for $C_4H_6BrFO_2$ ($M^+ - CH_2CO$) m/z 183.9536, found 183.9559.

Benzyl 2-bromo-2-fluoro-3-oxobutyrate (8b): colorless oil, in 79% yield; bp 82 °C (5×10^{-3} mmHg); IR (neat) 1760, 1750, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (3 H, d, J = 2.69 Hz, CH_3), 5.31 (2 H, s, CH_2), 7.36 (5 H, s, Ph); ^{19}F NMR ($CDCl_3$) δ −125.68 (br s); mass spectrum (EI mode), m/z 290, 288 (M^+), 209 (M^+ − Br), 91 ($PhCH_2^+$), 43 (CH_3CO^+); HRMS calcd for $C_{11}H_{10}Br^*FO_3$ (M^+) m/z 289.9777, found 289.9710. Calcd for $C_{11}H_{10}BrFO_3$ (M^+) m/z 287.9797, found 287.9695. Anal. Calcd for $C_{11}H_{10}BrFO_3$: C, 45.70; H, 3.49. Found: C, 45.61; H, 3.55.

Ethyl 2-bromo-2-fluoro-3-oxo-3-phenylpropionate (8c): colorless oil, 94% yield; bp 95 °C (1×10^{-2} mmHg); IR (neat) 1770, 1715, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (3 H, t, J = 7.08 Hz, CH_3), 4.37 (2 H, q, J = 7.08 Hz, CH_2), 7.45–8.10 (5 H, m, Ph); ^{19}F NMR ($CDCl_3$) δ −118.86 (br s); mass spectrum (EI mode), m/z 290, 288 (M^+), 245, 243 (M^+ − OEt), 217, 215 (M^+ − COOEt), 209 (M^+ − Br), 105 ($PhCO^+$); HRMS calcd for $C_{11}H_{10}Br^*FO_3$ (M^+) m/z 289.9777, found 289.9693. Calcd for $C_{11}H_{10}BrFO_3$ (M^+) m/z 287.9797, found 287.9736. Anal. Calcd for $C_{11}H_{10}BrFO_3$: C, 45.70; H, 3.49. Found: C, 45.45; H, 3.52.

Ethyl 2-Fluoro-2-nitro-3-oxobutyrate (9a). To an ice-cooled suspension of NaH (60% in mineral oil, 0.096 g, 2.4 mmol) in dry THF (30 mL) was syringed a solution of ethyl 2-nitro-3-oxobutyrate (**5a**) (0.462 g, 2.4 mmol) in dry THF (10 mL), and the resultant suspension was stirred at room temperature for 2 h. The suspension was subjected to fluorination with $FClO_3$ in the usual manner (0 °C, 2 h). Insoluble materials were removed by filtration and the filtrate was concentrated in vacuo to give **9a** in an almost pure state (100%) as a pale yellow oil: IR (neat) 1760, 1710, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (3 H, t, J = 7.08 Hz, CH_2CH_3), 2.45 (3 H, d, J = 2.68 Hz, $COCH_3$), 4.45 (2 H, q, J = 7.08 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.78 (CH_2CH_3), 24.79 ($COCH_3$), 65.55 (CH_2), 109.31 (d, J_{C-F} = 260.7 Hz, CF), 158.56 (d, J_{C-F} = 25.2 Hz, COO), 189.32 (d, J_{C-F} = 26.5 Hz, $COCH_3$); ^{19}F NMR ($CDCl_3$) δ −128.48 (br s); mass spectrum (EI mode), m/z 194 ($M + H^+$), 178 (M^+ − CH_3), 150 (M^+ − $COCH_3$), 73 (COOEt); HRMS calcd for $C_6H_9FNO_5$ ($M + H^+$) m/z 194.0463, found 194.0422.

Ethyl 2-Fluoro-2-(phenylthio)-3-oxobutyrate (11a). Fluorination of ethyl 2-(phenylthio)-3-oxobutyrate (**6a**) with $FClO_3$ in the usual manner (0 °C, 1.5 h) gave **11a** in 76% yield as a colorless oil after purification by silica gel chromatography: bp 106 °C (5×10^{-3} mmHg); IR (neat) 1760, 1740, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (3 H, t, J = 7.08 Hz, CH_2CH_3), 2.21 (3 H, d, J = 3.42 Hz, $COCH_3$), 4.20 (2 H, q, J = 7.08 Hz, CH_2), 7.33–7.59 (5 H, m, Ph); ^{19}F NMR ($CDCl_3$) δ −135.30 (q, J = 3.76 Hz); mass spectrum (EI mode), m/z 257 ($M + H^+$), 256 (M^+), 214 (M^+ − CH_2CO), 109 (SPh); HRMS calcd for $C_{12}H_{13}FO_3S$ (M^+) m/z 256.0568, found 256.0533. Anal. Calcd for $C_{12}H_{13}FSO_3$: C, 56.24; H, 5.11. Found: C, 56.28; H, 5.24.

Benzyl 2-Fluoro-2-(phenylthio)-3-oxobutyrate (11b). Fluorination of benzyl 2-(phenylthio)-3-oxobutyrate (**6b**) with $FClO_3$ in the usual manner (0 °C, 1.5 h) gave **11b** in 88% yield as a colorless oil after purification by silica gel chromatography: bp 148 °C (5×10^{-3} mmHg); IR (neat) 1760, 1740, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (3 H, d, J = 12.2 Hz, CH_3), 5.14 (2 H, AB q, J = 12.2 Hz, $\Delta\delta$ = 7.45 Hz, CH_2), 7.21–7.59 (10 H, m, Ph × 2); ^{19}F NMR ($CDCl_3$) δ −135.43 (br s); mass spectrum (EI mode), m/z 319 ($M + H^+$), 318 (M^+), 276 (M^+ − CH_2CO), 91 ($PhCH_2^+$); HRMS calcd for $C_{17}H_{15}FO_3S$ (M^+) m/z 318.0724, found 318.0694, calcd for $C_{15}H_{13}FO_2S$ (M^+ − CH_2CO) m/z 276.0619, found 276.0618. Anal. Calcd for $C_{17}H_{15}FO_3S$: C, 64.14; H, 4.75. Found: C, 64.42; H, 4.78.

General Procedure for Preparation of α-Fluoro-α-(benzenesulfonyl)-β-keto Esters (12a,c). To a stirred suspension of NaH (60% dispersion in mineral oil, 0.04 g, 1 mmol) in dry THF (15 mL) was syringed a solution of α-fluoro-β-keto esters (**3a,c**) (1 mmol) in THF (5 mL) under an argon atmosphere with stirring at room temperature for 0.5 h. To the mixture was added dropwise $PhSO_2Cl$ (0.177 g, 1 mmol) over 10 min, and the resultant mixture was stirred at room temperature for 2 h. The solvent was evaporated, Et_2O (5 mL) and water (10 mL) were added to the residue, and the organic layer was separated. The aqueous layer was extracted with Et_2O (5 mL × 3), and the combined ethereal layer was dried on $MgSO_4$. Evaporation of the solvent gave a pale yellow oil which was purified by preparative TLC to produce **12a,c**.

Ethyl 2-(benzenesulfonyl)-2-fluoro-3-oxobutyrate (12a): colorless oil, 53% yield: bp 100–102 °C (0.5 mmHg); IR (neat) 1760, 1735, 1385, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3 H, t, J = 7.08 Hz, CH_2CH_3), 2.44 (3 H, d, J = 4.64 Hz, $COCH_3$), 4.24 (2 H, q, J = 7.08 Hz, CH_2), 7.55–7.80 (5 H, m, Ph); ^{19}F NMR ($CDCl_3$) δ −132.86 (q, J = 4.64 Hz); mass spectrum (EI mode), m/z 284 ($M + H^+$), 244 ($M + H^+$ − OEt), 216 ($M^+ + 1$ − COOEt), 141 ($PhSO_2$), 77 (Ph); HRMS calcd for $C_9H_9FO_3S$ ($M + H^+$ − COOEt) m/z 216.0256, found 216.0226. Anal. Calcd for $C_{11}H_{13}FO_5S$: C, 50.00; H, 4.54. Found: C, 49.92; H, 4.52.

Ethyl 2-(benzenesulfonyl)-2-fluoro-3-oxo-3-phenylpropionate (12c): colorless needles (Et_2O/hexane), 64% yield: mp 97.0–97.5 °C; IR (KBr) 1731, 1381, 1073 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3 H, t, J = 7.08 Hz, CH_3), 4.39 (2 H, q, J = 7.08 Hz, CH_2), 7.1–7.70 (10 H, m, Ph × 2); ^{19}F NMR ($CDCl_3$) δ −140.94 (s); mass spectrum (EI mode), m/z 350 (M^+), 305 (M^+ − OEt), 141 ($PhSO_2$), 77 (Ph); HRMS calcd for $C_{17}H_{15}FO_5S$ (M^+) m/z 350.0623, found 350.0596. Anal. Calcd for $C_{17}H_{15}FO_5S$: C, 58.28; H, 4.32. Found: C, 58.23; H, 4.47.

1-(Benzenesulfonyl)-1-fluoropropan-2-one (17). Fluorination of 1-(benzenesulfonyl)propan-**2-one (16)** as a usual manner gave **17** in 59% yield as a colorless oil after purification by preparative TLC: bp 98 °C (5×10^{-3} mmHg); IR (neat) 1743, 1580, 1340, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (3 H, d, J = 3.91 Hz, CH_3), 5.47 (1 H, J = 49.07 Hz, CH), 7.61–7.98 (5 H, m, Ph); ^{19}F NMR ($CDCl_3$) δ −180.21 (dq, J = 49.64, 3.68 Hz); mass spectrum (EI mode), m/z 217 ($M + H^+$), 216 (M^+), 141 ($PhSO_2^+$), 77 (Ph^+); HRMS calcd for $C_9H_9FO_3S$ (M^+) m/z 216.0255, found 216.0240. Anal. Calcd for $C_9H_9FO_3S$: C, 49.99; H, 4.20. Found: C, 49.92; H, 4.21.

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Registry No. **3a**, 1522-41-4; **3b**, 139101-19-2; **3c**, 1479-22-7; **4a**, 141-97-9; **4b**, 5396-89-4; **4c**, 94-02-0; **5a**, 51026-98-3; **6a**, 27872-73-7; **6b**, 139101-20-5; **7a**, 100118-47-6; **8a**, 139101-21-6; **8b**, 139101-22-7; **8c**, 139101-23-8; **9a**, 139101-24-9; **11a**, 139101-25-0; **11b**, 139101-26-1; **12a**, 139101-27-2; **12c**, 139101-28-3; **16**, 5000-44-2; **17**, 139101-29-4; **18**, 139101-30-7.

On the Search for Diastereoselective Bisepoxidation of Template-Bound 1,5-Dienes

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We report here our efforts toward a novel template-based approach to the stereoselective bisepoxidation of 1,5-unsaturated hydrocarbon chains. This system attempts to exploit the conformational biases imposed on a hydrocarbon chain bearing distal sp^2 (alkene) centers by a large, rigid organic molecule. In broad terms, the strategy consists of coupling of template diol with a bisunsaturated diacid to provide a sterically biased macrocyclic bislactone.[1] Face-selective functionalization of the unsaturated moieties in the chain may then be possible as an external reagent should add from the less hindered peripheral face of the olefins. To the extent that the template imposes conformational restrictions on the attached diene-containing chain, high levels of remote relative asymmetric induction may be observed for the diacid substrate. Stereochemical control in bisepoxidations forms the basis for several

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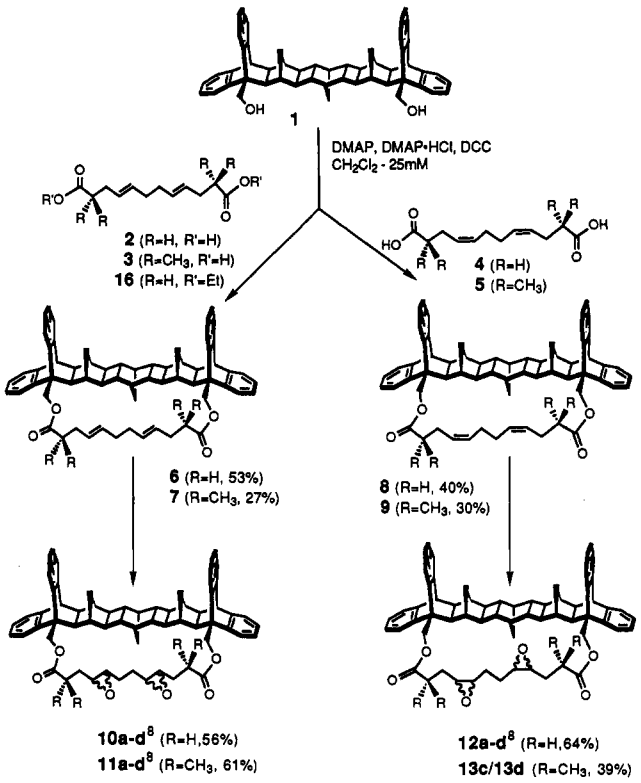
0022-3263/92/1957-2199$03.00/0

Scheme I



strategies directed toward the synthesis of polytetrahydrofuran-containing natural products, as reported by many authors.[2]

As a demonstration of this methodology, we have examined the bisepoxidation of template-bound dienes **6–9**. Coupling of the template **1** to the unsaturated diacids **2–5**[1] followed by epoxidation of bislactones **6–9** with mCPBA (CH_2Cl_2, 0 °C) was achieved in satisfactory yields (Scheme I). In each case, a bisepoxide product corresponding to a single TLC spot was isolated by flash column chromatography.[3]

For both the *E,E* and *Z,Z* unsubstituted cases **6** and **8**, respectively, and the *E,E* tetramethyl-substituted case **7**, the ^{13}C NMR spectra of the bisepoxide compounds **10–12** showed six epoxide carbon and three carbonyl carbon signals, indicating a mixture of stereoisomers. Separation of the stereoisomers of the bisepoxides formed from compounds **6** and **8**, i.e. **10a–d** and **12a–d**, respectively, was accomplished through HPLC and in each case led to isolation of two compounds in a nearly 1:1 ratio. For the diastereomeric mixture **10**, the first eluting stereoisomer

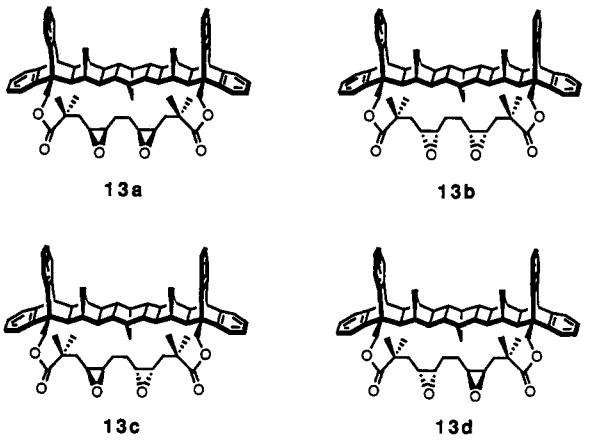


Figure 1. Isomers of bisepoxide **13**.

displays two epoxide carbon signals and one carbonyl carbon signal, while the remaining stereoisomer has four epoxide carbon and two carbonyl carbon signals. Analysis of the ^1H NMR spectra of the pure diastereomers of mixture **12** reveals that the first-eluting diastereomer has two doublets for the methylene protons adjacent to the template while the other stereoisomer displays three doublets. In both series **10** and **12**, the symmetry properties of the diastereomeric bisepoxides allow assignment of relative configuration. Thus, in each case, the first-eluting compound is one of the two possible meso diastereomers and the second-eluting compound is the enantiomeric pair. While the stereoisomeric bisepoxides formed from **7** were not individually characterized, examination of the crude ^{13}C NMR clearly indicates that bisepoxidation affords a 1:1 mixture of the meso and *d,l* diastereoisomers.

A more successful demonstration of remote relative asymmetric induction in this system was observed in the case of the *Z,Z* tetramethyl-substituted diene chain of substrate **9**. Structures **13a–d** (Figure 1) represent the four possible bisepoxides which can result from epoxidation of the *Z,Z* template-bound diene **9**. The ^{13}C NMR spectrum of bisepoxide **13**, isolated as a single compound following chromatography, shows just four epoxide carbon and two carbonyl carbon signals.[4] Thus, on the basis of the symmetry properties of the isomers **13a–d**, it is clear that only one diastereomer, the enantiomeric pair **13c/13d**, is formed.

The tetramethyl series **7** and **9** were chosen in the hope, apparently realized with **9** (vide infra), that methyl substitution would facilitate gauche turns at carbons a and a′ (cf. **14**) and hence furnish a maximally sterically biased parallel arrangement between the plane of the alkenes and the plane of the template. Molecular mechanics calculations[5] on diene **9** bear on this supposition—while 74 conformations within 2 kcal/mol of the "global" energy minimum **14** (Figure 2) were located, only nine of these conformers could reasonably be expected to afford bisepoxide products with a stereochemical outcome different than that reported for **13**. The remaining conformers all exposed the same relative faces of the two alkenes to peripheral attack.

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(4) As the yield of this particular bisepoxidation product (**13**) is diminished relative to the earlier cases, it is conceivable that stereoselectivity was an artifact of isolation. That this possibility was not the case can be ascertained by inspection of the ^1H and ^{13}C NMR spectra of the crude reaction product, which indicate that only the bisepoxide **13c/13d** was present.

(5) The Monte Carlo directed search subprogram of the Macromodel 3.1X was used. Rotations about all unconstrained bonds were allowed, and one thousand steps (starting geometries) were explored. Chang, G.; Guida, W. C.; Still, W. C.; *J. Am. Chem. Soc.* **1989**, *111*, 4379.

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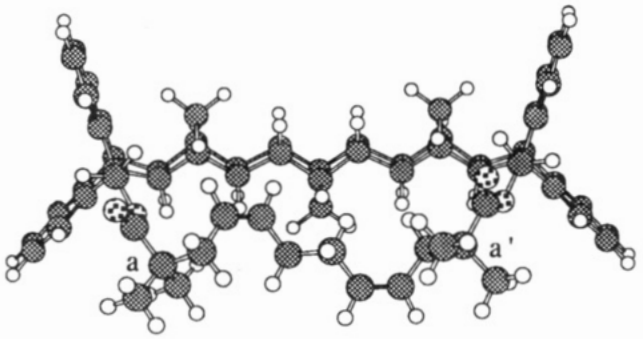

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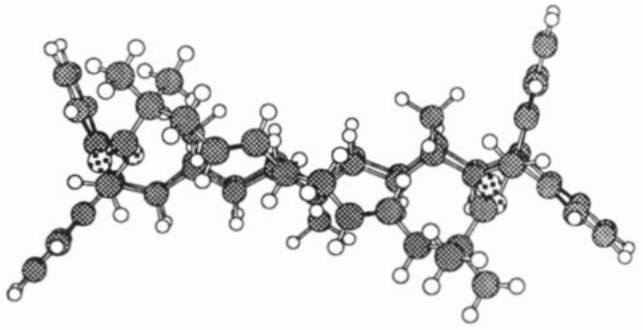

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Figure 2. "Global" minimum energy conformations.

A Boltzmann distribution of the energies associated with these 74 conformations revealed that the nine "rogue" conformers account for only 16% of the total population (298 K). In comparison to the *Z,Z* diene **9**, similar energy minimization calculations on the *E,E* diene **7** revealed a distinct difference in the conformer distribution. Inspection of the 64 conformations within 2 kcal/mol of the "global" energy minimum **15** (Figure 2) showed that 55% of the total population had the alkenes aligned for peripheral attack resulting in the formation of the *d,l* pair of **11** (similar to **13c/13d**) while 4% of the population would yield the meso diastereomer (similar to **13a/13b**). Strikingly different however, is the fact that 41% of the conformer population had the plane of one alkene aligned orthogonal to the plane of the template—a geometrical arrangement which makes prediction of epoxide stereochemistry problematical. Thus, this latter calculation shows that upon epoxidation of *E,E* diene **7**, a mixture of *d,l* and meso bisepoxide diastereomers is not unexpected. Of course, issues related to (1) differential conformer reactivity and (2) the conformational preferences of the intermediate monoepoxide/monoalkene complicate analysis of these "ground-state" calculations and provide a caveat about overinterpretation of these computational results. It should be noted that in a control experiment, epoxidation of an appropriate model system (diethyl ester **16**) resulted in a 1:1 mixture of two bisepoxides, indicating that these species have no inherent bias towards diastereoselection.

The production of a single diastereomeric bisepoxide from diene **9** represents a successful demonstration of this template-based methodology. Further efforts designed to expand on these observations are underway and may eventually provide a foundation for explorations in the area of stereocontrolled polytetrahydrofuran synthesis.

Experimental Section

All reagents were obtained from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise stated. PhH, Et_2O, and THF were purified by distillation from sodium/benzophenone ketyl under nitrogen. CH_2Cl_2 was distilled from CaH_2 under N_2. Solvents for flash chromatography[3] (Et_2O and hexane) were distilled from CaH_2 prior to use. Moisture- and oxygen-sensitive reactions were carried out in predried glassware under Ar.

Analytical TLC was performed using precoated silica gel (60 F_{254}) plates (E. Merck). HPLC was performed on a Waters 6000A semipreparative instrument equipped with an R-400 refractometer and 440 UV detector, using a ZORBAX-SIL silica gel column (25 cm × 20 mm, DuPont). The purity of all title compounds was judged to be ≥90% by ^1H and ^{13}C NMR determinations (see the supplementary material).

(*E,E*)-Diethyl 4,5:8,9-Diepoxydodecane-1,12-dioate. mCPBA (73 mg, 0.42 mmol) was added to a solution of (*E,E*)-diethyl dodeca-4,8-diene-1,12-dioate (**16**) (52 mg, 0.18 mmol) in 0.35 mL of dry CH_2Cl_2 at 0 °C. Additional mCPBA (31 mg, 0.18 mmol) and CH_2Cl_2 (0.35 mL) were added after 1.5 h. After an additional 30 min, the solution was poured into ice-cold 10% NaOH solution and extracted with ether. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by flash column chromatography using 25% hexane in ether as the eluent yielded 43 mg (76%) of (*E,E*)-diethyl 4,5:8,9-diepoxydodecane-1,12-dioate as a white solid: IR (neat) 1792, 1750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.14 (q, J = 7.15 Hz, 4 H), 2.80–2.75 (m, 4 H), 2.44 (t, J = 7.3 Hz, 4 H), 1.98–1.64 (m, 8 H), 1.26 (t, J = 7.15 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 60.5, 58.3, 58.0, 57.5, 57.46, 30.4, 28.7, 28.2, 27.1, 14.1 [the 4 epoxide peaks (2 from each diastereomer: 58.3, 58.0, 57.5, 57.46) were in approximately equal ratios]; MS-EI m/z (relative intensity) 269 (M^+ – OEt, 9), 224 (M^+ – 2OEt, 2); MS-CI m/z (relative intensity) 315 (MH^+, 10), 269 (M^+ – OEt, 22); HRMS calcd for $C_{14}H_{25}O_5$ 269.1389, found 269.1385.

C_s Template (*E,E*)-4,5:8,9-Diepoxydodecane-1,12-dioate (10). mCPBA (25 mg, 0.143 mmol) was added to a solution of C_s template-bound diene **6**[1] (50 mg, 0.057 mmol) in 0.1 mL of CH_2Cl_2 at 0 °C. The reaction stirred at 0 °C for 13 h, when additional mCPBA (25 mg, 0.143 mmol) in 0.1 mL of CH_2Cl_2 was added. The reaction mixture was stirred at 0 °C for an additional 3 h and then was warmed to rt and stirred for 7 h. The solution was washed with 10% NaOH, diluted with ether, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by flash column chromatography using 3% Et_2O in CH_2Cl_2 yielded 29 mg (56%) of **10** as a white solid. HPLC separation of the diastereomers was accomplished by eluting with 4% Et_2O in CH_2Cl_2. Spectral data for isomer **10a/10b**:[8] IR ($CDCl_3$) 1745 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.26–7.05 (m, 16 H), 5.31 (d, J = 11.4 Hz, 2 H), 5.10 (d, J = 11.4 Hz, 2 H), 4.17 (s, 2 H), 2.74–2.54 (m, 4 H), 2.05–0.86 (m, 34 H), –0.37 (d, J = 10.9 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.8, 145.3, 143.8, 142.8, 141.3, 126.1, 126.0, 125.6, 125.4, 124.4, 123.2, 121.3, 121.1, 63.2, 58.3, 57.5, 48.6, 48.3, 47.5, 47.3, 47.2, 42.8, 42.2, 42.1, 41.7, 41.5, 39.5, 31.3, 29.0, 28.9, 28.3, 28.1; MS (+FAB) m/z (relative intensity) 915.5 (M^+ + 1, 100); mp 192 °C dec. Spectral data for isomer **10c/10d**:[8] IR ($CHCl_3$) 1740 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.18–6.97 (m, 16 H), 5.38 (d, J = 11.4 Hz, 1 H), 5.24 (d, J = 11.4 Hz, 1 H), 5.04 (d, J = 11.4 Hz, 1 H), 4.95 (d, J = 11.3 Hz, 1 H), 4.10 (s, 1 H), 4.09 (s, 1 H), 2.64–2.41 (m, 4 H), 2.07–1.01 (m, 34 H), –0.45 (t, J = 10.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 172.8, 145.3, 143.8, 143.75, 142.8, 142.7, 141.3, 141.29, 126.1, 125.9, 125.6, 125.3, 124.3, 123.2, 121.5, 121.3, 121.2, 121.0, 63.3, 63.1, 58.1, 57.9, 57.4, 57.3, 48.5, 48.2, 48.1, 47.4, 47.3, 47.2, 47.1, 42.8, 42.7, 42.1, 42.07, 41.5, 41.4, 39.5, 31.2, 29.7, 28.9, 28.2, 28.1, 27.9; MS (+FAB) m/z (relative intensity) 915.5 (M^+ + 1, 100).

C_s Template (*Z,Z*)-4,5:8,9-Diepoxydodecane-1,12-dioate (12). By use of the procedure described above for bisepoxide **10**, C_s template-bound diene **8**[1] (36 mg, 0.039 mmol) was epoxidized with mCPBA (17 mg, 0.098 mmol) to afford 23 mg (64%) of **12** as a white solid, following flash chromatography on silica with 5% Et_2O in CH_2Cl_2 as eluent. HPLC separation of the diaste-

(8) **10a/10b–12a/12b** denote the meso diastereomers; **10c/10d–12c/12d** represent the *d,l* diastereomers.

reomers was accomplished by eluting with 4% Et_2O in CH_2Cl_2 and then 10% Et_2O in CH_2Cl_2. Spectral data for isomers **12a/12b**:[8] IR ($CHCl_3$) 1745 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24–7.06 (m, 16 H), 5.48 (d, J = 11.5 Hz, 2 H), 5.03 (d, J = 11.3 Hz, 2 H), 4.17 (s, 2 H), 2.95–2.60 (m, 4 H), 1.78–0.86 (m, 34 H), –0.33 (d, J = 14.2 Hz, 2 H); MS (+FAB) m/z (relative intensity) 915.0 (M^+ + 1, 100). Spectral data for isomers **12c/12d**:[8] IR ($CHCl_3$) 1745 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.23–7.02 (m, 16 H), 5.53 (d, J = 11.3 Hz, 1 H), 5.50 (d, J = 11.3 Hz, 1 H), 5.01 (d, J = 11.4 Hz, 2 H), 4.16 (s, 2 H), 3.05–2.60 (m, 4 H), 2.09–0.85 (m, 34 H), –0.39 (d, J = 11.3 Hz, 2 H); MS (+FAB) m/z (relative intensity) 915.3 (M^+ + 1, 100); ^{13}C NMR of mixture (75 MHz, $CDCl_3$) δ 172.8, 172.7, 172.6, 145.33, 145.29, 143.8, 143.7, 143.6, 143.55, 142.7, 141.2, 126.1, 125.9, 125.6, 125.3, 124.4, 123.1, 121.5, 121.46, 121.0, 62.8, 62.7, 62.6, 56.6, 56.2, 56.16, 56.14, 56.0, 55.9, 55.8, 48.5, 48.4, 47.74, 47.7, 47.6, 47.4, 47.3, 47.25, 47.0, 46.9, 42.6, 41.9, 41.7, 41.5, 39.3, 32.1, 31.9, 31.7, 28.7, 28.3, 25.2, 25.15, 25.0, 24.5, 24.3, 24.2.

(*E*,*E*)-2,2,11,11-Tetramethyldodeca-4,8-diene-1,12-dioic Acid (3). Isobutyryl chloride (1.62 mL, 15.4 mmol) and pyridine (1.25 mL, 15.4 mmol) were added sequentially to a solution of 1,7-octadiene-3,6-diol[6] (1.0 g, 7.01 mmol) in 23 mL of CH_2Cl_2 and stirred for 18 h at rt with formation of a white precipitate. The solution was concentrated, diluted with Et_2O, washed with 1 M H_3PO_4, dried (Na_2SO_4), concentrated in vacuo, and purified by flash column chromatography using 10% Et_2O in hexane as eluent to yield 1.31 g (66%) of 3,6-diisobutyroxy-1,7-octadiene as a colorless oil: IR (neat) 1745 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.71 (ddd, J = 17.4, 10.5, 6.0 Hz, 2 H), 5.23–5.08 (m, 6 H), 2.51 (heptet, J = 7.0 Hz, 2 H), 1.61 (t, J = 3.0 Hz, 4 H), 1.124 (d, J = 7.0 Hz, 6 H), 1.120 (d, J = 7.0 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 136.0, 116.3, 73.3, 33.8, 29.3, 18.7; MS m/z (relative intensity) 281 (M^+ – 1, 1.5), 124 (M^+ – $(CH_3)_2CHC(=O)CH(CH_3)CH{=}CH_2$, 14), 71 ($(CH_3)_2CHC(=O)^+$, 100); HRMS calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1852. Diisopropylamine (0.320 mL, 2.32 mmol) and *n*-BuLi (1.6 M in hexanes) (1.39 mL, 2.23 mmol) were added sequentially to 10 mL of THF at 0 °C. This mixture was cooled to –78 °C, a solution of 3,6-diisobutyroxy-1,7-octadiene (251 mg, 0.891 mmol) in 2 mL of THF was added, and the solution was stirred for 5 min as a yellow color appeared. A solution of *t*-BuMe$_2$SiCl (322 mg, 2.14 mmol) in 0.75 mL of hexane was added, and after 5 min, the reaction was warmed to rt and stirred for 24 h. The solution was diluted with Et_2O, washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. The crude reaction mixture was stirred with 1.5 mL of 5% aqueous HCl and 7.5 mL of THF at rt for 3 h, diluted with Et_2O, washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by flash column chromatography using 25% Et_2O in hexane as eluent afforded 158 mg (63%) of dicarboxylic acid **3** as a white solid: IR (CCl_4) 3600–3300, 1720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.46–5.30 (m, 4 H), 2.18 (d, J = 6.7 Hz, 4 H), 2.14 (t, J = 2.7 Hz, 4 H), 1.20 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 133.7, 125.6, 43.9, 42.8, 32.2, 24.5; MS m/z (relative intensity) 282 (M^+, 1.7), 236 (M^+ – HCO_2H, 23), 141 ($^1/_2M^+$, 85); HRMS calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1835.

C_s Template (*E*,*E*)-2,2,11,11-Tetramethyldodeca-4,8-diene-1,12-dioate (7). Oxalyl chloride (0.155 mL, 1.77 mmol) and DMF (1 drop) were added to a solution of diacid **3** (200 mg, 0.709 mmol) in 10 mL of dry CH_2Cl_2 and stirred at rt for 19 h. The reaction solution was concentrated in vacuo to afford 224 mg (99%) of (*E*,*E*)-2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioyl chloride as a brown oil: IR (CCl_4) 1810 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.45–5.40 (m, 4 H), 2.17 (d, J = 5.8 Hz, 4 H), 2.10 (m, 4 H), 1.18 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 133.6, 125.5, 43.7, 42.6, 32.3, 24.4. *n*-BuLi (1.6 M in hexanes) (0.250 mL, 0.400 mmol) was added to a solution of template C_s diol **1** (100 mg, 0.145 mmol) and triphenylmethane (2 mg) in 1.5 mL of THF at rt until a red color persisted. The above 1,12-dioyl chloride (51 mg, 0.160 mmol) was added dropwise, and the reaction mixture was stirred at rt for 48 h and then at reflux for an additional 4 h. The solution was diluted with THF, washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by flash column chromatography using 20% hexane in CH_2Cl_2 as eluent yielded 37 mg (27%) of dicarboxylate **7** as a white solid: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24–7.04 (m, 16 H), 5.38–5.27 (m, 4 H), 5.17 (d, J = 11.6 Hz, 2 H), 5.06 (d, J = 11.6 Hz, 2 H), 4.19 (d, J = 2.4 Hz, 2 H), 2.29–1.02 (m, 42 H), –0.34 (d, J = 11.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 145.1, 144.0, 142.5, 141.4, 133.2, 126.0, 125.9, 125.8, 125.4, 125.3, 124.3, 123.2, 121.2, 121.0, 63.5, 48.4, 48.1, 47.6, 47.2, 46.1, 44.9, 44.1, 42.6, 42.1, 41.9, 41.5, 41.3, 39.5, 32.8, 31.0, 28.9, 28.2, 25.7, 24.9, 24.0; MS (+FAB) m/z (relative intensity) 938.5 (M^+, 20); mp 240 °C dec.

C_s Template (*E*,*E*)-2,2,11,11-Tetramethyl-4,5:8,9-diepoxydodecane-1,12-dioate (11). By use of the procedure described above for bisepoxide **10**, C_s template-bound diene **7** (37 mg, 0.039 mmol) was epoxidized with mCPBA (54 mg, 0.316 mmol) to afford 23 mg (61%) of **11** as a white solid, following flash chromatography on silica with 3% Et_2O in CH_2Cl_2 as eluent (data provided for mixture of diastereomers): IR (CCl_4) 1740 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.24–7.05 (m, 16 H), 5.30–5.06 (m, 4 H), 4.19 (s, 2 H), 2.72–2.56 (m, 4 H), 2.04–0.87 (m, 4 H), 2.72–0.87 (m, 42 H), –0.34 (q, J = 11.6 Hz, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 177.4, 145.2, 144.0, 143.8, 142.7, 141.3, 126.1, 125.9, 125.5, 125.3, 124.3, 123.2, 121.3, 121.2, 120.9, 63.6, 57.4, 56.8, 56.7, 56.3, 55.9, 55.7, 48.4, 48.0, 47.7, 47.2, 47.1, 47.0, 46.9, 43.2, 42.7, 42.6, 42.3, 42.2, 41.8, 41.5, 41.3, 39.5, 29.4, 29.2, 28.7, 28.2, 26.5, 25.9, 25.2, 25.1, 24.7, 24.1; MS (+FAB) m/z (relative intensity) 971 (M^+, 10).

(*Z*,*Z*)-2,2,11,11-Tetramethyldodeca-4,8-diene-1,12-dioic Acid (5). A solution of anhydrous LiCl (110 mg, 2.58 mmol) and 2,4,6-collidine (0.358 mL, 2.71 mmol) in 2 mL of THF was added to a flask containing (*Z*,*Z*)-2,6-octadiene-1,8-diol[7] (175 mg, 1.23 mmol). The solution was cooled to 0 °C, treated with methanesulfonyl chloride (0.210 mL, 2.71 mmol), and warmed to rt. After stirring for 8 h, the heterogeneous yellow reaction mixture was poured into water, extracted with 1:1 ether/hexane, washed with saturated aqueous $CuSO_4$, dried (Na_2SO_4), and concentrated to furnish 194 mg (89%) of (*Z*,*Z*)-1,8-dichloro-2,6-octadiene as a yellow oil: IR (CCl_4) 2835, 1750, 1350 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.80–5.64 (m, 4 H), 4.09 (d, J = 7.3 Hz, 4 H), 2.24 (t, J = 3.2 Hz, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.7, 126.1, 39.2, 26.6; MS m/z (relative intensity) 179 (M^+, 2), 108 (M^+ – 2Cl, 39), 80 (M^+ – $2CH_2Cl$, 49); HRMS calcd for C_8H_{12} (M^+ – 2Cl) 108.0939, found 108.0950. Diisopropylamine (0.303 mL, 2.83 mmol) and *n*-BuLi (1.6 M in hexanes) (1.30 mL, 2.73 mmol) were added sequentially to 4 mL of THF at 0 °C. The solution was cooled to –78 °C when methyl isobutyrate (0.333 mL, 2.91 mmol) was added, and the mixture was stirred for 45 min. A solution of (*Z*,*Z*)-1,8-dichloro-2,6-octadiene in 2 mL of THF was added, and the reaction mixture was stirred at –78 °C for 3.5 h, warmed to 0 °C, and stirred for an additional 2 h. The solution was washed with brine, dried (Na_2SO_4), concentrated in vacuo, and purified by flash column chromatography, eluting with 5% Et_2O in hexane to afford 127 mg (49%) of (*Z*,*Z*)-dimethyl 2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioate as a colorless oil, as well as 36 mg of the monoester: IR (neat) 1735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.49–5.27 (m, 4 H), 3.66 (s, 6 H), 2.28 (dd, J = 7.4, 0.8 Hz, 2 H), 2.08 (t, J = 3.5 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.1, 131.8, 125.2, 51.7, 42.5, 37.8, 27.3, 24.8; MS m/z (relative intensity) 310 (M^+, 4), 279 (M^+ – OMe, 8), 250 (M^+ – HCO_2Me, 7), 209 (M^+ – $MeOC(O)C(CH_3)_2$, 17), 155 ($^1/_2M^+$, 57); HRMS calcd for $C_{18}H_{30}O_4$ 310.2144, found 310.2141. A solution of LiOH·H_2O (202 mg, 4.81 mmol) in 1 mL of H_2O was added to a solution of (*Z*,*Z*)-dimethyl 2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioate in 3 mL of DME and refluxed for 18 h. After cooling to rt, 1 M H_3PO_4 was added (creating a precipitate which dissolved upon further addition of H_3PO_4) and the product was extracted with ethyl acetate, washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo to afford 125 mg (99%) of diacid **5** as a colorless oil: IR (CCl_4) 1720 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.51–5.31 (m, 4 H), 2.28 (d, J = 6.9 Hz, 4 H), 2.05 (t, J = 2.8 Hz, 4 H), 1.18 (s, 12 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 184.4, 132.2, 124.7, 42.6, 38.0, 32.5, 27.3, 24.5; MS m/z (relative intensity) 282 (M^+, 16), 236 (M^+ – HCO_2H, 39), 141 ($^1/_2M^+$, 79); HRMS calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1843.

C_s Template (*Z*,*Z*)-2,2,11,11-Tetramethyldodeca-4,8-diene-1,12-dioate (9). Oxalyl chloride (0.086 mL, 0.980 mmol) and DMF (1 drop) were added to a solution of diacid **5** (125 mg, 0.443 mmol) in 6 mL of dry CH_2Cl_2 and stirred at rt for 19 h. The reaction solution was concentrated in vacuo to afford 138 mg (98%) of (*Z*,*Z*)-2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioyl chloride as a brown oil: IR (neat) 1820 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$) δ 5.48–5.38 (m, 4 H), 2.30 (d, J = 7.3 Hz, 4 H), 2.07 (t, J = 2.9 Hz, 4 H), 1.21 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 132.3, 124.6, 42.8, 38.3, 27.4, 24.4. *n*-BuLi (1.6 M in hexanes) (0.520 mL, 0.832 mmol) was added to a solution of template C_s diol **1** (200 mg, 0.289 mmol) and triphenylmethane (2 mg) in 3 mL of THF at rt until a red color persisted. The above 1,12-dioyl chloride (101 mg, 0.318 mmol) was added dropwise, and the solution was stirred at rt for 20 h and then at reflux for 25 h. The solution was diluted with THF, washed with brine, dried (Na_2SO_4), and concentrated. Purification of the residue by flash column chromatography using 20% hexane in CH_2Cl_2 as eluent yielded 82 mg (30%) of dicarboxylate **9** as a white solid: IR (CCl_4) 1745 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.21–7.01 (m, 16 H), 5.44 (m, 2 H), 5.20 (d, J = 11.5 Hz, 2 H), 5.10 (m, 2 H), 5.01 (d, J = 11.5 Hz, 2 H), 4.14 (d, J = 5.9 Hz, 2 H), 2.22 (d, J = 7.2 Hz, 4 H), 2.00 (s, 4 H), 1.80–0.82 (m, 34 H), –0.46 (d, J = 11.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 145.2, 143.9, 142.6, 141.3, 131.7, 126.1, 125.9, 125.4, 125.3, 124.9, 124.3, 123.2, 121.3, 121.0, 63.0, 48.4, 48.3, 47.5, 47.4, 47.1, 47.0, 42.7, 41.8, 41.6, 41.3, 39.2, 38.1, 29.7, 28.3, 27.3, 24.9, 23.9; MS (+FAB) *m/z* (relative intensity) 939 (M^+ + 1, 65), 940 (M^+ + 2, 100).

C_S Template (*Z,Z*)-2,2,11,11-Tetramethyl-4,5:8,9-diepoxydodecane-1,12-dioate (13). By use of the procedure described above for bisepoxide **10**, C_s template-bound diene **9** (30 mg, 0.039 mmol) was epoxidized with mCPBA (24 mg, 0.141 mmol) to afford 12 mg (39%) of **13** as a white solid, following flash chromatography on silica with 3% Et_2O in CH_2Cl_2 as eluent: IR (CCl_4) 1735 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.23–7.06 (m, 16 H), 5.29 (d, J = 8.6 Hz, 1 H), 5.23 (d, J = 11.3 Hz, 1 H), 5.17 (d, J = 9.8 Hz, 1 H), 5.12 (d, J = 11.4 Hz, 1 H), 4.19 (s, 2 H), 2.92–2.79 (m, 4 H), 2.03–0.73 (m, 42 H), –0.38 (t, J = 8.6 Hz, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 177.7, 177.3, 145.2, 143.9, 143.8, 142.7, 142.6, 141.3, 141.2, 126.1, 126.0, 125.9, 125.5, 125.4, 125.3, 124.4, 123.2, 121.2, 120.9, 63.4, 63.2, 55.9, 55.4, 54.0, 53.9, 48.4, 48.2, 47.3, 47.2, 47.0, 42.7, 42.4, 42.1, 41.9, 41.7, 41.5, 41.3, 41.1, 39.4, 39.2, 38.7, 38.4, 31.9, 29.7, 29.3, 29.0, 28.8, 28.3, 26.1, 25.9, 25.6, 25.3, 24.4, 23.9, 22.7, 14.1; MS (+FAB) *m/z* (relative intensity) 971.8 (M^+ + 1, 100); mp 160 °C dec.

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Registry No. **1**, 110224-49-2; **3**, 139200-08-1; **5**, 139200-09-2; **6**, 124461-66-1; **7**, 139344-58-4; **8**, 124578-44-5; **9**, 139200-10-5; **10a**, 139200-11-6; **10b**, 139342-21-5; **10c/d**, 139342-22-6; **11a**, 139200-12-7; **11b**, 139342-23-7; **11c/d**, 139342-24-8; **12a**, 139342-25-9; **12b**, 139342-26-0; **12c/d**, 139342-27-1; **13c/d**, 139342-28-2; **16**, 124461-71-8; **16** diepoxy (isomer 1), 139200-13-8; **16** diepoxy (isomer 2), 139342-29-3; isobutyryl chloride, 79-30-1; 1,7-octadiene-3,6-diol, 70475-66-0; 3,6-diisobutyroxy-1,7-octadiene, 139200-14-9; (*E,E*)-2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioyl chloride, 139200-15-0; (*Z,Z*)-2,6-octadiene-1,8-diol, 84117-75-9; (*Z,Z*)-1,8-dichloro-2,6-octadiene, 84117-76-0; methyl isobutyrate, 547-63-7; (*Z,Z*)-dimethyl 2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioate, 139200-16-1; (*Z,Z*)-2,2,11,11-tetramethyldodeca-4,8-diene-1,12-dioyl chloride, 139200-17-2.

Supplementary Material Available: ^1H and ^{13}C spectra for all compounds described in the Experimental Section (31 pages). Ordering information is given on any current masthead page.

Recent Reviews. 25

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Major English-language sources of critical reviews are covered. Encyclopedic treatises, annual surveys such as *Specialist Periodical Reports*, and compilations of symposia proceedings are omitted.

This installment of Recent Reviews covers principally the latter part of the 1991 literature. Previous installment: *J. Org. Chem.* **1992**, *57*(1), 412–416. For regularly issued journals and series volumes, the coverage in this installment continues from the last item included in Recent Reviews 24.

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10. Hazai, Laszlo. 3(2*H*)-Isoquinolones and their saturated derivatives. **1991**, *52*, 156–188.
11. Queguiner, Guy; Marsais, Francis; Snieckus, Victor; Epsztajn, Jan. Directed metalation and π-deficient azaaromatics: Strategies of functionalization of pyridines, quinolines, and diazines. **1991**, *52*, 189–295 ff.

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