), 6.69 (br d, 1H, H(5), ^3J = 7.6 Hz), 6.90−6.95 (m, 1H, H(6)), 6.95−7.07 (m, 6H, 2Ar except H(5) and H(6)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 21.2 (CH_3), 33.3 ($CH_2(1)$), 35.2 (CH(2)), 38.6 ($CH_2(3)$), 46.6 (CH(4)), 52.60 and 52.63 (2OMe), 57.6 (CH), 126.15 and 126.17 (CH(6) and CH(8)), 128.8 (2 *m*-CH), 128.9 (CH(7)), 129.3 (2 *o*-CH), 129.6 (CH(5)), 135.7 (*p*-C), 136.1 (C(8a)), 139.6 (C(4a)), 143.5 (*i*-C), 168.8 and 168.9 (2COO).

The following are data for compound *trans*-**5b** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.90−1.97 (m, 2H, $CH_2(3)$), 2.23 (s, 3H, Me), 2.52−2.62 (m, 1H, H(2)), 2.59−2.67 (m, 1H, *syn*-H(1)), 2.96 (dd, 1H, *anti*-H(1), ^3J = 16.0 and 4.6 Hz), 3.29 (d, 1H, H(2′), ^3J = 8.3 Hz), 3.59 and 3.63 (both s, 2 × 3H, 2 OMe), 4.17 (dd, 1H, H(4), ^3J = 5.3 and 5.1 Hz), 6.81 (br d, 1H, H(5), ^3J = 8.0 Hz), 6.84−7.07 (m, 7H, 2Ar except H(5)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 21.1 (CH_3), 30.3 ($CH_2(1)$), 33.3 (CH(2)), 36.0 ($CH_2(3)$), 43.3 (CH(4)), 52.46 and 52.48 (2OMe), 56.4 (CH)), 126.3 and 126.5 (CH(6) and CH(8)), 128.6, 129.1, 129.3, and 129.6 (2 *o*-CH, 2 *m*-CH, CH(5) and CH(7)), 135.6 (*p*-C), 135.9 (C(8a)), 137.9 (C(4a)), 143.7 (*i*-C), 168.9 and 169.0 (2COO).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-*tert*-butylphenyl)-1,2,3,4-tetrahydronaphthalene (5c).** The title compound was prepared according to the general procedure from cyclopropane **1a** (150 mg, 0.64 mmol), 4-(*tert*-butyl)styrene (**2c**) (512 mg, 3.20 mmol), and $GaCl_3$ (118 mg, 0.67 mmol) as a mixture of diastereomers (*cis*:*trans* = 2.5:1) in 120 mg yield (48%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3008, 2958, 1732 (O═CO), 1451, 1437 cm^{-1}. MS (*m*/*z* (rel intens, %)): 394 (15, M^+), 363 (4, $M^+ - OCH_3$), 262 (100), 247 (28), 217 (9), 205 (100), 178 (16), 158 (40), 143 (49), 133 (63), 119 (25), 100 (19), 91(39), 69 (16), 57 (67). HRMS: calcd for $C_{25}H_{30}O_4$ M + H 395.2217, M + Na 417.2036, M + K 433.1776, found *m*/*z* 395.2214, 417.2033, 433.1775.

The following are data for compound *cis*-**5c** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.32 (s, 9H, *t*-Bu), 1.65 (ddd, 1H, *syn*-H(3), ^2J = 12.7 Hz, ^3J = 12.2 and 12.2 Hz), 2.16 (dddd, 1H, *anti*-H(3), ^2J = 12.7 Hz, ^3J = 5.4 and 2.5 Hz, ^4J = 2.1 Hz), 2.68−2.77 (m, 1H, H(2)), 2.81 (dd, 1H, *anti*-H(1), ^3J = 15.5 and 11.7 Hz), 2.92 (ddd, 1H, *syn*-H(1), ^2J = 15.5 Hz, ^3J = 4.2 Hz, ^4J = 2.1 Hz), 3.36 (d, 1H, CH, ^3J = 8.5 Hz), 3.73 and 3.78 (both s, 2 × 3H, 2 OMe), 4.10 (dd, 1H, H(4), ^3J = 12.2 and 5.4 Hz), 6.78 (br d, 1H, H(5), ^3J = 7.8 Hz), 6.98−7.16 (m, 3H, H(6)−H(8)), 7.05−7.10 (m, 2H, 2 *o*-H), 7.28−7.33 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 31.6 (CMe_3), 34.4 ($CH_2(1)$), 34.6 (CMe_3), 35.3 (CH(2)), 38.6 ($CH_2(3)$), 46.5 (CH(4)), 52.61 and 52.62 (2OMe), 57.6 (CH), 125.5 (2 *m*-CH), 126.11 and 126.14 (CH(6) and CH(8)), 128.5 (2 *o*-CH), 129.0 (CH(7)), 129.7 (CH(5)), 135.8 (C(8a)), 139.7 (C(4a)), 143.3 (*i*-C), 149.4 (*p*-C), 168.87 and 168.93 (2COO).

The following are data for compound *trans*-**5c** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.29 (s, 9H, *t*-Bu), 1.97−2.03 (m, 2H, $CH_2(3)$), 2.57−2.69 (m, 1H, H(2)), 2.66−2.76 (m, 1H, *syn*-H(1)), 3.04 (dd, 1H, *anti*-H(1), ^3J = 15.9 and 4.5 Hz), 3.29 (d, 1H, CH, ^3J = 8.3 Hz), 3.66 and 3.70 (both s, 2 × 3H, 2 OMe), 4.25 (dd, 1H, H(4), $^3J \approx$ 5.1 and 5.2 Hz), 6.90−6.94 (m, 2H, 2 *o*-H), 6.96 (br d, 1H, H(5), ^3J = 7.5 Hz), 6.98−7.16 (m, 3H, H(6), H(7) and H(8)), 7.24−7.28 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 30.5 (CH(2)), 31.6 (3 Me, *t*-Bu), 33.3 ($CH_2(1)$), 34.5 (C, *t*-Bu), 36.0 ($CH_2(3)$), 43.2 (CH(4)), 52.43 and 52.45 (2OMe), 56.5 (CH), 125.2 (2 *m*-CH), 126.2 (CH(6)), 126.4 (CH(8)), 128.4 (2 *o*-CH), 129.3 (CH(7)), 130.5 (CH(5)), 136.0 (C(8a)), 138.0 (C(4a)), 143.6 (*i*-C), 148.9 (*p*-C), 169.0 and 169.1 (2COO).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (5d).** The title compound was prepared according to the general procedure from cyclopropane **1a** (150 mg, 0.64 mmol), 4-methoxystyrene (**2d**) (429 mg, 3.20 mmol), and $GaCl_3$ (118 mg, 0.67 mmol) as a mixture of diastereomers (*cis*:*trans* = 3.5:1) in 86 mg yield (37%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2956, 2839, 1751, 1732 (O═CO), 1610, 1512, 1437 cm^{-1}. MS (*m*/*z* (rel intens, %)): 368 (10, M^+), 250 (31), 236 (100), 221 (14), 209 (15), 178 (14), 165 (14), 142 (22), 128 (39), 121 (48), 69 (12). HRMS: calcd for $C_{22}H_{24}O_5$ M + H 369.1697, M + Na 391.1516, found *m*/*z* 369.1691, 391.1515.

The following are data for compound *cis*-**5d** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.64 (ddd, 1H, *syn*-H(3), ^2J = 12.5 Hz, ^3J = 12.0 and 12.1 Hz), 2.14 (dddd, 1H, *anti*-H(3), ^2J = 12.5 Hz, ^3J = 5.3 and 2.8 Hz, ^4J = 2.2 Hz), 2.67−2.77 (m, 1H, H(2)), 2.76 (dd, 1H, *anti*-H(1), ^2J = 15.0 Hz, ^3J = 11.5 Hz), 2.92 (ddd, 1H, *syn*-H(1), ^2J = 15.0 Hz, ^3J = 7.8 Hz, ^4J = 2.2 Hz), 3.37 (d, 1H, CH, ^3J = 8.4 Hz), 3.73, 3.78, and 3.79 (all s, 3 × 3H, 3 OMe), 4.08 (dd, 1H, H(4), ^3J = 12.1 and 5.3 Hz), 6.79 (br d, 1H, H(5), ^3J = 7.8 Hz), 6.82−6.86 (m, 2H, 2 *m*-H), 6.98−7.10 (m, 3H, H(6)−H(8)), 7.06−7.10 (m, 2H, 2 *o*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.2 ($CH_2(1)$), 35.1 (CH(2)), 38.5 ($CH_2(3)$), 46.1 (CH(4)), 55.34, 52.55, and 52.57 (3 OMe), 57.5 (CH), 114.0 (2 *m*-CH), 126.1, 126.3 (CH(6) and CH(7)), 128.4 (CH(8)), 128.9 (2 *o*-CH), 129.4 (CH(5)), 135.6 (C(8a)), 139.6 (C(4a)), 145.1 (*i*-C), 158.2 (*p*-C), 168.7 and 168.8 (2COO).

The following are data for compound *trans*-**5d** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.96−2.01 (m, 2H, $CH_2(3)$), 2.57−2.68 (m, 1H, H(2)), 2.64−2.74 (m, 1H, *syn*-H(1)), 3.02 (dd, 1H, *anti*-H(1), ^2J = 16.0 Hz, ^3J = 4.3 Hz), 3.36 (d, 1H, H(2′), ^3J = 8.4 Hz), 3.67, 3.71, and 3.77 (all s, 3 × 3H, 3 OMe), 4.24 (dd, 1H, H(4), $^3J \approx$ 5.0 and 5.1 Hz), 6.73−6.77 (m, 2H, 2 *m*-H), 6.86−6.89 (m, 2H, 2 *o*-H), 6.94 (br d, 1H, H(5), ^3J = 8.0 Hz), 7.06−7.20 (m, 3H, H(6)−H(8)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 30.2 (CH(2)), 33.2 ($CH_2(1)$), 36.0 ($CH_2(3)$), 43.8 (CH(4)), 55.29, 52.38, and 52.42 (3 OMe), 56.4 (CH), 113.2 (2 *m*-CH), 126.2 and 126.3 (CH(6) and CH(8)), 128.2 (2 *o*-CH), 129.2 (CH(7)), 130.3 (CH(5)), 135.6 (C(8a)), 138.8 (C(4a)), 142.5 (*i*-C), 157.5 (*p*-C), 168.8 and 168.9 (2COO).

DOI: 10.1021/acs.joc.5b01179
J. Org. Chem. 2015, 80, 8225−8235

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(2-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (5e).** The title compound was prepared according to the general procedure from cyclopropane **1a** (150 mg, 0.64 mmol), 2-methoxystyrene (**2e**) (429 mg, 3.20 mmol), and $GaCl_3$ (118 mg, 0.67 mmol) as a mixture of diastereomers (*cis*:*trans* = 7:1) in 96 mg yield (42%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2956, 2839, 1732 (O═CO), 1610, 1583, 1512, 1494, 1451, 1375, 1337, 1301, 1245 cm^{-1}. MS (*m*/*z* (rel intens, %)): 368 (11, M^+), 250 (33), 236 (100), 221 (18), 209 (19), 178 (14), 165 (15), 142 (24), 128 (44), 121 (53), 108 (8), 100 (10), 91 (9), 59 (27). HRMS: calcd for $C_{22}H_{24}O_5$ M + NH_4 386.1962, M + Na 391.1516, found: *m*/*z* 386.1960, 391.1512.

The following are data for compound *cis*-**5e** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.70 (ddd, 1H, *syn*-H(3), ^2J = 12.6 Hz, ^3J = 12.1 and 11.9 Hz), 2.12 (dddd, 1H, *anti*-H(3), ^2J = 12.6 Hz, ^3J = 5.5 and 2.6 Hz, ^4J = 2.2 Hz), 2.67−2.77 (m, 1H, H(2)), 2.81 (dd, 1H, *anti*-H(1), ^2J = 15.3 Hz, ^3J = 11.6 Hz), 2 0.91 (ddd, 1H, *syn*-H(1), ^2J = 15.3 Hz, ^3J = 4.1 Hz, ^4J = 2.2 Hz), 3.38 (d, 1H, CH, ^3J = 8.3 Hz), 3.73, 3.76, and 3.77 (all s, 3 × 3H, 3 OMe), 4.61 (dd, 1H, H(4), ^3J = 11.9 and 5.5 Hz), 6.74 (br d, 1H, H(5), ^3J = 7.6 Hz), 6.85−6.92 (m, 2H), 6.95−7.02 (m, 2H), 7.04−7.09 (m, 2H) and 7.17−7.23 (m, 1H) (2Ar except H(5)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.4 (CH_2(1)), 35.4 (CH(2)), 36.2 (CH_2(3)), 39.7 (br, CH(4)), 52.56 and 52.57 (2COOMe), 55.7 (OMe), 57.7 (CH), 111.2 (CH(3′)), 121.0 (CH(5′)), 125.7, 126.1, 127.6, 128.9, 129.0, and 129.8 (CH(5)−CH(8), CH(4′) and CH(6′)), 134.8 (C(1′)), 135.9 (C(8a)), 139.7 (C(4a)), 157.7 (C(2′)), 168.94 and 169.02 (2COO).

The following are data for compound *trans*-**5e** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.90 (ddd, 1H, H_a(3), ^2J = 13.1 Hz, ^3J = 10.8 and 5.9 Hz), 1.97−2.04 (m, 2H, H_b(3)), 2.51−2.62 (m, 1H, H(2)), 2.65−2.72 (m, 1H, *syn*-H(1)), 3.01 (dd, 1H, *anti*-H(1), ^2J = 16.3 Hz, ^3J = 5.5 Hz), 3.35 (d, 1H, H(2′), ^3J = 8.3 Hz), 3.68, 3.70, and 3.76 (all s, 3 × 3H, 3 OMe), 4.66 (dd, 1H, H(4), ^3J = 5.9 and 3.6 Hz), 6.85−7.25 (m, 8H, 2 Ar).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-(1-butyl)-1,2,3,4-tetrahydronaphthalene (5f).** The title compound was prepared according to the general procedure from cyclopropane **1a** (235 mg, 1.0 mmol), 1-hexene (**2f**) (176 mg, 2.1 mmol), and $GaCl_3$ (187 mg, 1.06 mmol) as a mixture of diastereomers (*cis*:*trans* = 1:1.6) in 300 mg yield (93%). Both diastereomers were partially separated by chromatography according to the general procedure.

The following are data for compound **5f**, enriched by the *cis*-isomer (*cis*:*trans* = 2:1). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3008, 2957, 2932, 2873, 2862, 1732 (O═CO), 1603, 1491, 1452, 1437, 1379, 1297, 1273 cm^{-1}. MS (*m*/*z* (rel intens, %)): 318 (3, M^+), 287 (7, $M^+ - OCH_3$), 255 (2), 186 (100), 143 (25), 129 (66), 115 (13), 91 (6), 59 (19). HRMS: calcd for $C_{19}H_{26}O_4$ M + Na 341.1723, M+K 357.1463, found *m*/*z* 341.1716, 357.1461. ^1H NMR ($CDCl_3$, 400.1 MHz for *cis*-**5f**): δ 0.85−0.98 (m, 3H, CH_3(4′)), 1.20−1.36 (m, 2H, CH_2(2′)), 1.22−1.43 (m, 2H, CH_2(3′)), 1.23 (ddd, 1H, *syn*-H(3), ^2J = 12.6 Hz, ^3J = 12.1 and 11.7 Hz), 1.50−1.64 (m, 1H, CH_a(1′)), 1.84−1.96 (m, 1H, CH_b(1′)), 2.05 (dddd, 1H, *anti*-H(3), ^2J = 12.6 Hz, ^3J = 5.4 and 2.6 Hz, ^4J = 2.4 Hz), 2.46−2.57 (m, 1H, H(2)), 2.62 (dd, 1H, *anti*-H(1), ^2J = 15.5 Hz, ^3J = 12.0 Hz), 2.77 (ddd, 1H, *syn*-H(1), ^2J = 15.5 Hz, ^3J = 4.2 Hz, ^4J = 2.4 Hz), 2.86−2.98 (m, 1H, H(4)), 3.35 (d, 1H, CH, ^3J = 8.4 Hz), 3.77 (s, 6H, 2 OMe), 7.05−7.22 (m, 3H, CH(6), C(7) and CH(8)), 7.25−7.29 (m, 1H, CH(5)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 14.2 (CH_3), 23.2 (CH_2(3′)), 28.4 (CH_2(2′)), 34.0 (CH_2(3)), 34.6 (CH_2(1)), 34.8 (CH(2)), 35.7 (CH_2(1′)), 38.0 (CH(4)), 52.45 and 52.49 (2OMe), 57.7 (CH), 125.6, 126.2, and 129.1 (CH(6), CH(7) and CH(8)), 127.0 (CH(5)), 136.0 (C(8a)), 139.9 (C(4a)), 168.93 and 169.01 (2COO).

The following are data for compound **5f**, enriched by the *trans*-isomer (*cis*:*trans* = 1:3). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2956, 2932, 2873, 2861, 1751, 1732 (O═CO), 1491, 1452, 1436, 1379, 1337, 1297, 1272 cm^{-1}. MS (*m*/*z* (rel intens, %)): 318 (2, M^+), 287 (5, $M^+ - OCH_3$), 255 (2), 226 (2), 201 (5), 186 (100), 169 (4), 143 (13), 129 (75), 115 (13), 101 (9), 91 (7), 59 (15). HRMS: calcd for $C_{19}H_{26}O_4$ M + H 319.1904, M + Na 341.1723, M + K 357.1463, found *m*/*z* 319.1905, 341.1720, 357.1463. ^1H NMR ($CDCl_3$, 400.1 MHz for *trans*-**4f**): δ 0.85−0.98 (m, 3H, CH_3(4′)), 1.22−1.43 (m, 2H, CH_2(3′)), 1.31−1.47 (m, 2H, CH_2(2′)), 1.55−1.67 (m, 2H, CH_2(1′)), 1.84−1.93 (m, 2H, CH_2(3)), 2.57 (dd, 1H, *syn*-H(1), ^2J = 15.9 Hz, ^3J = 10.8 Hz), 2.64−2.77 (m, 1H, H(2)), 2.74−2.87 (m, 1H, H(4)), 2.88 (ddd, 1H, *anti*-H(1), ^2J = 15.9 Hz, ^3J = 4.7 Hz, ^4J = 1.3 Hz), 3.34 (d, 1H, CH), ^3J = 8.9 Hz), 3.77 (s, 6H, 2 OMe), 7.00−7.05 (m, 1H, CH(8)), 7.05−7.20 (m, 3H, CH(5), CH(6) and CH(7)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 14.2 (CH_3), 22.8 (CH_2(3′)), 30.0 (C(2′)), 30.2 (C(2)), 30.6 (C(3)), 33.7 (C(1)), 37.2 (C(1′)), 37.7 (C(4)), 52.45 and 52.48 (2OMe), 57.5 (CH), 125.8, 125.9, and 129.0 (C(5), C(6) and C(7)), 129.1 (C(8)), 134.8 (C(8a)), 141.1 (C(4a)), 168.99 and 169.04 (2COO).

2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4,4-diphenyl-1,2,3,4-tetrahydronaphthalene (5g). The title compound was prepared according to the general procedure from cyclopropane **1a** (100 mg, 0.43 mmol), 1,1-diphenylethylene (**2g**) (310 mg, 1.72 mmol) and $GaCl_3$ (83 mg, 0.47 mmol) in 107 mg yield (61%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3010, 2954, 1733 (O═CO), 1492, 1455, 1437, 1282, 1244 cm^{-1}. MS (*m*/*z* (rel intens, %)): 414 (1, M^+), 383 (2, $M^+ - OCH_3$), 282 (100), 204 (24), 191 (45), 179 (30), 115 (15), 91 (10). HRMS: calcd for $C_{27}H_{26}O_4$ M + Na 437.1723, found *m*/*z* 437.1732. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.35−2.46 (m, 1H, H(2)), 2.48 (dd, 1H, *anti*-H(1), ^2J = 12.3 Hz, ^3J = 12.0 Hz), 2.65 (ddd, 1H, *syn*-H(1), ^2J = 12.3 Hz, ^3J = 1.8 Hz, ^4J = 1.8 Hz), 2.81 (dd, 1H, H_a(3), ^2J = 16.7 Hz, ^3J = 10.4 Hz), 2.94 (ddd, 1H, H_b(3), ^2J = 16.7 Hz, ^3J = 6.0 Hz, ^4J = 1.8 Hz), 3.33 (d, 1H, CH, ^3J = 8.1 Hz), 3.68 and 3.70 (both s, 2 × 3H, 2 OMe), 6.68 (br d, 1H, H(5), ^3J = 7.6 Hz), 6.97−7.04 (m, 2H, 2 *o*-H′), 6.98−7.07 (m, 2H, H(6) and H(7)), 7.04−7.09 (m, 2H, 2 *o*-H″), 7.12−7.17 (m, 1H, H(8)), 7.13−7.21 (m, 2H, *p*-H″), 7.17−7.25 (m, 2H, 2 *m*-H″), 7.19−7.26 (m, 2H, *p*-H′), 7.25−7.33 (m, 2H, 2 *m*-H′). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 31.2 (CH(2)), 34.0 (CH_2(1)), 42.5 (CH_2(3)), 52.46 and 52.51 (2 OMe), 54.4 (C(4)), 57.7 (CH), 125.7, 126.3, 126.5, 126.6, 129.4, and 131.7 (CH(5)−CH(8) and 2 *p*-CH), 127.9, 128.0, 129.3, and 129.6 (2 × 2 *o*-CH and 2 × 2 *m*-CH), 135.9, 142.1, 146.0, and 149.4 (C(4a), C(8a) and 2 *i*-C), 168.7 and 168.8 (2COO).

(2*RS*,4*SR*)- and (2*RS*,4*RS*)-2-(1,3-dimethoxy-1,3-dioxopropan-2-yl)-4-methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (5h). The title compound was prepared according to the general procedure from cyclopropane **1a** (200 mg, 0.85 mmol), α-methylstyrene (**2h**) (296 mg, 2.55 mmol), and $GaCl_3$ (157 mg, 0.89 mmol) as a mixture of diastereomers (2*RS*,4*SR*:2*RS*,4*RS* = 1.5:1) in 134 mg total yield (45%). Both diastereomers were partially separated by chromatography according to the general procedure.

The following are data for compound (2*RS*,4*SR*)-**5h** (major diastereomer, ∼85% purity). colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3008, 2956, 2931, 2871, 1750, 1732 (O═CO), 1599, 1494, 1437, 1377, 1341, 1274 cm^{-1}. MS (*m*/*z* (rel intens, %)): 352 (4, M^+), 338 (19), 323 (19), 303 (3), 235 (3), 220 (93), 205 (100), 191 (12), 178 (16), 143 (49), 129 (34), 115 (33), 105 (39), 91 (77), 77 (11), 59 (13). HRMS: calcd for $C_{22}H_{24}O_4$ M + H 353.1747, M + Na 375.1567, M + K 391.1306, found: *m*/*z* 353.1744, 375.1562, 391.1304. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.74 (s, 3H, Me), 1.76−1.94 (m, 2H, CH_2(3)), 2.59−2.95 (m, 3H, H(2) and CH_2(1)), 3.32 (d, 1H, CH, ^3J = 8.5 Hz), 3.73 and 3.78 (both s, 2 × 3H, 2 OMe), 6.75 (br d, 1H, H(5), ^3J = 7.7 Hz), 6.97−7.30 (m, 8H, 2Ar except H(5)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 29.2 (Me), 32.3 (CH(2)), 34.7 (CH_2(1)), 44.4 (C(4)), 46.6 (CH_2(3)), 52.51 and 52.57 (2 OMe), 57.5 (CH), 125.85, 125.89, 126.4, and 129.0 (CH(6), CH(7), CH(8) and *p*-CH), 127.4 and 128.2 (2 *o*-CH and 2 *m*-CH), 129.7 (CH(5)), 134.9 (C(8a)), 144.9 (C(4a)), 151.4 (*i*-C), 168.75 and 168.82 (2COO).

The following are data for ompound (2*RS*,4*RS*)-**5h** (minor diastereomer, ∼95% purity). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2955, 2935, 2875, 2847, 1732 (O═CO), 1597, 1493, 1437, 1376, 1341, 1293, 1253 cm^{-1}. MS (*m*/*z* (rel intens, %)): 352 (1, M^+), 303 (3), 220 (97), 205 (100), 192 (10), 178 (15), 143 (18), 129 (21), 115 (11), 105 (19), 91 (23), 77 (6), 59 (6). HRMS: calcd for $C_{22}H_{24}O_4$ M + Na 375.1567, M + K 391.1306, found *m*/*z* 375.1562, 391.1319. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.74 (s, 3H, Me), 1.77

DOI: 10.1021/acs.joc.5b01179
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(dd, 1H, *syn*-H(3), ^2J = 12.8 Hz, ^3J = 11.7 Hz), 2.13 (ddd, 1H, *anti*-H(3), ^2J = 12.8 Hz, ^3J = 2.4 Hz, ^4J = 2.0 Hz), 2.26−2.37 (m, 1H, H(2)), 2.70 (dd, 1H, *syn*-H(1), ^2J = 16.3 Hz, ^3J = 11.6 Hz), 2.90 (ddd, 1H, *anti*-H(1), ^2J = 16.3 Hz, ^3J = 5.3 Hz, ^4J = 2.0 Hz), 3.26 (d, 1H, CH, ^3J = 8.0 Hz), 3.63 and 3.67 (both s, 2 × 3H, 2 OMe), 6.94−6.99 (m, 2H, 2 *o*-H), 7.10−7.16 (m, 1H, *p*-H), 7.11−7.17 (m, 1H, H(8)), 7.15−7.27 (m, 3H, H(5)−H(7)), 7.18−7.25 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 30.8 (CH_2(2)), 31.1 (Me), 34.2 (CH_2(1)), 43.7 (C(4)), 44.6 (CH_2(3)), 52.38 and 52.43 (2 OMe), 57.3 (CH), 125.9 (*p*-CH), 126.4, 126.5, and 128.5 (CH(5), C(6) and CH(7)), 127.3 (2 *o*-CH), 128.0 (2 *m*-CH), 129.4 (CH(8)), 136.0 (C(8a)), 142.5 (C(4a)), 150.1 (*i*-C), 168.7 and 168.9 (2COO).

2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene (5i). The title compound was prepared according to the general procedure from cyclopropane **1a** (200 mg, 0.85 mmol), isobutylene (**2i**) (57 mg, 1.02 mmol), and $GaCl_3$ (150 mg, 0.85 mmol) in 213 mg yield (86%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3011, 2957, 2930, 2868, 1732 (C═O), 1602, 1490, 1436, 1366, 1302, 1292 cm^{-1}. MS (*m*/*z* (rel intens, %)): 262 (75), 247 (21), 205 (11), 158 (76), 143 (100), 128 (23), 115 (12), 91 (8), 59 (10). HRMS: calcd for $C_{17}H_{22}O_4$ M + H 291.1591, M + Na 313.1410, M + K 329.1150, found *m*/*z* 291.1604, 313.1415, 329.1152. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.29 and 1.33 (both s, 2 × 3H, 2 Me), 1.47 (dd, 1H, H_a(3), ^2J = 12.8 Hz, ^3J = 12.0 Hz), 1.69 (ddd, 1H, H_b(3), ^2J = 12.8 Hz, ^3J = 2.3 Hz, ^4J = 2.6 Hz), 2.63−2.74 (m, 1H, H(2)), 2.61 (dd, 1H, *anti*-H(1), ^2J = 14.6 Hz, ^3J = 12.2 Hz), 2.82 (ddd, 1H, *syn*-H(1), ^2J = 14.6 Hz, ^3J = 3.6 Hz, ^4J = 2.6 Hz), 3.34 (d, 1H, CH, ^3J = 8.4 Hz), 3.77 and 3.78 (both s, 2 × 3H, 2 OMe), 7.02 (br d, 1H, H(5), ^3J = 7.5 Hz), 7.07 (ddd, 1H, H(6), ^3J = 7.5 and 7.4 Hz, ^4J = 1.3 Hz), 7.15 (br dd, 1H, H(7), ^3J = 7.4 and 7.6 Hz), 7.31 (br dd, 1H, H(8), ^3J = 7.6 Hz, ^4J = 1.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 31.71 and 31.73 (2 Me), 32.3 (CH_2(2)), 35.0 (CH_2(1)), 35.1 (C(4)), 43.7 (CH_2(3)), 52.55 and 52.59 (2 OMe), 57.7 (CH), 125.7 (CH(6)), 126.4 (CH(7)), 126.6 (CH(8)), 129.2 (CH(5)), 134.4 (C(8a)), 145.0 (C(4a)), 169.01 and 169.03 (2COO).

2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3,4-diphenyl-1,2,3,4-tetrahydronaphthalene (5j). The title compound was prepared according to the general procedure from cyclopropane **1a** (200 mg, 0.85 mmol), *trans*-stilbene (**2j**) (612 mg, 3.40 mmol), and $GaCl_3$ (158 mg, 0.90 mmol) as a single diastereomer in 285 mg yield (81%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3020, 2955, 1746, 1730 (O═CO), 1493, 1453, 1437, 1224, 1208 cm^{-1}. MS (*m*/*z* (rel intens, %)): 414 (2, M^+), 383 (3, $M^+ - OCH_3$), 282 (100), 215 (4), 204 (13), 191 (40), 179 (31), 165 (10), 115 (7), 91 (8). HRMS: calcd for $C_{27}H_{26}O_4$ M + H 415.1904, M + Na 437.1723, found: *m*/*z* 415.1914, 437.1733. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.97 (dddd, 1H, H(2), ^3J = 11.2, 11.0, 3.8, and 3.0 Hz), 3.04 (dd, 1H, *anti*-H(1), ^2J = 16.0 Hz, ^3J = 3.0 Hz), 3.19 (dd, 1H, H(3), ^3J = 11.2 and 10.8 Hz), 3.35 (d, 1H, CH, ^3J = 3.8 Hz), 3.48 (dd, 1H, *syn*-H(1), ^2J = 16.0 Hz, ^3J = 11.0 Hz), 3.62 and 3.68 (both s, 2 × 3H, 2 OMe), 4.22 (d, 1H, H(4), ^3J = 10.8 Hz), 6.72 (br d, 1H, H(5), ^3J = 7.7 Hz), 6.76−6.83 (m, 2H, 2 *o*-H″), 6.90−6.96 (m, 2H, *o*-H′), 6.99−7.04 (m, 1H, H(6)), 7.03−7.11 (m, 3H, 2 *m*-H″ and *p*-H″), 7.10−7.15 (m, 1H, H(7)), 7.13−7.20 (m, 2H, 2 *m*-H′), 7.15−7.19 (m, 1H, H(8)), 7.19−7.16 (m, 2H, *p*-H′). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 32.3 (CH_2(1)), 40.0 (CH(2)), 51.9 and 52.5 (2 OMe), 52.9 (CH), 53.2 (CH(3)), 55.2 (C(4)), 126.1 (together CH(6), CH(7) and *p*-CH″), 126.8 (*p*-C′), 128.0 (2 *m*-CH″), 128.47 and 128.52 (2 *o*-CH′ and 2 *m*-CH′), 128.7 (CH(8)), 129.4 (2 *o*-CH″), 129.9 (CH(5)), 136.1 (C(8a)), 139.5 (C(4a)), 141.7 (*i*-C′), 145.1 (*i*-C″), 168.7 and 169.9 (2COO).

(2*RS*,3*SR*,4*SR*)- and (2*RS*,3*RS*,4*RS*)-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-3-methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (5k). The title compound was prepared according to the general procedure from cyclopropane **1a** (250 mg, 1.07 mmol), *β*-methylstyrene (**2k**) (505 mg, 4.28 mmol), and $GaCl_3$ (198 mg, 1.12 mmol) as a mixture of diastereomers (2*RS*,3*SR*,4*SR*:2*RS*,3*RS*,4*RS* = 1.2:1) in 335 mg total yield (89%). Both diastereomers were fully separated by chromatography according to the general procedure.

The following are data for compound (2*RS*,3*SR*,4*SR*)-**5k** (major diastereomer). Colorless powder. Mp: 98−100 °C. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2956, 2931, 2875, 2852, 1731 (C═O), 1600, 1493, 1452, 1437, 1380, 1316, 1285, 1251 cm^{-1}. MS (*m*/*z* (rel intens, %)): 352 (1, M^+), 338 (2), 321 (5), 220 (100), 205 (86), 191 (20), 179 (46), 165 (19), 142 (20), 129 (47), 105 (18), 91 (62), 93 (12), 59 (10). HRMS: calcd for $C_{22}H_{24}O_4$ M + Na 375.1567, found *m*/*z* 375.1562. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 0.92 (d, 3H, Me, ^3J = 6.5 Hz), 2.04 (ddq, 1H, H(3), ^3J = 10.3, 9.8, and 6.5 Hz), 2.46 (dddd, 1H, H(2), ^3J = 10.8, 9.8, 5.0, and 4.5 Hz), 2.88 (dd, 1H, *anti*-H(1), ^2J = 16.1 Hz, ^3J = 4.5 Hz), 3.23 (dd, 1H, *syn*-H(1), ^2J = 16.1 Hz, ^3J = 10.8 Hz), 3.61 (d, 1H, H(4), ^3J = 10.3 Hz), 3.73 and 3.76 (both s, 2 × 3H, 2 OMe), 3.76 (d, 1H, CH, ^3J = 5.0 Hz), 6.63 (br d, 1H, H(5), ^3J = 7.8 Hz), 6.94−7.00 (m, 1H, H(6)), 7.03−7.10 (m, 2H, H(7) and H(8)), 7.09−7.14 (m, 2H, 2 *o*-H), 7.19−7.25 (m, 1H, *p*-H), 7.25−7.32 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 17.7 (Me), 32.2 (CH_2(1)), 39.8 (CH(2)), 41.0 (CH(3)), 52.2 and 52.5 (2 OMe), 53.5 (CH), 54.9 (CH(4)), 125.9 (CH(7)), 126.0 (CH(6)), 126.4 (*p*-CH), 128.5 (CH(8) and 2 *m*-CH), 129.66 (CH(5)), 129.68 (2 *o*-CH), 136.1 (C(8a)), 139.8 (C(4a)), 145.6 (*i*-C), 168.9 and 169.8 (2COO).

The following are data for compound (2*RS*,3*RS*,4*RS*)-**5k** (minor diastereomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3007, 2956, 2885, 2846, 1732 (C═O), 1600, 1493, 1448, 1384, 1332, 1279, 1262 cm^{-1}. MS (*m*/*z* (rel intens, %)): 352 (1, M^+), 321 (1), 220 (100), 205 (39), 191 (9), 179 (13), 165 (7), 129 (14), 105 (10), 91 (19), 59 (4). HRMS: calcd for $C_{22}H_{24}O_4$ M + Na 375.1567, M + K 391.1306, found *m*/*z* 375.1556, 391.1298. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.01 (d, 3H, Me, ^3J = 7.0 Hz), 2.09 (ddq, 1H, H(3), ^3J = 7.0, 2.6, and 2.4 Hz), 2.60 (dd, 1H, H(1)-a, ^2J = 15.8 Hz, ^3J = 11.4 Hz), 2.67 (dddd, 1H, H(2), ^3J = 11.4, 10.5, 4.4, and 2.6 Hz), 2.91 (dd, 1H, H(1)-b, ^2J = 15.8 Hz, ^3J = 4.4 Hz), 3.39 (d, 1H, CH, ^3J = 10.5 Hz), 3.53 and 3.70 (both s, 2 × 3H, 2 OMe), 4.02 (d, 1H, H(4), ^3J = 2.4 Hz), 6.87−6.94 (m, 2H, 2 *o*-H), 6.97 (br d, 1H, H(5), ^3J = 7.5 Hz), 7.07−7.19 (m, 3H, H(7), H(8) and *p*-H), 7.18−7.27 (m, 1H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 14.2 (Me), 29.2 (CH_2(1)), 32.4 (CH(2)), 37.5 (CH(3)), 52.26 and 52.45 (2 OMe), 52.29 (CH), 55.4 (CH(4)), 126.0, 126.2, and 126.3 (CH(6), CH(7) and *p*-CH), 128.1 (2 *m*-CH), 128.7 (2 *o*-CH), 128.9 (CH(8)), 131.4 (CH(5)), 135.4 (C(8a)), 135.9 (C(4a)), 146.4 (*i*-C), 168.4 and 169.0 (2COO).

(4b*SR*,8a*SR*,9*RS*)-9-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4b-phenyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (5l). The title compound was prepared according to the general procedure from cyclopropane **1a** (100 mg, 0.43 mmol), phenylcyclohexene (**2l**) (344 mg, 2.15 mmol), and $GaCl_3$ (79 mg, 0.45 mmol) as a single diastereomer in 90 mg yield (53%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3011, 2936, 2857, 1731 (O═CO), 1605, 1493, 1478, 1450, 1436, 1311, 1266 cm^{-1}. MS (*m*/*z* (rel intens, %)): 392 (2, M^+), 361 (1, $M^+ - OMe$), 332 (3, $M^+ - HCO_2Me$), 302 (1), 274 (4), 260 (100), 217 (28), 203 (21), 169 (19), 141 (30), 115 (34), 100 (25), 91 (67), 59 (78). HRMS: calcd for $C_{25}H_{28}O_4$ M + H 393.2060, M + Na 415.1880, M + K 431.1619, found *m*/*z* 393.2056, 415.1873, 431.1621. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.06 (dddd, 1H, CH_a(8), ^2J = 13.2 Hz, ^3J = 10.7, 10.1, and 3.2 Hz), 1.32−1.45 and 1.52−1.66 (both m, 2 × 1H, CH_2(7)), 1.50 (br dddd, 1H, CH_b(8), ^2J = 13.2 Hz, ^3J = 4.7, 3.9, and 3.5 Hz), 1.56−1.70 (m, 2H, CH_2(6)), 1.87 (ddd, 1H, H_a(5), ^2J = 14.7 Hz, ^3J = 9.8 and 5.1 Hz), 2.15 (br dd, 1H, H_a(10), ^2J = 14.9 Hz, ^3J = 10.3 Hz), 2.31 (br ddd, 1H, H_b(5), ^2J = 14.7 Hz, ^3J = 4.3 and 4.1 Hz), 2.39 (dddd, 1H, H(9), ^3J = 10.3, 9.8, 6.6, and 3.9 Hz), 2.46 (ddd, 1H, H(8a), ^3J = 10.1, 3.9, and 3.9 Hz), 2.67 (dd, 1H, H_b(10), ^2J = 14.9 Hz, ^3J = 6.6 Hz), 3.24 (d, 1H, H(2′), ^3J = 9.8 Hz), 3.67 and 3.81 (both s, 2 × 3H, 2 OMe), 7.02−7.28 (m, 9H, 2 Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 22.9 (CH_2(6)), 25.5 (br, CH_2(7)), 31.8 (br, CH_2(8)), 32.2 (CH_2(10)), 38.7 (br, CH_2(5)), 39.5 (br, CH(9)), 43.2 (CH(8a)), 48.6 (C(4b)), 52.5 and 52.6 (2 OMe), 57.2 (br, CH(2′)), 126.1 (CH, Ar), 126.3 (2CH, Ar), 127.3 (2CH, Ar), 128.5 (3CH, Ar), 128.9 (CH, Ar), 136.9 (C(10a)), 142.2 (br) and 148.7 (C(4a) and *i*-C), 169.0 and 169.6 (2COO).

(4b*SR*,8a*SR*,9*RS*)-9-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (5m). The title compound was prepared according to the general procedure from cyclopropane **1a** (100 mg, 0.43 mmol), cyclohexene (**2m**) (212 mg, 2.58 mmol), and $GaCl_3$ (79 mg, 0.45 mmol) as a single diastereomer

DOI: 10.1021/acs.joc.5b01179
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in 57 mg yield (42%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3011, 2953, 2934, 2858, 1734 (O═CO), 1602, 1494, 1450, 1436, 1372, 1305, 1289, 1255 cm^{-1}. MS (*m*/*z* (rel intens, %)): 316 (1, M^+), 285 (1, $M^+ - OCH_3$), 235 (2), 224 (2), 184 (100), 169 (6), 155 (8), 141 (47), 133 (22), 115 (19), 91 (13), 59 (11). HRMS: calcd for $C_{19}H_{24}O_4$ M + Na 339.1567, found *m*/*z* 339.1565. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.07 (dt, 1H, $J \approx 12.7$ and 3.6 Hz), 1.14 (tt, 1H, $J \approx 12.8$ and 3.2 Hz), 1.21−1.29 (m, 1H), 1.40−1.54 (m, 2H), 1.61−1.71 (m, 1H), 1.62−1.69 (m, 1H), 1.82−1.91 (m, 1H), 2.43−2.52 (m, 1H) [for all H from $CH_2(5)-CH_2(8)$ and CH(8a)], 2.61 (dd, 1H, $H_a(10)$, $^2J = 14.9$ Hz, $^3J = 12.4$ Hz), 2.69 (dddd, 1H, H(9), $^3J = 12.4$, 10.6, 4.2, and 2.4 Hz), 2.78 (dd, 1H, $H_b(10)$, $^2J = 14.9$ Hz, $^3J = 4.2$ Hz), 3.05−3.12 (m, 1H, H(4b)), 3.48 (d, 1H, H(2′), $^3J = 10.6$ Hz), 3.77 and 3.78 (both s, 2 × 3H, 2 OMe), 7.04 (br d, 1H, H(1) or H(4), $^3J \approx 7.5$ Hz), 7.11 (ddt, 1H, H(2) or H(3), $^3J \approx 7.3$ Hz, $^{4,5}J \approx 1.3$ and 1.0 Hz), 7.17 (dt, 1H, H(2) or H(3), $^3J \approx 7.5$ Hz, $^{4,5}J \approx 1.3$ Hz), 7.33 (br d, 1H, H(1) or H(4), $^3J \approx 7.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 20.9, 21.1, 26.2, 29.3, and 30.5 ($CH_2(5)-CH_2(8)$ and $CH_2(10)$), 37.9, 38.9, and 39.2 (CH(4b), CH(8a) and CH(9)), 52.58 and 52.62 (2 OMe), 55.4 (CH), 125.6, 126.4, 126.5, and 129.2 (CH(1)−CH(4)), 135.6 and 137.5 (C(4a) and C(10a)), 169.0 and 169.1 (2 COO).

(6*RS*,6a*SR*,11b*RS*)- and (6*SR*,6a*SR*,11b*RS*)-6-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6,6a,7,11b-tetrahydro-5*H*-benzo[*c*]fluorene (5n). The title compound was prepared according to the general procedure from cyclopropane **1a** (100 mg, 0.43 mmol), indene (**2n**) (299 mg, 2.58 mmol), and $GaCl_3$ (79 mg, 0.45 mmol) as a mixture of diastereomers (6*RS*,6a*SR*,11b*RS*:6*RS*,6a*SR*,11b*SR* ≈ 2.5:1) in 80 mg total yield with 70−80% purity (40%). A crude mixture of diastereomers was purified and separated by PTLC according to the general procedure to give single diastereomers with 90−95% purity, but the quantity of substances was small due to its very poor separation during chromatography. Compound **5n** has a low stability in solution and very easily oxidizes in air.

The following are data for compound (6*RS*,6a*SR*,11b*RS*)-**5n** (major diastereomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 2956, 2929, 2853, 1734 (O═CO), 1602, 1519, 1457, 1437, 1284 cm^{-1}. MS (*m*/*z* (rel intens, %)): 350 (2, M^+), 319 (4, $M^+ - OCH_3$), 287 (1), 259 (2), 231 (5), 218 (100), 202 (20), 189 (5), 178 (5), 133 (5), 115 (6), 91 (2), 59 (4). HRMS: calcd for $C_{22}H_{22}O_4$ M + H 351.1591, M + Na 373.1410, found *m*/*z* 351.1592, 373.1416. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.55−2.62 (m, 1H, H(6)), 2.71 (dd, 1H, $^3J = 15.8$ Hz, $^3J = 7.3$ Hz), 2.78−2.93 (m, 3H) and 3.14 (dd, 1H, $^3J = 15.6$ Hz, $^3J = 7.6$ Hz) (H(6a), $CH_2(5)$ and $CH_2(7)$), 3.51 (d, 1H, CH, $^3J = 8.3$ Hz), 3.72 and 3.74 (both s, 2 × 3H, 2 OMe), 4.35 (d, 1H, H(11b), $^3J = 7.7$ Hz), 7.03−7.08 (m, 1H), 7.10−7.23 (m, 5H) and 7.29−7.36 (m, 2H) (2Ar).

The following are data for compound (6*RS*,6a*SR*,11b*SR*)-**5n** (minor diastereomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3008, 2958, 2925, 1734 (O═CO), 1601, 1520, 1457, 1437, 1289 cm^{-1}. MS (*m*/*z* (rel intens, %)): 319 (2, $M^+ - OCH_3$), 286 (3), 271 (3), 260 (16), 218 (100), 203 (22), 178 (9), 165 (7), 141 (7), 133 (14), 115 (24), 91 (22), 59 (35). HRMS: calcd for $C_{22}H_{22}O_4$ M + H 351.1591, M + Na 373.1410, found *m*/*z* 351.1586, 373.1410. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.67−3.05 (m, 6H, H(6), H(6a), $CH_2(5)$ and $CH_2(7)$), 3.50 (d, 1H, CH, $^3J = 10.8$ Hz), 3.76 and 3.81 (both s, 2 × 3H, 2 OMe), 4.46 (d, 1H, H(11b), $^3J = 7.6$ Hz), 7.01 (br d, 1H, $^3J = 6.8$ Hz), 7.06 (br dd, 1H, $^3J \approx 6.7$ and 6.9 Hz), 7.09−7.21 (m, 4H), 7.48 (br d, 1H, $^3J = 7.8$ Hz), 7.54 (br d, 1H, $^3J = 6.9$ Hz) (2Ar).

(6*RS*,6a*SR*,12b*RS*)-6-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene (5o). The title compound was prepared according to the general procedure from cyclopropane **1a** (150 mg, 0.64 mmol), dihydronaphthalene (**2o**) (250 mg, 1.92 mmol), and $GaCl_3$ (118 mg, 0.67 mmol) as a single diastereomer in 102 mg yield (44%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3032, 3011, 2955, 2929, 1732 (O═CO), 1492, 1451, 1436, 1243, 1159 cm^{-1}. MS (*m*/*z* (rel intens, %)): 364 (1, M^+), 333 (2, $M^+ - OCH_3$), 232 (100), 217 (22), 204 (12), 191 (6), 178 (8), 141 (9), 133 (20), 117 (25), 91(9), 69 (18), 59 (15). HRMS: calcd for $C_{23}H_{24}O_4$ M + Na 387.1567, found *m*/*z* 387.1569. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.26−1.39 (m, 1H, *anti*-H(7)), 1.65−1.74 (m, 1H, *syn*-H(7)), 2.17−2.28 (m, 2H, H(6) and H(6a)), 2.69−2.88 (m, 4H, $CH_2(5)$ and $CH_2(8)$), 3.62 (d, 1H, CH, $^3J = 7.6$ Hz), 3.74 and 3.77 (both s, 2 × 3H, 2 OMe), 4.03 (d, 1H, H(12b), $^3J = 4.9$ Hz), 6.71 (br d, 1H, H(1), $^3J = 7.4$ Hz), 7.05−7.12 (m, 1H, H(2)), 7.11−7.16 (m, 2H, H(3) and H(4)), 7.10−7.23 (m, 4H, H(9)−H(12)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 27.7 ($CH_2(7)$), 29.1 ($CH_2(8)$), 31.7 ($CH_2(5)$), 37.1 (CH(6a)), 40.1 (CH(6)), 42.0 (CH(12b)), 52.5 (2 OMe), 56.1 (CH), 125.4 (CH(10)), 126.1 (CH(3)), 126.2 (CH(2)), 126.5 (CH(11)), 127.5 (CH(4)), 127.8 (CH(1)), 129.2 (CH(9)), 131.1 (CH(12)), 136.56 and 136.58 (C(4a) and C(8a)), 137.2 (C(12a)), 140.7 (C(12c)), 169.13 and 169.16 (2 COO).

(1*S,2*S**,3*R**)-1,3-Bis(1,3-dimethoxy-1,3-dioxopropan-2-yl)-2-phenyl-1,2,3,4-tetrahydronaphthalene (5p).** The title compound was prepared according to the general procedure from cyclopropane **1a** (200 mg, 0.85 mmol), styrylmalonate **2p** (200 mg, 0.85 mmol), and $GaCl_3$ (165 mg, 0.94 mmol) as a single diastereomer in 332 mg yield (83%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3020, 2955, 2921, 1733 br (O═CO), 1602, 1519, 1494, 1454, 1437 cm^{-1}. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.54 (dddd, 1H, H(3), $^3J = 12.5$, 10.4, 4.2, and 3.8 Hz), 2.88 (dd, 1H, *anti*-H(4), $^2J = 15.0$, $^3J = 3.8$ Hz), 3.03 (dd, 1H, *syn*-H(4), $^2J = 15.0$, $^3J = 12.5$ Hz), 3.28 and 3.71 (both s, 2 × 3H, 2OMe at C(2′)), 3.32 (dd, 1H, H(2), $^3J = 10.4$ and 4.9 Hz), 3.33 (d, 1H, CH, $^3J = 4.2$ Hz), 3.59 and 3.69 (both s, 2 × 3H, 2OMe), 3.78 (d, 1H, H(2′), $^3J = 7.6$ Hz), 3.84 (dd, 1H, H(1), $^3J = 7.6$ and 4.9 Hz), 7.09 (m, 2H, 2 *o*-CH), 7.13−7.22 (m, 5H, H(5), H(6), H(7), H(8) and *o*-CH), 7.26 (m, 2H, 2 *m*-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 31.9 ($CH_2(4)$), 43.2 (CH(3)), 47.1 (CH(2)), 47.4 (CH(1)), 52.0 and 52.2 (2OMe at C(2′)), 52.3 and 52.4 (2OMe), 53.6 (CH), 57.1 (CH(2′)), 126.6, 127.0, 127.1, 128.5, and 128.7 (*p*-CH, CH(5), CH(6), CH(7) and CH(8)), 128.4 (2 *o*-CH), 128.7 (2 *m*-CH), 135.6 (C(8a)), 138.7 (C(4a)), 144.6 (*i*-C), 168.2 and 168.7 (2COO at C(2′)), 168.9 and 169.2 (2COO). MS (*m*/*z* (rel intens, %)): 468 (1, M^+), 437 (2, $M^+ - OCH_3$), 376 (1), 336 (18), 317 (3), 305 (7), 276 (4), 217 (6), 204 (100), 133 (7), 115 (11), 91 (7), 69 (4), 59 (11). HRMS: calcd for $C_{26}H_{28}O_8$ M + H 469.1857, M + Na 491.1676, found *m*/*z* 469.1848, 491.1669.

(1*S,2*S**,3*R**)-1,3-Bis(1,3-dimethoxy-1,3-dioxopropan-2-yl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydronaphthalene (5q).** The title compound was prepared according to the general procedure from cyclopropane **1a** (93 mg, 0.40 mmol), styrylmalonate **2q** (100 mg, 0.40 mmol), and $GaCl_3$ (74 mg, 0.42 mmol) as a single diastereomer in 146 mg yield (76%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3020, 2955, 2919, 1733 br (O═CO), 1658, 1644, 1512, 1435, 1423 cm^{-1}. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.49 (dddd, 1H, H(3), $^3J = 12.8$, 10.5, 4.3, and 3.9 Hz), 2.87 (dd, 1H, *anti*-H(4), $^2J = 15.0$, $^3J = 3.9$ Hz), 3.00 (dd, 1H, *syn*-H(4), $^2J = 15.0$, $^3J = 12.8$ Hz), 3.30−3.38 (m, 2H, CH and H(2)), 3.30, 3.61, 3.70, and 3.71 (all s, 4 × 3H, 4OMe), 3.72−3.81 (m, 2H, H(1) and H(2′)), 6.95 (m, 2H, 2 *m*-CH, $^3J_{HF} = 8.8$ Hz), 7.05 (m, 2H, 2 *o*-CH, $^4J_{HF} = 5.3$ Hz), 7.05−7.30 (m, 4H, H(5)−H(8)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 32.0 ($CH_2(4)$), 43.4 (CH(3)), 46.2 (CH(2)), 47.6 (CH(1)), 52.0, 52.3, 52.4, and 52.5 (4OMe), 53.6 (CH), 57.0 (CH(2′)), 115.5 (d, 2 *m*-CH, $^2J_{CF} = 21.2$ Hz), 126.7, 127.2, 128.5, and 128.8 (CH(5)−CH(8)), 129.8 (d, 2 *o*-CH, $^3J_{CF} = 7.8$ Hz), 135.3 (C(8a)), 138.6 (C(4a)), 140.6 (d, *i*-C, $^4J_{CF} = 3.1$ Hz), 161.8 (d, *p*-CF, $^1J_{CF} = 245.5$ Hz), 168.2, 168.7, 168.8, and 169.1 (4COO). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −116.6 (tt, 1F, *p*-CF, $^3J_{HF} = 8.8$, $^4J_{HF} = 5.3$ Hz). MS (*m*/*z* (rel intens, %)): 486 (2, M^+), 455 (4, $M^+ - OCH_3$), 423 (2), 394 (1), 354 (14), 323 (7), 294 (12), 263 (12), 233 (41), 223 (100), 204 (95), 175 (17), 149 (12), 133 (85), 115 (64), 100 (45), 91 (21), 69 (53), 59 (100). HRMS: calcd for $C_{26}H_{27}FO_8$ M + H 487.1763, M + Na 509.1582, M + K 525.1322, found *m*/*z* 487.1762, 509.1582, 525.1320.

(1*S,2*S**,3*R**)-1,3-Bis(1,3-dimethoxy-1,3-dioxopropan-2-yl)-7-fluoro-2-phenyl-1,2,3,4-tetrahydronaphthalene (5r).** The title compound was prepared according to the general procedure from cyclopropane **1b** (80 mg, 0.32 mmol), styrylmalonate **2p** (74 mg, 0.32 mmol), and $GaCl_3$ (59 mg, 0.22 mmol) as a single diastereomer in 78 mg yield (51%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3020, 2974, 2955, 2920, 1734 br (O═CO), 1642, 1616, 1511, 1501, 1454, 1437 cm^{-1}. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 2.52 (dddd, 1H, H(3), $^3J = 12.6$,

DOI: 10.1021/acs.joc.5b01179
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10.6, 4.3, and 3.9 Hz), 2.87 (dd, 1H, *anti*-H(4), ^2J = 14.9, ^3J = 4.3 Hz), 2.96 (dd, 1H, *syn*-H(4), ^2J = 14.9, ^3J = 12.6 Hz), 3.26−3.38 (m, 2H, CH and H(2)), 3.33, 3.60, 3.70, and 3.71 (all s, 4 × 3H, 4OMe), 3.74−3.87 (m, 2H, H(1) and H(2′)), 6.85−6.96 (m, 2H, H(6) and H(8)), 7.03−7.33 (m, 6H, H(5) and Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 31.4 (CH_2(4)), 43.1 (CH(3)), 46.9 (CH(2)), 47.4 (CH(1)), 52.2, 52.3, 52.5, and 52.7 (4OMe), 53.5 (CH), 56.8 (CH(2′)), 114.0 (d, CH(6) or CH(8), $^2J_{CF}$ = 21.2 Hz), 115.4 (d, CH(6) or CH(8), $^2J_{CF}$ = 21.9 Hz), 127.3 (*p*-CH), 128.5 and 118.9 (2 *o*-CH and 2 *m*-CH), 129.9 (d, CH(5), $^3J_{CF}$ = 7.9 Hz), 134.4 (d, C(4a), $^4J_{CF}$ = 2.5 Hz), 137.7 (d, C(8a), $^3J_{CF}$ = 7.0 Hz), 144.2 (*i*-C), 161.6 (d, C(7), $^1J_{CF}$ = 244.1 Hz), 168.1, 168.7, 168.8, and 169.3 (4COO). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −117.0 (dddt, 1F, CF(7), $^3J_{HF}$ ≈ 8.9 and 8.6, $^4J_{HF}$ ≈ 5.6, $^6J_{HF}$ ≈ 1 Hz). HRMS: calcd for $C_{26}H_{27}FO_8$ M + Na 509.1582, M + K 525.1322, found *m*/*z* 509.1573, 525.1311.

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6-fluoro-4-phenyl-1,2,3,4-tetrahydronaphthalene (5s).** The title compound was prepared according to the general procedure from cyclopropane **1b** (252 mg, 1.0 mmol), styrene (**2a**) (624 mg, 6 mmol), and $GaCl_3$ (176 mg, 1.0 mmol) as a mixture of diastereomers (*cis*:*trans* = 8:1) in 347 mg yield (82%). The major *cis*-isomer was isolated in pure form by chromatography on a SiO_2 plate.

The following are data for compound *cis*-**5s** (major isomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3010, 2955, 2928, 1733 (O═CO), 1602, 1590, 1496, 1454, 1437 cm^{-1}. MS (*m*/*z* (rel intens, %)): 356 (1, M^+), 325 (1, $M^+ - OCH_3$), 224 (100), 209 (12), 196 (15), 183 (8), 159 (8), 146 (35), 133 (32), 115 (7), 91 (100), 59 (15). HRMS: calcd for $C_{21}H_{21}FO_4$ M + Na 379.1316, M + K 395.1055, found *m*/*z* 379.1309, 395.1054. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.65 (ddd, 1H, *syn*-H(3), ^2J = 12.0 Hz, ^3J = 12.1, 12.0 Hz), 2.16 (dddd, 1H, *anti*-H(3), ^2J = 12.0 Hz, ^3J = 5.4, 2.3 Hz, ^4J = 2.6 Hz), 2.63−2.72 (m, 1H, H(2)), 2.71−2.79 (m, 1H, *anti*-H(1)), 2.89 (ddd, 1H, *syn*-H(1), ^2J = 14.7 Hz, ^3J = 4.3 Hz, ^4J = 2.6 Hz), 3.37 (d, 1H, CH, ^3J = 8.3 Hz), 3.72 and 3.77 (both s, 2 × 3H, 2 OMe), 4.07 (br dd, 1H, H(4), ^3J = 12.1 and 5.4 Hz), 6.44 (ddd, 1H, H(5), ^4J = 2.7 and 0.9 Hz, $^3J_{HF}$ = 10.2 Hz), 6.79 (dddd, 1H, H(7), ^3J = 8.5 Hz, ^4J = 2.7 Hz, ^5J = 0.6 Hz, $^3J_{HF}$ = 8.4 Hz), 7.03 (dd, 1H, H(8), ^3J = 8.5 Hz, $^4J_{HF}$ = 5.9 Hz), 7.12−7.16 (m, 2H, 2 *o*-H), 7.21−7.27 (m, 1H, *p*-H), 7.28−7.34 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 33.5 (CH_2(1)), 35.1 (CH(2)), 37.9 (CH_2(3)), 47.0 (CH(4)), 52.59 and 52.61 (2OMe), 57.3 (CH), 113.4 (d, CH(7), $^2J_{CF}$ =21.5 Hz), 115.7 (d, CH(5), $^2J_{CF}$ =21.4 Hz), 126.8 (*p*-CH), 128.78 and 128.81 (2 *o*-CH and 2 *m*-CH), 130.2 (d, CH(8), $^3J_{CF}$ = 7.8 Hz), 131.2 (d, C(8a), $^4J_{CF}$ = 2.8 Hz), 141.4 (d, C(4a), $^3J_{CF}$ = 6.7 Hz), 145.5 (*i*-C), 161.2 (d, C(6)F, $^1J_{CF}$ = 243.6 Hz), 168.7 and 168.8 (2COO). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −117.6 (ddd, 1F, CF(6), $^3J_{HF}$ = 10.2 and 8.4 Hz, $^4J_{HF}$ = 5.9 Hz).

The following are data for compound *trans*-**5s** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.97−2.02 (m, 2H, CH_2(3)), 2.58−2.74 (m, 2H, H(2) and *syn*-H(1)), 2.94−3.04 (m, 1H, *anti*-H(1)), 3.35 (d, 1H, CH, ^3J = 8.2 Hz), 3.66 and 3.70 (both s, 2 × 3H, 2 OMe), 4.24 (dd, 1H, H(4), ^3J ≈ 5.3 and 5.3 Hz), 6.64 (dd, 1H, H(5), ^4J = 2.7 Hz, $^3J_{HF}$ = 9.7 Hz), 6.86 (ddd, 1H, H(7), ^3J = 8.3 Hz, ^4J = 2.7 Hz, $^3J_{HF}$ = 8.4 Hz), 7.09 (dd, 1H, H(8), ^3J = 8.3 Hz, $^4J_{HF}$ = 6.2 Hz), 7.21−7.34 (m, 5H, Ph).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-6-chloro-4-phenyl-1,2,3,4-tetrahydronaphthalene (5t).** The title compound was prepared according to the general procedure from cyclopropane **1c** (200 mg, 0.75 mmol), styrene (**2a**) (624 mg, 6.0 mmol), and $GaCl_3$ (132 mg, 0.75 mmol) as a mixture of diastereomers (*cis*:*trans* = 9:1) in 195 mg yield (70%). The major *cis*-isomer was isolated in pure form by chromatography on a SiO_2 plate.

The following are data for compound *cis*-**5t** (major isomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3012, 2955, 2929, 1733 (O═CO), 1596, 1485, 1454, 1436 cm^{-1}. MS (*m*/*z* (rel intens, %)): 372 (6, M^+), 341 (6, $M^+ - OCH_3$), 240 (100), 205 (29), 178 (15), 162 (5), 91 (2). HRMS: calcd for $C_{21}H_{21}ClO_4$ M + Na 395.1021, M + K 411.0760, found *m*/*z* 395.1015, 411.0754. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.65 (ddd, 1H, *syn*-H(3), ^2J = 12.3 Hz, ^3J = 12.1, 12.1 Hz), 2.17 (dddd, 1H, *anti*-H(3), ^2J = 12.3 Hz, ^3J = 7.9, 5.4 Hz, ^4J = 2.2 Hz), 2.62−2.69 (m, 1H, H(2)), 2.77 (dd, 1H, *anti*-H(1), ^2J = 13.4 Hz, ^3J = 11.5 Hz), 2.91 (ddd, 1H, *syn*-H(1), ^2J = 13.4 Hz, ^3J = 5.7 Hz, ^4J = 2.2 Hz), 3.37 (d, 1H, CH, ^3J = 8.1 Hz), 3.73 and 3.78 (both s, 2 × 3H, 2 OMe), 4.07 (dd, 1H, H(4), ^3J = 12.1 and 5.4 Hz), 6.74 (dd, 1H, H(5), ^4J = 2.0 and 1.0 Hz), 7.02 (br d, 1H, H(8), ^3J = 8.3 Hz), 7.07 (ddd, 1H, H(7), ^3J = 8.3 Hz, ^4J = 2.0 Hz, ^5J = 0.9 Hz), 7.12−7.16 (m, 2H, 2 *o*-H), 7.21−7.27 (m, 1H, *p*-H), 7.28−7.34 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 33.7 (CH_2(1)), 34.9 (CH(2)), 38.1 (CH_2(3)), 46.9 (CH(4)), 52.59 and 52.61 (2OMe), 57.2 (CH), 126.4 (CH(7)), 126.8 (*p*-CH), 128.78 and 128.82 (2 *o*-CH and 2 *m*-CH), 128.8 (CH(5)), 130.2 (CH(8)), 131.7 (C(6)Cl), 134.1 (C(8a)), 141.2 (C(4a)), 145.4 (*i*-C), 168.6 and 168.7 (2COO).

The following are data for compound *trans*-**5t** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.95−2.01 (m, 2H, CH_2(3)), 2.55−2.72 (m, 2H, H(2) and *syn*-H(1)), 2.99 (dd, 1H, *anti*-H(1), ^2J = 15.7 Hz, ^3J = 3.8 Hz), 3.34 (d, 1H, CH, ^3J = 8.4 Hz), 3.64 and 3.68 (both s, 2 × 3H, 2 OMe), 4.23 (dd, 1H, H(4), ^3J ≈ 5.2 and 5.2 Hz), 6.93 (d, 1H, H(5), ^4J = 2.0 Hz), 6.95−7.35 (m, 7H, 2Ar except H(5)).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-8-chloro-4-phenyl-1,2,3,4-tetrahydronaphthalene (5u).** The title compound was prepared according to the general procedure from cyclopropane **1e** (150 mg, 0.56 mmol), styrene (**2a**) (349 mg, 3.36 mmol), and $GaCl_3$ (133 mg, 0.75 mmol) as a mixture of diastereomers (*cis*:*trans* = 7:1) in 83 mg yield (40%). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3014, 2955, 2873, 2857, 1734 (O═CO), 1602, 1567, 1494, 1454, 1438, 1375, 1337, 1257 cm^{-1}. MS (*m*/*z* (rel intens, %)): 372 (3, M^+), 341 (3, $M^+ - OCH_3$), 309 (2), 240 (100), 205 (74), 178 (56), 162 (43), 133 (96), 115 (31), 100 (24), 91 (100), 69 (25), 59 (50). HRMS: calcd for $C_{21}H_{21}ClO_4$ M + Na 395.1021, found *m*/*z* 395.1019.

The following are data for compound *cis*-**5u** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.67 (ddd, 1H, *syn*-H(3), ^2J = 12.4 Hz, ^3J = 12.3 and 12.2 Hz), 2.15 (dddd, 1H, *anti*-H(3), ^2J = 12.4 Hz, ^3J = 5.3 and 2.3 Hz, ^4J = 2.4 Hz), 2.61 (dd, 1H, *anti*-H(1), ^2J = 16.3 Hz, ^3J = 11.8 Hz), 2.66−2.75 (m, 1H, H(2)), 3.16 (ddd, 1H, *syn*-H(1), ^2J = 16.3 Hz, ^3J = 4.2 Hz, ^4J = 2.4 Hz), 3.43 (d, 1H, CH, ^3J = 8.3 Hz), 3.74 and 3.80 (both s, 2 × 3H, 2 OMe), 4.12 (dd, 1H, H(4), ^3J = 12.3 and 5.3 Hz), 6.66 (ddd, 1H, H(5), ^3J = 7.9 Hz, ^4J = 1.2 and 1.2 Hz), 6.94 (dd, 1H, H(6), ^3J = 7.9 and 7.8 Hz), 7.10−7.16 (m, 2H, 2 *o*-H), 7.19 (ddd, 1H, H(7), ^3J = 7.8 Hz, ^4J = 1.2, ^5J = 1.1 Hz), 7.21−7.27 (m, 1H, *p*-H), 7.27−7.33 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 32.0 (CH_2(1)), 34.9 (CH(2)), 37.5 (CH_2(3)), 47.3 (CH(4)), 52.61 and 52.67 (2 OMe), 57.3 (CH), 126.69, 126.72, 127.0, and 128.1 (CH(5), CH(6), CH(7) and *p*-CH), 128.7 and 128.8 (2 *o*-CH and 2 *m*-CH), 133.8, 134.2, 142.0, and 145.9 (C(4a), C(8a), C(8) and *i*-C), 168.71 and 168.76 (2 COO).

The following are data for compound *trans*-**5u** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.96−2.06 (m, 2H, CH_2(3)), 2.55−2.77 (m, 2H, H(2) and *syn*-H(1)), 3.09−3.17 (m, 1H, *anti*-H(1)), 3.38 (d, 1H, CH, ^3J = 7.9 Hz), 3.67 and 3.70 (both s, 2 × 3H, 2 OMe), 4.31 (dd, 1H, H(4), ^3J = 4.8 and 4.8 Hz), 6.90 (br d, 1H, H(5), ^3J = 7.6 Hz), 6.95−7.00 (m, 2H, 2 *o*-H), 7.05 (dd, 1H, H(6), ^3J = 7.8 and 7.6 Hz), 7.16−7.34 (m, 4H, H(7), *p*-H and 2 *m*-H).

***cis*- and *trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-7-chloro-4-phenyl-1,2,3,4-tetrahydronaphthalene (5v).** The title compound was prepared according to the general procedure from cyclopropane **1d** (200 mg, 0.75 mmol), styrene (**2a**) (468 mg, 4.5 mmol), and $GaCl_3$ (145 mg, 0.83 mmol) as a mixture of two diastereomers (*cis*:*trans* = 6:1) in 165 mg yield (59%). The major *cis*-isomer was isolated in pure form by chromatography.

The following are data for compound *cis*-**5v** (major isomer). Colorless thick oil. IR ($CHCl_3$): $\tilde{\nu}$ 3015, 2955, 1733 (O═CO), 1597, 1485, 1454, 1436 cm^{-1}. MS (*m*/*z* (rel intens, %)): 372 (7, M^+), 341 (8, $M^+ - OCH_3$), 240 (100), 215 (5), 205 (51), 178 (29), 162 (13), 133 (22), 115 (6), 91 (22), 59 (13). HRMS: calcd for $C_{21}H_{21}ClO_4$ M + H 373.1201, M + Na 395.1021, found *m*/*z* 373.1193, 395.1016. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.65 (ddd, 1H, *syn*-H(3), ^2J = 12.3 Hz, ^3J = 12.1, 12.1 Hz), 2.18 (dddd, 1H, *anti*-H(3), ^2J = 12.3 Hz, ^3J = 5.4, 2.4 Hz, ^4J = 2.0 Hz), 2.63−2.73 (m, 1H, H(2)), 2.74−2.85 (m, 1H, *anti*-H(1)), 2.91 (ddd, 1H, *syn*-H(1), ^2J = 13.3 Hz, ^3J = 4.3 Hz, ^4J = 2.0 Hz), 3.37 (d, 1H, CH, ^3J = 8.2 Hz), 3.74 and 3.78 (both s, 2 × 3H, 2 OMe), 4.07 (dd, 1H, H(4), ^3J = 12.1 and 5.4 Hz), 6.69 (dd, 1H, H(5),

DOI: 10.1021/acs.joc.5b01179
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^3J = 8.4 Hz, ^4J = 0.7 Hz), 6.97 (dd, 1H, H(6), ^3J = 8.4 Hz, ^4J = 2.2 Hz), 7.09 (d, 1H, H(8), ^4J = 2.2 Hz), 7.11−7.14 (m, 1H, *p*-H), 7.20−7.27 (m, 2H, 2 *o*-H), 7.27−7.35 (m, 2H, 2 *m*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.0 (CH_2(1)), 34.8 (CH(2)), 38.2 (CH_2(3)), 46.5 (CH(4)), 52.59 and 52.61 (2OMe), 57.2 (CH), 126.3 (CH(6)), 126.7 (*p*-CH), 128.6 (CH(8)), 128.73 and 128.76 (2 *o*-CH and 2 *m*-CH), 130.9 (CH(5)), 131.7 (C(7)Cl), 137.6 (C(8a)), 137.9 (C(4a)), 145.6 (*i*-C), 168.61 and 168.69 (2COO).

The following are data for compound *trans*-**5v** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.97−2.03 (m, 2H, CH_2(3)), 2.55−2.67 (m, 1H, H(2)), 2.65−2.75 (m, 1H, *syn*-H(1)), 3.01 (dd, 1H, *anti*-H(1), ^3J = 16.6 and 4.9 Hz), 3.35 (d, 1H, CH, ^3J = 8.5 Hz), 3.66 and 3.70 (both s, 2 × 3H, 2 OMe), 4.24 (dd, 1H, H(4), $^3J \approx$ 5.1 and 5.1 Hz), 6.85−7.30 (m, 8H, 2Ar).

***cis*/*trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenyl-1,2,3,4-tetrahydroanthracene (5w) and *cis*/*trans*-2-(1,3-Dimethoxy-1,3-dioxopropan-2-yl)-4-phenyl-1,2,3,4-tetrahydrophenanthrene (5x).** The title compounds were prepared according to the general procedure from cyclopropane **1f** (150 mg, 0.53 mmol), styrene (**2a**) (386 mg, 3.71 mmol), and $GaCl_3$ (93 mg, 0.53 mmol) in 125 mg total yield (62%). Colorless thick oil. HRMS: calcd for $C_{25}H_{24}O_4$ M + H 389.1747, M + Na 411.1567, M + K 427.1306, found *m*/*z* 389.1738, 411.1571, 427.1305. The compounds obtained were partially separated by column chromatography on silica gel to give a mixture of *cis*-**5w** and *cis*-**5x**, pure *trans*-**5x**, and a mixture of *trans*-**5w** and *trans*-**5x**. The calculated yields by NMR are 25% for **5w** (*cis*:*trans* = 1.9:1) and 37% for **5y** (*cis*:*trans* = 1:2.3).

The following are data for compound *cis*-**5w** (major isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.76 (ddd, 1H, *syn*-H(3), ^2J = 12.6 Hz, ^3J = 12.5 and 12.2 Hz), 2.24 (dddd, 1H, *anti*-H(3), ^2J = 12.6 Hz, ^3J = 5.3 and 2.7 Hz, ^4J = 2.4 Hz), 2.76−2.85 (m, 1H, H(2)), 2.98 (dd, 1H, *anti*-H(1), ^2J = 16.1 Hz, ^3J = 12.4 Hz), 3.17 (ddd, 1H, *syn*-H(1), ^2J = 16.1 Hz, ^3J = 4.3 Hz, ^4J = 2.4 Hz), 3.41 (d, 1H, CH, ^3J = 8.7 Hz), 3.74 and 3.80 (both s, 2 × 3H, 2 OMe), 4.28 (dd, 1H, H(4), ^3J = 12.5 and 5.3 Hz), 7.21 (s, 1H, H(10)), 7.21−7.26 (m, 2H, 2 *o*-H), 7.22−7.30 (m, 1H, *p*-H), 7.29 (dd, 1H, H(7), ^3J = 7.5 and 7.1 Hz), 7.30−7.37 (m, 2H, 2 *m*-H), 7.35 (dd, 1H, H(6), ^3J = 8.2 and 7.1 Hz), 7.53 (d, 1H, H(8), ^3J = 7.5 Hz), 7.58 (s, 1H, H(9)), 7.70 (d, 1H, H(5), ^3J = 8.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.7 (CH_2(1)), 35.3 (CH(2)), 38.5 (CH_2(3)), 47.3 (CH(4)), 52.6 (2 OMe), 57.5 (CH), 125.2 (CH(7)), 125.6 (CH(6)), 126.6 (*p*-CH), 127.0 (CH(5)), 127.1 (CH(9)), 127.5 (CH(8)), 128.1 (CH(10)), 128.7 (2 *m*-CH), 129.0 (2 *o*-CH), 132.2, 132.3, 134.4, 138.3, and 146.4 (C(4a), C(8a), C(9a), C(10a) and *i*-C), 168.8 (2 COO).

The following are data for compound *trans*-**5x** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.05−2.18 (m, 2H, CH_2(3)), 2.68−2.78 (m, 1H, H(2)), 2.91 (dd, 1H, *anti*-H(1), ^2J = 16.3 Hz, ^3J = 9.6 Hz), 3.23 (dd, 1H, *syn*-H(1), ^2J = 16.3 Hz, ^3J = 5.1 Hz), 3.41 (d, 1H, CH, ^3J = 8.8 Hz), 3.68 and 3.71 (both s, 2 × 3H, 2 OMe), 4.48 (dd, 1H, H(4), ^3J = 5.7 and 5.7 Hz), 7.02−7.07 (m, 2H, 2 *o*-H), 7.16−7.24 (m, 1H, *p*-H), 7.23−7.29 (m, 2H, 2 *m*-H), 7.31−7.37 and 7.35−7.41 (both m, 2 × 1H, H(6) and H(7)), 7.42 and 7.63 (both s, 2 × 1H, H(9) and H(10)), 7.60−7.64 and 7.72−7.76 (both m, 2 × 1H, H(5) and H(8)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 30.8 (CH(2)), 33.7 and 36.0 (CH_2(1) and CH_2(3)), 43.7 (CH(4)), 52.44 and 52.46 (2 OMe), 56.3 (CH), 125.3, 125.6, 126.2, 127.1, 127.2, 127.5, and 128.5 (7CH(Ar)), 128.4 and 128.8 (2 *o*-CH and 2 *m*-CH), 132.43, 132.47, 134.6, 137.0, and 146.6 (C(4a), C(8a), C(9a), C(10a) and *i*-C), 168.8 (2 COO).

The following are data for compound *cis*-**5x** (minor isomer). ^1H NMR ($CDCl_3$, 400.1 MHz): δ 1.59 (ddd, 1H, *syn*-H(3), ^2J = 13.1 Hz, ^3J = 12.4 and 10.2 Hz), 2.51 (br ddd, 1H, *anti*-H(3), ^2J = 13.1 Hz, ^3J = 7.7 and 2.7 Hz), 2.61−2.69 (m, 1H, H(2)), 2.86−3.01 (m, 2H, CH_2(1)), 3.37 (d, 1H, CH, ^3J = 8.9 Hz), 3.73 and 3.77 (both s, 2 × 3H, 2 OMe), 4.78 (dd, 1H, H(4), ^3J = 10.2 and 7.4 Hz), 6.96−7.02 (m, 2H, 2 *o*-H), 7.07−7.13 (m, 1H, *p*-H), 7.14 (dd, 1H, H(7), ^3J = 8.2 and 7.3 Hz), 7.15−7.20 (m, 2H, 2 *m*-H), 7.24 (d, 1H, H(10), ^3J = 8.4 Hz), 7.28 (dd, 1H, H(6), ^3J = 8.0 and 7.3 Hz), 7.54 (d, 1H, H(5), ^3J = 8.2 Hz), 7.67 (d, 1H, H(9), ^3J = 8.4 Hz), 7.73 (d, 1H, H(8), ^3J = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 34.7 (CH(2)), 35.9 (CH_2(1)), 40.9 (CH_2(3)), 44.0 (CH(4)), 52.5 and 52.6 (2 OMe), 57.0 (CH), 124.7 (CH(6)), 125.5 (CH(7)), 125.6 (CH(8)), 125.8 (*p*-CH), 127.2 (CH(9)), 127.4 (2 *o*-CH), 127.9 (CH(10)), 128.5 (CH(5)), 128.8 (2 *m*-CH), 132.1, 132.7, 133.2, 135.4, and 148.7 (C(4a), C(4b), C(8a), C(10a) and *i*-C), 168.78 and 168.84 (2 COO).

The following are data for compound *trans*-**5x** (major isomer). Colorless thick oil. HRMS: calcd for $C_{25}H_{24}O_4$ M + H 389.1747, M + Na 411.1567, M + K 427.1306, found *m*/*z* 389.1743, 411.1575, 427.1313. ^1H NMR ($CDCl_3$, 400.1 MHz): δ 2.08 (ddd, 1H, H(3)-a, ^2J = 12.5 Hz, ^3J = 12.5 and 5.1 Hz), 2.17 (dddd, 1H, H(3)-b, ^2J = 12.5 Hz, ^3J = 2.5 and 1.8 Hz, ^4J = 1.5 Hz), 2.57−2.66 (m, 1H, H(2)), 2.90 (dd, 1H, *anti*-H(1), ^2J = 16.9 Hz, ^3J = 11.5 Hz), 3.16 (ddd, 1H, *syn*-H(1), ^2J = 16.9 Hz, ^3J = 5.1 Hz, ^4J = 1.5 Hz), 3.35 (d, 1H, CH, ^3J = 7.8 Hz), 3.64 and 3.70 (both s, 2 × 3H, 2 OMe), 4.87 (dd, 1H, H(4), ^3J = 5.1 and 1.8 Hz), 6.97−7.03 (m, 2H, 2 *o*-H), 7.10−7.17 (m, 1H, *p*-H), 7.17−7.24 (m, 2H, 2 *m*-H), 7.26 (br dd, 1H, H(7), ^3J = 8.5 and 6.9 Hz), 7.27 (d, 1H, H(10), ^3J = 8.5 Hz), 7.34 (ddd, 1H, H(6), ^3J = 8.1 and 6.9 Hz, ^4J = 1.2 Hz), 7.61 (d, 1H, H(8), ^3J = 8.5 Hz), 7.70 (d, 1H, H(9), ^3J = 8.5 Hz), 7.77 (br d, 1H, H(5), ^3J = 8.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 29.2 (CH(2)), 34.1 and 36.5 (CH_2(1) and CH_2(3)), 41.4 (CH(4)), 52.36 and 52.41 (2 OMe), 57.1 (CH), 124.4 (CH(8)), 124.9 (CH(6)), 126.1 (*p*-CH), 126.2 (CH(7) or CH(10)), 127.3 (CH(9)), 127.8 (CH(7) or CH(10)), 128.3 (2 *m*-CH), 128.4 (2 *o*-CH and CH(5)), 131.8, 132.2, 132.7, 134.2, and 145.8 (C(4a), C(4b), C(8a), C(10a) and *i*-C), 168.7 and 168.9 (2 COO).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

2D NMR data for the key compounds and NMR spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01179.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (Project 14-13-01054).

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DOI: 10.1021/acs.joc.5b01179
J. Org. Chem. 2015, 80, 8225−8235