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A Mild Stereo- and Enantiospecific Conversion of 2,3-Diaryl-Substituted Oxiranes into 2,2-Dimethyl-1,3-Dioxolanes by an Acetone/Amberlyst 15 System

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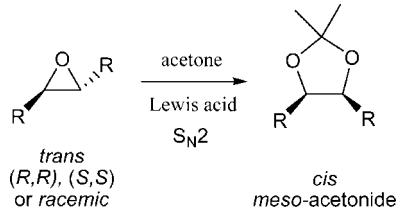
Amberlyst 15 is an efficient catalyst for the reaction of aryl-substituted oxiranes with acetone to prepare 2,2-dimethyl-1,3-dioxolanes in high yields. *trans*-2,3-Diaryloxiranes afford *trans*-acetonides enantiospecifically at room temperature, and the use of enantiopure 2,3-diaryloxiranes results in no loss of stereochemical integrity in the resulting *trans*-acetonides.

Introduction

The 2,2-dimethyl-1,3-dioxolane (acetonide) group is a widely used protecting group for vicinal diols. The preparation of acetonides usually involves the reaction of the diol with acetone, 2,2-dimethoxypropane, or 2-methoxypropene under acidic conditions.[1]

The direct conversion of epoxides to the corresponding acetonides has been described with the use of different Lewis acid catalysts. Among the most recent catalysts, with various degrees of success in terms of yield and selectivity, are anhydrous $SnCl_2$,[2] tin(IV) tetraphenylporphyrin perchlorate,[3] 2,4,4,6-tetrabromo-2,5-cyclohexadienone,[4] bismuth(III) salts,[5] various titanium complexes,[6] $[(C_5Me_5)Ir(NaMe)_3]$,[7] $RuCl_3$,[8] CH_3ReO_3,[9] $Cu(OTf)_2$,[10,11] $Er(OTf)_3$,[12] $BF_3{\cdot}Et_2O$,[13] $LiBF_4$,[14] and heteropoly-acids.[15] Many of these catalysts are strong Lewis acids and are not suitable in the presence of other functional groups. Heterogeneous catalysts, such as K-10 montmorillonite[16] and various zeolites,[17] have also been studied in order to find milder reaction conditions. However, examples with 2,3-disubstituted oxiranes bearing at least one aryl group have been reported only occasionally. The conversion of epoxides into acetonides by the above-mentioned systems usually occurs through a general S_N2 mechanism, with inversion of configuration at the oxiranyl carbon approached by acetone. Thus, *trans*-symmetrical 2,3-disubstituted oxiranes lead invariably to *meso*-acetonides as the main reaction product (Scheme 1).



Scheme 1.

Herein we report the direct conversion of di- and trisubstituted epoxides into 2,2-dimethyl-1,3-dioxolanes (acetonides) by acetone in the presence of the acid resin Amberlyst 15.

Results and Discussion

During our studies on metal halide promoted opening reactions of diaryl epoxides,[18] we observed the formation of a considerable amount (up to 30%) of by-products, along with the expected halohydrins, when the reaction was performed in acetone. These results prompted us to investigate the acetone/Amberlyst 15 system as a reagent with a variety of aryl epoxides (Scheme 2). The results are shown in Table 1.

We started by studying the behavior of styrene oxide (**1a**) in the presence of different amounts of Amberlyst 15, at different reaction temperatures, and with acetone as the solvent. We noted that although the acetonide could be formed by the use of very small quantities of resin (20 mg/mmol of substrate), the best results, in terms of yield and reaction time, were obtained using a 220 mg/mmol ratio at

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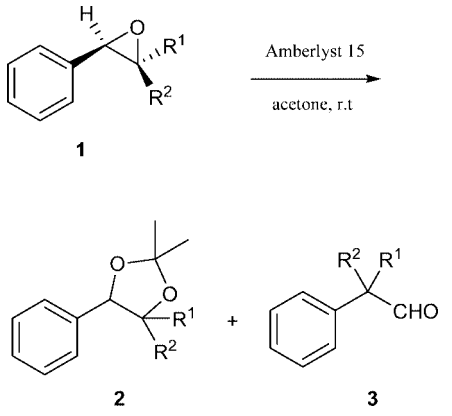
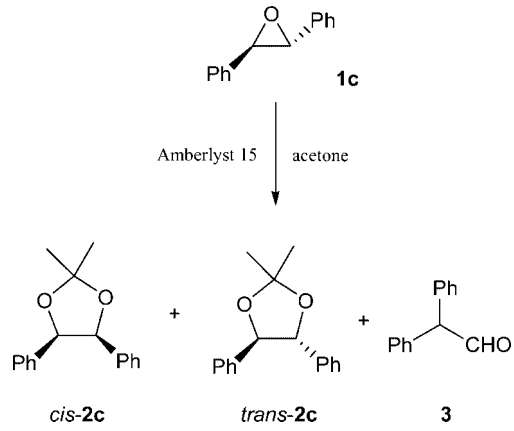


Scheme 2.



Scheme 3.

Table 1. Conversion of aryl epoxides into acetonides.

Entry	1[a]	R^1	R^2	Time [h]	*cis*-2[b]	*trans*-2[b]	3[b]
1	**1a**	H	H	12	82[c]		18
2	**1b**	CH_3	H	12	28[c]	38[c]	–
3	**1c**	Ph	H	1	13	53	23[d]
4	**1d**	Ph	Ph	8	82[e]		18[e]

[a] All reactions were performed with 220 mg of Amberlyst 15 per millimol of substrate and in a 0.1 M acetone solution of the substrate at room temperature. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] 34% of the corresponding diols were detected. [d] 11% of unidentified product. [e] Isolated yield.

room temperature. Under these conditions, the dioxolane **2a** ($R^1 = R^2 = H$) was obtained in 82% yield, together with an 18% yield of phenylacetaldehyde (entry 1). Triphenyloxirane (**1d**) also gave a high yield of the corresponding acetonide **2d** (entry 4).

In the case of *trans*-2,3-disubstituted oxiranes such as *trans*-β-methylstyrene (**1b**) and *trans*-stilbene (**1c**; entries 2 and 3, respectively), we noted an interesting stereoselectivity towards *trans*-acetonides, with a clear retention of configuration at the oxiranyl carbon atoms.

In order to study the stereoselectivity of this transformation, the 2,3-disubstituted model *trans*-stilbene oxide (**1c**) was allowed to react under different conditions (Scheme 3). The most significant results of the effect of temperature on stereoselectivity of acetonide formation are collected in Table 2.

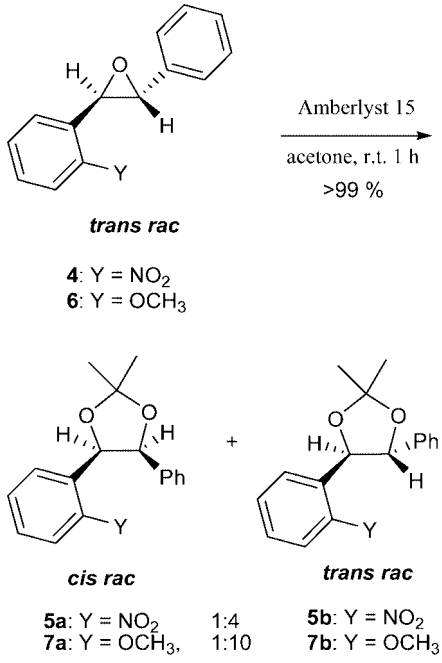
We first of all noted a slightly higher lability of the corresponding 2,3-diaryl products due to the presence of acidic traces, with respect to dioxolanes **2a** and **2d**, thus leading to several by-products. However, after an initial neutralization with $NaHCO_3$ these by-products were almost totally avoided. As can be seen, high yields of acetonides were obtained after reasonable reaction times, with temperatures ranging between 25 and –78 °C; only traces of by-product were detected. At –78 °C, a higher amount of Amberlyst 15 was required to lead the reaction to completion (entry 6). From the data shown in Table 2, it is clear that the temperature has a strong effect on the stereoselectivity of the reaction. At room temperature, the corresponding acetonides were obtained in high yield, with a *cis*/*trans* ratio of 2/3 (entry 1). Running the reaction at 40 °C, the *trans*/*cis* ratio of the products decreased slightly (4/3.6) and a considerable amount of the aldehyde **3** was formed (24%). Upon lowering the temperature, the formation of the *cis* isomer increased, and it became the major reaction product below –10 °C. While the formation of the *cis*-acetonide can be easily explained by a classical S_N2 oxiranyl ring opening with inversion of configuration, the *trans* isomer implies the formation of an acyclic cationic-type intermediate, which has already been suggested in the reactions with metal halides as nucleophiles.[19] Upon lowering the temperature, the formation of the acyclic intermediate becomes slower, while the S_N2 opening with inversion of configuration becomes more competitive.

Table 2. Conversion of *trans*-stilbene oxide (**1c**) into acetonides.

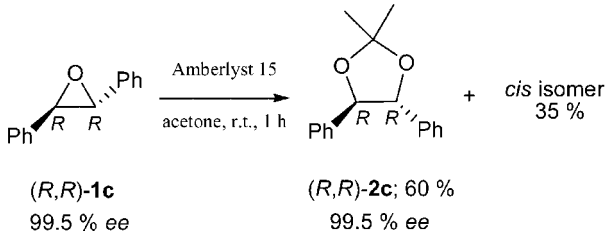
Entry[a]	Temp. [°C]	Time [h]	Conv.[b]	*cis*-**2c** [%][b]	*trans*-**2c** [%][b]	**3** [%][b]
1	25	1	100	40	60	–
2	0	3	100	50	50	–
3	–10	8	100	55	45	–
4	–50	12	100	67	24	9
5	–78	10.5	37	80	16	4
6[c]	–78	10.5	100	75	25	–

[a] All reactions were performed with 300 mg of Amberlyst 15 per millimol of substrate and in 0.1 M acetone solution of the substrate. The workup was performed by neutralization with $NaHCO_3$ s.s. [b] Determined by ^{1}H NMR analysis on the crude mixture. [c] 660 mg of Amberlyst 15 per millimol of substrate.

This stereochemical outcome prompted us to submit optically pure (*R*,*R*)-**1c** to the standard conditions at room temperature (Scheme 4). No loss of stereochemical integrity of the corresponding *trans*-acetonide was obtained, which proved that no epimerization occurs during the oxiranyl ring opening.[20] After easy chromatographic purification, *trans*-(*R*,*R*)-acetonide **2c** was obtained in good isolated yield. This method represents the first direct enantioselective access to this acetonide from the parent epoxide.

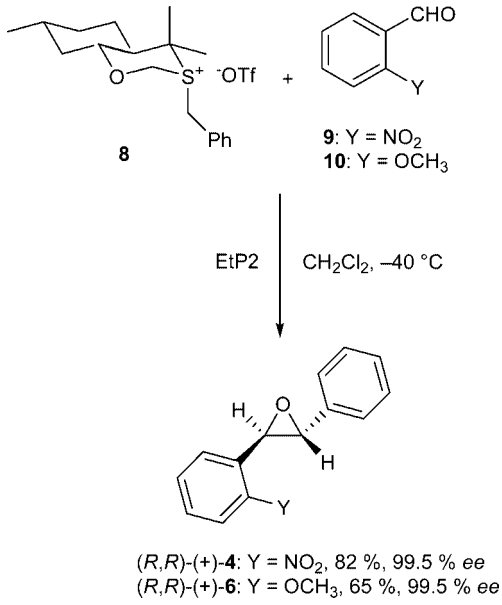


Scheme 4.



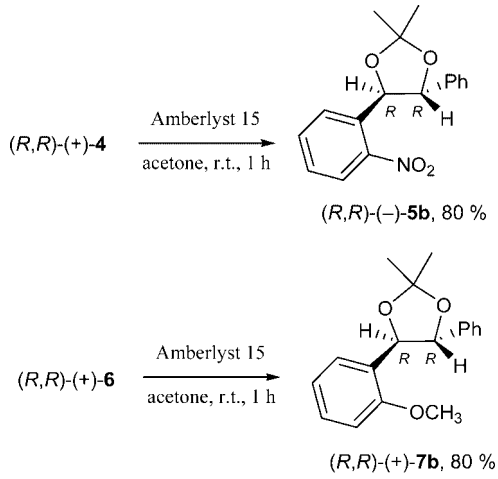
We then extended our procedure to racemic nonsymmetrical 2,3-diaryloxiranes, which can be easily prepared, in racemic form, by the reaction of benzylidene sulfur ylide, generated from the corresponding sulfonium salts under phase-transfer conditions, with the appropriate aryl aldehyde.[19a] *ortho*-Nitro and *ortho*-methoxy *trans*-epoxides **4** and **6** were prepared in this way and submitted to our standard conditions; both epoxides produced the corresponding acetonides quantitatively, with a *trans*/*cis* ratio of between 4:1 and 10:1 (Scheme 4).

Nonracemic *trans*-epoxides **4** and **6**[21] were prepared in good yield and more than 99.5% *ee* (as determined by HPLC) from the pure (*R*,*R*,*R*,S_S)-(–)-sulfonium salt **8**,[22] commercial 2-nitro- and 2-methoxybenzaldehydes, and the phosphazene base EtP2 [EtN=P(NMe$_2$)$_2${N=P(NMe$_2$)$_3$}] to generate the sulfur ylide (Scheme 5).



Scheme 5. Synthesis of enantiopure *ortho*-substituted diaryl epoxides.

Once submitted to our standard conditions, the optically active epoxides afforded the corresponding new (*R*,*R*) *trans*-acetonides **5b** and **7b** in high yield with no loss of stereochemical integrity (Scheme 6). The *cis*-acetonides were not formed in these cases.



Scheme 6. Synthesis of enantiopure *trans*-acetonides.

In conclusion, these results show that Amberlyst 15 is an efficient catalyst for the enantiospecific conversion of mono- and diaryl-substituted epoxides directly to their 2,2-dimethyl-1,3-dioxolane derivatives, which are useful intermediates in the synthesis of functionalized diaryl glycols.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded at 300 (or 500) and 75 (or 125) MHz, respectively. Mass spectra were recorded with a Hewlett–Packard 6890 chromatograph equipped with a HP 5973 mass detector. Commercially available reagents were used without further purification. All reactions were monitored by TLC on silica

gel-coated plates. Column chromatography was carried out using 60–240 mesh silica gel at atmospheric pressure.

General Procedure. Preparation of 2,2-Dimethyl-4-phenyl-1,3-dioxolane (2a): Amberlyst 15 (220 mg) was added in one portion to a solution of styrene oxide **1a** (1 mmol) in acetone (10 mL) at room temperature and the mixture was allowed to stir until the reaction was complete (by TLC and GC analysis). The Amberlyst was filtered off and $NaHCO_3$ s.s. (10 mL) was poured into the solution. The solvent was then evaporated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed. The crude product was purified by silica gel chromatography (*n*-hexane/Et_2O, 4:1) to give **2a** (146 mg; 82% yield) as a colorless oil whose ^1H and ^{13}C NMR spectra were identical to those reported in the literature.[2]

***cis*- and *trans*-2,2,5-Trimethyl-4-phenyl-1,3-dioxolanes (2b):** Epoxide **1b** (1 mmol), acetone (10 mL), and Amberlyst 15 (220 mg) at room temperature yielded **2b** (126 mg; 66%) together with 34% of the corresponding 1-phenyl-1,2-propandiol. ^1H NMR (300 MHz, $CDCl_3$) of a 66:34 mixture with the diols: δ = 1.09 (d, ^3J = 6.5 Hz, 3 H, *cis*, 28%), 1.29 (d, ^3J = 6.0 Hz, 3 H, *trans*, 38%), 1.47 (s, 3 H, *cis*, 28%), 1.52 (s, 3 H, *trans*, 38%), 1.56 (s, 3 H, *trans*, 38%), 1.64 (s, 3 H, *cis*, 28%), 3.86 (qd, $^3J_1$ = 6.0, $^3J_2$ = 8.5 Hz, 1 H, *trans*, 38%), 4.02 (qd, $^3J_1$ = 6.5, $^3J_2$ = 4.0 Hz, 1 H, *cis*, 28%), 4.47 (d, ^3J = 8.5 Hz, 1 H, *trans*, 38%), 4.69 (d, ^3J = 4.0 Hz, 1 H, *cis*, 28%), 7.2–7.4 (m, 5 H) ppm.

***trans*-2,2-Dimethyl-4,5-diphenyl-1,3-dioxolane (2c):** Epoxide **1c** (1 mmol), acetone (10 mL), and Amberlyst 15 (300 mg) at room temperature yielded *trans*-**2c** (152 mg; 60%) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 9:1) as an oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.69 (s, 6 H), 4.76 (s, 2 H), 7.30–7.50 (m, 10 H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$): δ = 27.2, 85.4, 109.3, 126.7, 128.2, 128.4, 128.5, 130.2, 133.7, 136.7 ppm. MS: *m*/*z* (%) 197 (6) $[M - 57]^+$, 179 (7) $[M - 75]^+$, 148 (100). $C_{17}H_{18}O_2$ (254.32): calcd. C 80.28, H 7.13; found C 80.1, H 7.2.

trans-(4*R*,5*R*)-**2c** was obtained from (2*R*,3*R*)-**1c**[19b] in 60% yield [99.5% *ee*;[20] $[\alpha]_D^{25}$ = +50 (*c* = 0.7, $CHCl_3$)] using the same procedure.

***cis*-2,2-Dimethyl-4,5-diphenyl-1,3-dioxolane (2c):** Epoxide **1c** (1 mmol), acetone (10 mL) and Amberlyst 15 (300 mg), at –78 °C, yielded *cis*-**2c** (191 mg; 75%) after chromatographic purification on silica gel (petroleum ether/diethyl ether = 9:1) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 3 H), 1.84 (s, 3 H), 5.53 (br. s, 2 H), 6.90–7.20 (m, 10 H).

2,2-Dimethyl-4,4-5-triphenyl-1,3-dioxolane (2d): Epoxide **1d** (1 mmol), acetone (10 mL), and Amberlyst 15 (220 mg) at room temperature yielded **2d** (271 mg; 82%) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 9:1) as a white solid (m.p. 113 °C from ethanol).[23] ^1H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 3 H), 1.83 (s, 3 H), 5.64 (s, 1 H), 7.0–7.50 (m, 15 H) ppm.

***trans*-2,2-Dimethyl-4-(2-nitrophenyl)-5-phenyl-1,3-dioxolane (5b):** (*E*)-2-(2-Nitrophenyl)-3-phenyloxirane **4** (1 mmol), acetone (10 mL) and Amberlyst 15 (300 mg) at room temperature yielded **5b** (239 mg; 80%) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 7:3) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 6 H), 4.79 (d, ^3J = 8.5 Hz, 1 H), 5.49 (d, ^3J = 8.5 Hz, 1 H), 7.21 (m, 2 H), 7.29 (m, 3 H), 7.46 (dd, $^3J_1$ = $^3J_2$ = 8.0 Hz, 1 H), 7.66 (dd, $^3J_1$ = $^3J_2$ = 8.0 Hz, 1 H), 7.73 (d, ^3J = 8.0 Hz, 1 H), 7.82 (d, ^3J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 27.2, 79.7, 85.8, 109.8, 124.3, 126.5, 128.6, 128.7, 128.8, 129.0, 131.0, 132.8, 135.5 ppm. IR (neat): $\tilde{\nu}$ = 2926, 1531, 1383, 1234, 1057, 757, 699. MS: *m*/*z* (%) 284 (2) $[M - 15]^+$, 193 (9), 135 (100). $C_{17}H_{17}NO_4$ (299.32): calcd. C 68.21, H 5.72, N 4.68; found C 68.1, H 5.6, N 4.6.

trans-(4*R*,5*R*)-**5b** was obtained from (2*R*,3*R*)-**4** in 80% isolated yield [99.5% *ee*; HPLC Chiralcel OD, *n*-hexane/2-propanol 95:5, 0.5 mL min^{-1}, t_R = 11.41 min. $[\alpha]_D^{25}$ = –6.0 (*c* = 2, $CHCl_3$)] using the same procedure.

***cis*-2,2-Dimethyl-4-(2-nitrophenyl)-5-phenyl-1,3-dioxolane (5a):** (*E*)-2-(2-Nitrophenyl)-3-phenyloxirane **4** (1 mmol), acetone (10 mL), and Amberlyst 15 (300 mg) at room temperature yielded **5b** (59.8 mg; 20%) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 7:3) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 6 H), 5.0 (d, ^3J = 4.0 Hz, 1 H), 5.57 (d, ^3J = 4.0 Hz, 1 H), 7.40 (m, 9 H) ppm. MS: *m*/*z* (%) 284 (2) $[M - 15]^+$, 193 (9), 135 (100). $C_{17}H_{17}NO_4$ (299.32): calcd. C 68.21, H 5.72, N 4.68; found C 68.1, H 5.6, N 4.6.

***trans*-4-(2-Methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (7b):** (*E*)-2-(2-Methoxyphenyl)-3-phenyloxirane **6** (1 mmol), acetone (10 mL), and Amberlyst 15 (300 mg) at room temperature yielded **7b** (199 mg; 70%) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 9:1) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.67 (s, 3 H), 1.68 (s, 3 H), 3.32 (s, 3 H), 4.77 (d, ^3J = 8.0 Hz, 1 H), 5.27 (d, ^3J = 8.0 Hz, 1 H), 6.75 (d, ^3J = 8.0 Hz, 1 H), 7.02 (dd, $^3J_1$ = $^3J_2$ = 8.0 Hz, 1 H), 7.30 (m, 6 H), 7.59 (d, ^3J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.2, 54.8, 79.3, 84.7, 108.9, 110.6, 120.7, 125.2, 126.6, 126.8, 127.2, 127.7, 128.0, 129.0, 137.6, 157.2 ppm. IR (neat): $\tilde{\nu}$ = 2984, 2931, 1495, 1251, 1055, 894, 754, 698. MS: *m*/*z* (%) 284 (1) $[M^+]$, 269 (2) $[M - 15]^+$, 227 (10) $[M - 57]^+$, 178 (100), 148 (99). $C_{18}H_{20}O_3$ (284.35): calcd. C 76.03, H 7.09; found C 75.9, H 7.0.

trans-(4*R*,5*R*)-**7b** was obtained from (2*R*,3*R*)-**6** in 80% isolated yield [99.5% *ee*; HPLC Chiralcel OJ, *n*-hexane/2-propanol 99:1, 0.5 mL min^{-1}, t_R = 31.95 min. $[\alpha]_D^{25}$ = +13 (*c* = 0.4, $CHCl_3$)] using the same procedure.

***cis*-4-(2-Methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (7a):** This compound was isolated (28 mg, 10% yield) after chromatographic purification on silica gel (petroleum ether/diethyl ether, 9:1) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.61 (s, 3 H), 1.81 (s, 3 H), 3.61 (s, 3 H), 5.53 (d, ^3J = 7.5 Hz, 1 H), 5.81 (d, ^3J = 7.5 Hz, 1 H), 6.47 (d, ^3J = 8.0 Hz, 1 H), 6.76 (dd, $^3J_1$ = $^3J_2$ = 8.0 Hz, 1 H), 7.01 (m, 5 H), 7.29 (m, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.2, 26.7, 54.6, 76.3, 81.07, 108.9, 119.8, 126.2, 126.6, 126.7, 126.9, 127.2, 127.4, 127.8, 138.3, 155.0 ppm.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and characterization data for epoxides (2*R*,3*R*)-**4** and (2*R*,3*R*)-**6**. ^1H and ^{13}C NMR spectra of compounds *trans*-**2c**, **-5b**, and **-7b**.

Acknowledgments

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