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# Sulfinyl Group as an Intramolecular Nucleophile: Synthesis of Bromohydrins from β-Methyl-γ,δ-unsaturated Sulfoxides with High 1,2-Asymmetric Induction†

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**Abstract:** Bromohydrins have been prepared from β-methyl-γ,δ-unsaturated sulfoxides with high regio- and stereoselectivity. The reaction proceeds via neighboring group participation of the sulfinyl moiety with inversion of sulfoxide configuration as proven by an $^{18}O$ labeling study and X-ray crystallography.

A large number of dense vicinally functionalized compounds are present in nature. The obvious and arguably the best method of introducing a vicinal functionality is by a nucleophilic attack, initiated by the addition of an electrophile to an alkene. Neighboring group participation has been put to use for introducing the nucleophile, with site and face selectivity in electrophile-mediated functionalization of olefins.[1] As a goal toward the heterofunctionalization of olefins using the pendant sulfoxide as the nucleophile,[2] we report herein the preparation of bromohydrins from β-methyl-γ,δ-unsaturated sulfoxides with excellent 1,2-asymmetric induction.

It was desirable to react each of the diastereomeric sulfoxides **3** and **4** with *N*-bromosuccinimide (NBS) to probe the influence of sulfoxide configuration on the outcome of the reaction. The sulfoxides **3** and **4** were synthesized in a short sequence of reactions that began with the Michael addition of thiophenol to methacrolein, promoted by triethylamine, to afford aldehyde **1**. Subsequently, Wittig reaction[3] and other routine transformations yielded the sulfides **2**. The trans and cis ester (**2a**) were separated by chromatography, and the pure ester **2a** was used in the next step. The mixture of olefins resulting from the reaction of the aldehyde **1** with benzylphosphonium salt was subjected to treatment with thiophenol in the presence of catalytic AIBN in THF to yield exclusively the trans ester **2d**. Oxidation of the sulfides with $NaIO_4$[4] afforded an equimolar mixture of sulfoxides **3** and **4**, which were separated by column chromatography. The trans alkene **3d** was prepared by thiophenol-catalyzed thermal isomerization of **3a**[5] (Scheme 1).

The unsaturated sulfoxides **3** and **4**, upon treatment with a slight excess of NBS in toluene at ambient temperature, afforded the product bromohydrins (Table 1). A cursory examination of Table 1 reveals that all the unsaturated sulfoxides, except **3c**, react highly stereoselectively. The stereochemical outcome of the reaction is explained using **4b** as a representative (Scheme 2). The attack by the electrophilic bromonium ion on the less hindered face of the olefin in its stable conformation (a principle of allylic 1,3-strain[6]), followed by the nucleophilic sulfinyl group intramolecularly, would yield the sulfoxonium salt, which on hydrolysis by attack of water on sulfur[7] would yield the regioisomeric products. The olefin **3d** also affords regioisomeric bromohydrins, while the other substrates react regiospecifically. Each of the isomeric bromohydrins arising from **3d** and **4b** was individually transformed, by treatment with a base, to afford an identical epoxide, proving beyond doubt their regioisomeric relationship (Scheme 2). The stabilization of a partial positive charge at the benzylic position would account for the formation of products by 6-endo opening from the sulfoxides **3c** and **4c**.

The orientation of the hydroxyl group relative to the $C_2$-Me in bromohydrin **5a**, was established by transforming it into the acetonide **9** (Scheme 3), the structure of which was established by COSY and coupling constant data.[8] The sulfoxide **3b**, by analogy with **3a**, is expected to afford bromohydrin **5b**. Debromination of product **5d** with tributyltin hydride afforded **7**, identical in all respects to the product obtained from bromohydrin **5a**, thus establishing the relative orientation of the methyl and hydroxyl groups in **5d**. Trans addition[9] of the electrophile and the nucleophile across the double bond predicates that the relative orientation of the bromine and hydroxyl groups in the product depend on the olefin geometry. Transforming them individually into an identical sulfone proved that bromohydrins **5a** and **6a** differ due to the difference in sulfoxide configuration. The same exercise proved the isomeric nature of products **5b**/**6b** and **5c**/**6c**.

Neighboring sulfinyl group participation in the reaction has been demonstrated conclusively by carrying out the reaction of substrates **3c** and **4a** in the presence of $^{18}O$-labeled water. The resulting products **10** and **12** revealed $M^+$ peaks in the mass spectrum two units greater than those of the product obtained using unlabeled water. If the added water were the nucleophile, the labeled oxygen

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(3) Olefin **2a** was prepared using Still's reagent: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.

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(8) Assignment of configuration to 1,3-diols by comparing the coupling constants of the derived acetonides has been widely used in the literature. For excellent examples, see: (a) Barrett, A. G. M.; Tam, W. *J. Org. Chem.* **1997**, *62*, 4655. (b) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560.

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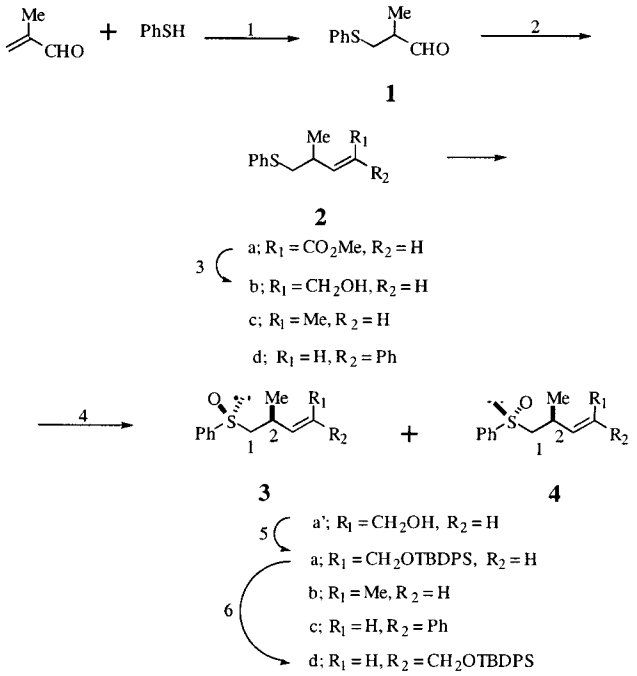
**SCHEME 1**[a]



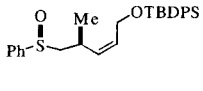
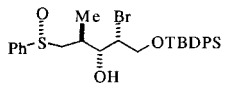
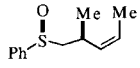
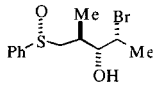
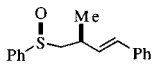
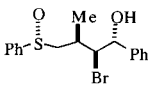
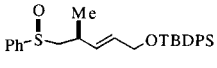
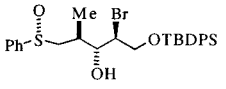
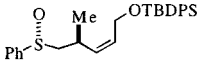
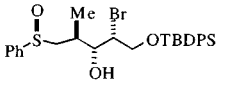
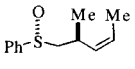
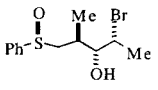
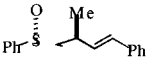
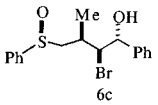

[a] Reaction conditions: (1) Catalytic DBU, PhH, rt, 16h, 85%. (2) (a) $(CF_3CH_2O)_2P(O)CH_2CO_2Me$, NaH, THF, −78 °C, 3 h, **2a** = 80%, cis:trans = 8.5:1.5; (b) $EtPPh_3Br$, *n*-BuLi, THF, from −78 °C to rt, 16 h, **2c** = 85% cis only; (c) $PhCH_2PPh_3Br$, *n*-BuLi, THF, from −78 °C to rt, 16 h, **2d** = 80%, cis:trans 1:3. (3) $AlH_3$, $Et_2O$, 0 °C, 2 h, **2b** = 93%. (4) $NaIO_4$, MeOH, $H_2O$, rt, 16 h, 95%, **3**:**4** = 1:1. (5) TBDPS-Cl, imidazole, DMF, rt, 2 h, 78%. (6) PhSH, AIBN, PhH, 80 °C, 4 h, 80%.

would be on the hydroxyl group and the reduction of the sulfinyl moiety would yield products with $M^+$ peaks again two units greater than those obtained when unlabeled water was used. Reduction of the sulfinyl moiety[10] in **10** and **12**, however, afforded products with a loss of 18 mass units, indicating that the labeled oxygen is on sulfur and, therefore, proving beyond doubt intramolecular sulfinyl participation (Scheme 4).

The relative orientation of the sulfinyl oxygen and the $C_2$-Me group in sulfoxide **3c** was confirmed to be syn by single-crystal X-ray diffraction.[11] The relative stereochemistries in sulfoxides **3a** and **3b** were deduced by comparing the chemical shifts of $C_1$, $C_2$, and the $C_2$-Me protons to those in **3c** (Table 2). The sulfoxides **4a**−**c** also reveal striking similarities in their $^1$H NMR spectra. Inspection of Table 2 reveals that the $C_2$-H in sulfoxides **3a**−**c** resonates downfield relative to the $C_2$-H of the corresponding sulfoxides **4a**−**c**; $C_2$-Me in **3a**−**c** appears upfield relative to $C_2$-Me in **4a**−**c**. Also, the difference in the chemical shifts of the methylene protons, flanked by the sulfinyl moiety and $C_2$, is larger in **3a**−**c** in comparison to that observed for the corresponding diastereomeric sulfoxides **4a**−**c**. The structure of the bromohydrin **5c** was secured by X-ray crystallography.[11]

The X-ray structure established the relative orientation of the sulfinyl oxygen, $C_2$-Me, bromo, and hydroxyl groups in **5c**. The crystallization of racemic **3c** and **5c** in enantiomorphous space groups by spontaneous resolution[12] may be noted.

**TABLE 1. Regio- and Stereoselectivity of Bromohydrin Formation**[a]

| Entry | Substrate | Product | Yield (%) (Anti : Syn) ($C_2/C_3$) |
|---|---|---|---|
| 1 |  3a |  5a | 90 (> 95 : < 5) |
| 2 |  3b |  5b | 85 (> 95 : <5) |
| 3 |  3c |  5c | 75 (1 : 3) |
| 4 |  3d |  5d | 85 (> 95 : < 5)[b] |
| 5 |  4a |  6a | 80 (> 95 : < 5) |
| 6 |  4b |  6b | 75 (>95 : <5 )[c] |
| 7 |  4c |  6c | 90 (<5 : >95) |

[a] All reactions were done on a 0.25 mmol scale using 1.2 equiv of NBS and 1.7 equiv of water in toluene as the solvent (0.25 M). [b] Regioisomeric bromohydrins are obtained in a 1:2 ratio; the minor isomer is depicted [c] Regioisomeric bromohydrins are obtained in a 3:2 ratio; the major isomer is depicted. The ratio was determined from $^1$H NMR spectra. The yield refers to the combined yield of the mixture of regiomers.

In conclusion, we have demonstrated the utility of the sulfinyl moiety as a neighboring group to afford vicinally functionalized products with good stereo- and regioselectivity. The extent of asymmetric induction is determined by the stereocenter at $C_2$, the double-bond geometry, and to some extent the sulfoxide configuration. This study also helps to assign the relative configuration of *β*-alkyl sulfoxides by inspection of their $^1$H NMR data. The use of the methodology in the synthesis of bioactive natural products is in progress and will be reported in due course.

## Experimental Section

NBS was freshly recrystallized from hot water before use. NMR spectra were recorded on a 200 and 400 MHz spectrometer.

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(11) See Supporting Information.

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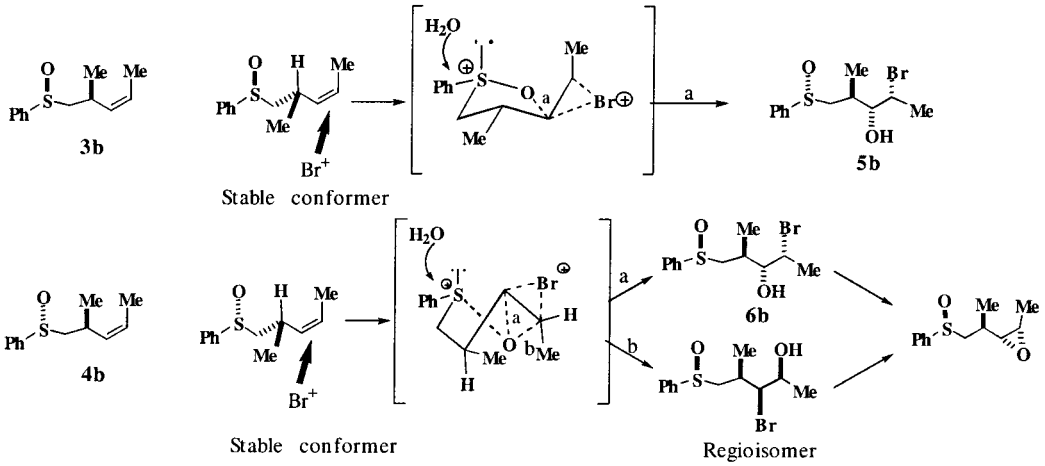
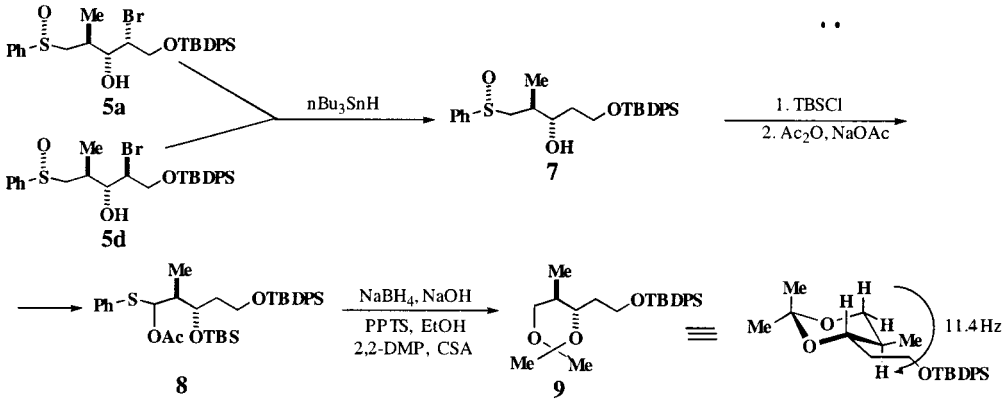
**SCHEME 2**




**SCHEME 3**




**SCHEME 4**

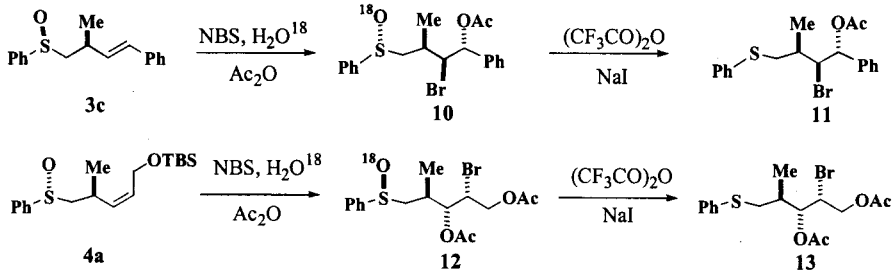



**TABLE 2. Chemical Shift Data of Sulfoxides 3 and 4**

| sulfoxide | $C_2$-H | $C_2$-Me | difference in $\delta$ of $C_1$-H | sulfoxide | $C_2$-H | $C_2$-Me | difference in $\delta$ of $C_1$-H |
|---|---|---|---|---|---|---|---|
| **3c** | 3.05 | 1.25 | 0.25 | **4c** | 3.0 | 1.38 | 0.29 |
| **3a** | 2.92 | 1.04 | 0.33 | **4a** | 2.77 | 1.13 | 0.23 |
| **3b** | 3.20 | 1.10 | 0.33 | **4b** | 3.06 | 1.20 | 0.29 |

$^1$H NMR and $^{13}$C NMR samples were internally referenced to TMS (0.00 ppm). Column chromatography was performed with 60−120 mesh silica gel. The sulfoxides **3** and **4** were prepared from sulfides **2** following the literature procedure.

**General Procedure for the Preparation of Sulfoxides 3 and 4.** To a solution of the sulfide **2** (15 mmol) in methanol (150 mL) cooled at 0 °C was added dropwise a solution of $NaIO_4$ (18 mmol) in water (75 mL), and the mixture was allowed to stir for 12 h and gradually attain rt. The solid was filtered and the filtrate concentrated. The aqueous layer was extracted with EtOAc. The organic layer was washed successively with water, brine, dried over $Na_2SO_4$, and concentrated to yield a 1:1 mixture of sulfoxides **3** and **4**, which were separated by column chromatography using EtOAc/petroleum ether as the eluent.

**Sulfoxide (3a):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.04 (bs, 12H), 2.40 (dd, $J$ = 13.16, 9.11 Hz, 1H), 2.73 (dd, $J$ = 13.16, 5.06 Hz, 1H), 2.92 (m, 1H), 4.30 (d, $J$ = 6.33 Hz, 2H), 5.25 (m, 1H), 5.70 (m, 1H), 7.30−7.70 (m, 15H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 19.1, 20.9, 26.8, 28.3, 60.3, 65.7, 123.8, 127.5, 127.6, 129.1, 129.5, 130.9, 133.8, 135.5, 144.8; MS (EI, $m/z$) 405 ($M^+ - C_4H_9$), 229, 199.

**Sulfoxide (4a):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.03 (s, 9H), 1.13 (d, $J$ = 6.33 Hz, 3H), 2.50 (dd, $J$ = 12.66, 8.86 Hz, 1H), 2.73 (dd, $J$ = 12.66, 5.06 Hz, 1H), 2.77 (m, 1H), 4.19 (d, $J$

= 6.33 Hz, 2H), 5.23 (m, 1H), 5.56 (m, 1H), 7.30−7.68 (m, 15H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 19.6, 20.3, 26.9, 27.9, 60.2, 65.1, 124.1, 127.7, 129.2, 129.6, 130.9, 133.9, 135.6, 144.0; MS (EI, *m*/*z*) 405 ($M^+ - C_4H_9$).

**Sulfoxide (3b):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.10 (d, $J$ = 7.10 Hz, 3H), 1.72 (d, $J$ = 7.10 Hz, 3H), 2.48 (dd, $J$ = 12.94, 10.60 Hz, 1H), 2.81 (dd, $J$ = 12.94, 4.71 Hz, 1H), 3.20 (m, 1H), 5.22 (m, 1H), 5.62 (m, 1H), 7.43−7.62 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 12.8 20.0, 27.0, 65.7, 124.0, 124.3, 129.0, 130.6, 133.1, 144.5; MS (EI, *m*/*z*) 208 ($M^+$), 145, 131.

**Sulfoxide (4b):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.20 (d, $J$ = 7.0 Hz, 3H), 1.61 (d, $J$ = 7.0 Hz, 3H), 2.51 (dd, $J$ = 12.68, 9.86 Hz, 1H), 2.80 (dd, $J$ = 12.68, 6.76 Hz, 1H), 3.06 (m, 1H), 5.20 (m, 1H), 5.40 (m, 1H), 7.42−7.62 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 13.0, 20.9, 27.2, 66.3, 123.7, 125.7, 129.0, 130.6, 132.8, 145.1; MS (EI, *m*/*z*) 208 ($M^+$), 145, 131.

**Sulfoxide (3c):** solid; mp 83−84 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.25 (d, $J$ = 6.45 Hz, 3H), 2.65 (dd, $J$ = 12.90, 9.68 Hz, 1H), 2.90 (dd, $J$ = 12.90, 5.38 Hz, 1H), 3.05 (m, 1H), 6.12 (dd, $J$ = 15.48, 8.17 Hz, 1H), 6.59 (d, $J$ = 15.48, 1H), 7.20−7.40 (m, 5H), 7.45−7.68 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 20.8, 32.8, 65.8, 123.8, 126.2, 127.3, 128.4, 129.1, 130.8, 130.9, 132.0, 136.9, 144.9; MS (FAB, *m*/*z*) 271 ($M^+$ + H), 221, 193.

**Sulfoxide (4c):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.38 (d, $J$ = 6.60 Hz, 3H), 2.67 (dd, $J$ = 13.10, 10.48 Hz, 1H), 2.94−3.14 (m, 2H), 6.12 (dd, $J$ = 16.60, 9.52 Hz, 1H), 6.41(d, $J$ = 16.60, 1H), 7.20−7.40 (m, 5H), 7.45−7.70 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 19.4, 32.1, 65.1, 123.9, 126.0, 127.4, 128.4, 129.2, 129.8, 130.9, 132.7, 136.8, 144.2; MS (FAB, *m*/*z*) 271 ($M^+$+ H).

**Sulfoxide (3d):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.06 (s, 9H), 1.14 (d, $J$ = 6.40 Hz, 3H), 2.53 (dd, $J$ = 12.72, 8.91 Hz, 1H), 2.80 (dd, $J$ = 12.72, 5.08 Hz, 1H), 2.82 (m, 1H), 4.20 (m, 2H), 5.70 (m, 2H), 7.30−7.70 (m, 15H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 19.3, 19.4, 26.9, 32.1, 64.0, 65.9, 123.9, 127.6, 129.2, 129.6, 130.9, 133.9, 135.5, 145.0; MS (EI, *m*/*z*) 405 ($M^+ - C_4H_9$), 229, 199.

**General Procedure for the Preparation of Bromohydrins 5/6.** To a stirred solution of the unsaturated sulfoxide **3**/**4** (0.25 mmol) in toluene (1 mL) at room temperature was added water (8 $\mu$L, 1.7 equiv) followed by NBS (54 mg, 1.2 equiv) in one portion. The solution was stirred until TLC examination showed consumption of the starting material. The reaction mixture was diluted with ether and the organic phase washed with saturated $NaHCO_3$, water, and brine, and dried ($Na_2SO_4$). The solvent was evaporated to afford a residue, which was purified by column chromatography using EtOAc/petroleum ether as the eluent.

**Bromohydrin 5a:** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.06 (s, 9H), 1.55 (d, $J$ = 6.30 Hz, 3H), 2.41 (m, 1H), 2.61 (dd, $J$ = 12.60, 7.04 Hz, 1H), 3.22 (dd, $J$ = 12.60, 4.03 Hz, 1H), 3.57 (d, $J$ = 8.80 Hz, 1H), 3.86−4.12 (m, 3H), 7.40−7.58 (m, 9H), 7.63−7.72 (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 16.6, 19.2, 26.8, 34.7, 57.9, 62.4, 65.6, 73.2, 124.1, 127.9, 129.3, 130.0, 131.0, 133.2, 135.5, 135.6, 144.3; MS (FAB, *m*/*z*) 559, 501.

**Bromohydrin 5b:** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.24 (d, $J$ = 6.36 Hz, 3H), 1.76 (d, $J$ = 6.36 Hz, 3H), 2.44 (m, 1H), 2.59 (dd, $J$ = 12.72, 8.14 Hz, 1H), 3.04 (dd, $J$ = 12.72, 3.82 Hz, 1H), 3.19 (dd, $J$ = 6.11, 3.82 Hz, 1H), 4.26 (m, 1H), 7.50−7.68 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 17.5, 23.4, 34.8, 54.8, 60.8, 77.7, 124.2, 129.3, 131.2, 144.3; MS (EI, *m*/*z*) 304, 286.

**Bromohydrin 5c:** solid; mp 160−162 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.33 (d, $J$ = 6.33 Hz, 3H), 2.61 (dd, $J$ = 13.16, 8.86 Hz, 1H), 2.89 (dd, $J$ = 13.16, 3.80 Hz, 1H), 3.05 (m, 1H), 4.25 (dd, $J$ = 8.86, 2.0 Hz, 1H), 4.80 (d, $J$ = 8.86, 1H), 7.34 (bs, 5H), 7.45−7.58 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.3, 30.0, 65.3, 66.0, 76.0, 124.0, 127.0, 128.4, 128.5, 129.3, 131.1, 141.6, 144.0; MS (FAB, *m*/*z*) 366, 348, 271.

**Bromohydrin 5d and Regioisomer (Inseparable Mixture):** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.05−1.28 (m, 12 H), 2.60−3.0 (m, 3H), 3.80−4.15 (m, 4H), 7.35−7.68 (m, 15H).

**Bromohydrin 6a:** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.02 (d, $J$ = 6.70 Hz, 3H), 1.06 (s, 9H), 2.39 (m, 1H), 2.92 (dd, $J$ = 13.10, 3.81 Hz, 1H), 3.10 (dd, $J$ = 13.10, 3.81 Hz, 1H), 3.66 (d, $J$ = 8.57 Hz, 1H), 3.94−4.15 (m, 3H), 7.33−7.52 (m, 9H), 7.58−7.70 (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 17.3, 19.8, 26.9, 34.7, 57.9, 61.2, 65.5, 72.4, 124.2, 127.9, 129.3, 129.9, 131.1, 133.7, 135.6, 144.0; MS (FAB, *m*/*z*) 559, 501.

**Bromohydrin 6b:** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.03 (d, $J$ = 6.70 Hz, 3H), 1.77 (d, $J$ = 6.70 Hz, 3H), 2.33 (m, 1H), 2.84−3.08 (m, 2H), 3.53 (bs, 1H), 4.26 (m, 1H), 7.46−7.62 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 16.9, 23.1, 34.2, 55.2, 61.7, 78.4, 124.0, 129.3, 131.1, 144.2; MS (EI, *m*/*z*) 304, 286.

**Bromohydrin 6c:** liquid; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.18 (d, $J$ = 6.33 Hz, 3H), 2.77 (dd, $J$ = 10.13, 8.0 Hz, 1H), 2.89−3.07 (m, 2H), 4.72 (d, $J$ = 8.10, 1H), 4. 82 (d, $J$ = 8.10, 1H), 7.31−7.60 (m, 10H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 15.4, 29.7, 64.1, 64.2, 76.0, 123.9, 127.0, 128.5, 128.6, 129.4, 131.1, 141.5, 143.7; MS (FAB, *m*/*z*) 366, 348, 271.

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**Supporting Information Available:** Experimental details for compounds **1**, **2a**−**d**, **7**, and **9** and crystallographic data for **3c** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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