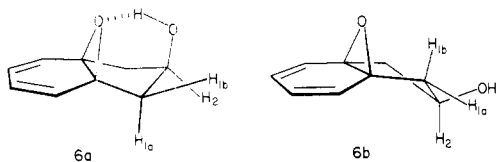


observed couplings  $J(H_{1b}/H_2)$  and  $J(H_{1a}/H_2)$  indicate that **6** may be conformationally mobile, showing contributions from both extremes of geometry, **6a** and **6b**.<sup>12</sup>



The coupling  $J(H_2/OH)$  as a function of solvent composition (Figure 1) is closely approximated by the quadratic eq 1, where  $M$  represents the mole percent of *tert*-butyl alcohol =

$$[1.53 \times 10^{-4}M^2 + 1.46 \times 10^{-2}M + 6.91] \text{ Hz} \quad (1)$$

butyl alcohol in the *tert*-butyl alcohol/dimethyl- $d_6$  sulfoxide mixture. Equation 1 has been derived empirically for the *syn*-hydroxy epoxide **6** and is not intended to apply directly to other systems such as **1** or **3**. Undoubtedly, the coefficients in eq 1 reflect not only the propensity for hydrogen bonding to the epoxide in conformation **6a** vs. hydrogen bonding to the solvent but also reflect the energetics of the conformational change  $\mathbf{6a} \rightleftharpoons \mathbf{6b}$  as hydrogen bonding to solvent molecules becomes significant. Thus, for different conformationally mobile systems the coefficients, if not the nature, of the corresponding equation will change.

Both conformational<sup>10</sup> and rate data have been obtained for diol epoxides **1-4**<sup>11</sup> and other diol epoxides.<sup>13</sup> The data presented herein show that the propensity for *intramolecular* hydrogen bonding in *syn*-diol epoxides such as **1** and **3** may depend critically on solvent composition. Conformational assignments based on <sup>1</sup>H NMR spectra obtained in solvents such as dimethyl- $d_6$  sulfoxide<sup>10,11a,c</sup> need not apply to solvent systems<sup>11,13</sup> used for nucleophilic addition rate studies.

The *syn*-diol epoxides **1** and **3**<sup>11a</sup> and three *syn*-diol epoxides derived from benzo[*a*]anthracene<sup>13</sup> react with *p*-nitrophenylthiolate from 60 to 330 times faster than their corresponding anti isomers in 98 mol % *tert*-butyl alcohol/2 mol % dimethyl sulfoxide. By contrast, in 25% EtOH/75% aqueous buffer (pH 7.4), diol epoxides **3** and **4** react at nearly equal rates, the anti isomer actually reacting somewhat faster.<sup>11a</sup> The pronounced solvent dependence has been ascribed to conformational effects in the alcohol/water system.<sup>11a</sup> The present results clearly show that *intramolecular* hydrogen bonding will be enhanced in *syn*-diol epoxides (cf. Figure 1) in 98% *tert*-butyl alcohol/2% dimethyl sulfoxide. In the alcohol/water system hydrogen bonding to the solvent may be dominant. The entropic advantage of an *intramolecular* hydrogen bond, thus, will be manifested only in the nonaqueous solvent system. A similar rate effect is seen for isomers **3** and **4** in dioxane/water mixtures. The rate acceleration for the *syn* isomer **3**, seen as the proportion of the organic solvent increases, has been discussed also by Bruice.<sup>11c</sup>

Rate studies for nucleophilic addition of thiolates to **6** in *tert*-butyl alcohol/dimethyl sulfoxide mixtures were precluded by the lack of reactivity of *p*-nitrophenylthiolate toward **6**. Other thiolates, such as LiSMe which is known to add to **6** in *tert*-butyl alcohol/water,<sup>12</sup> cannot be used due to their low solubility in *tert*-butyl alcohol/dimethyl sulfoxide mixtures. The instability of **6** in *tert*-butyl alcohol/water<sup>12</sup> precludes as well kinetic measurements in this solvent system.

## Experimental Section

<sup>1</sup>H NMR of *syn*-2-Hydroxyindan **3a,7a**-Oxide (**6**). The epoxy alcohol (**6**) was prepared by our published procedure.<sup>12</sup> Solutions of **6** (0.2 M) were prepared in volumetrically measured mixtures of *tert*-butyl alcohol (J. T. Baker, reagent grade dried statically over activated 4-Å molecular sieves) and dimethyl- $d_6$  sulfoxide (Merck, 99.5%). Nine samples prepared in this fashion contained 100, 89.0, 82.2, 65.3, 48.1, 36.2, 18.5, 10.9, and 0 mol % *tert*-butyl alcohol. The last sample, containing only dimethyl- $d_6$  sulfoxide as solvent, also contained ca. 1% tetramethylsilane (for spectrometer lock). The hydroxyl region of the <sup>1</sup>H NMR spectrum of **6**<sup>12</sup> was swept at a rate of 1.0 Hz/6.0 s with a sweep width of 50.0 Hz (Hitachi Perkin-Elmer R-24B NMR spectrometer). The spectrometer was locked on the *tert*-butyl alcohol methyl signal for all samples except the dimethyl- $d_6$  sulfoxide sample which was locked on internal tetramethylsilane. The hydroxyl region in each sample was swept four or five times and the average observed couplings were calculated: 10.03 Hz (100 mol % *tert*-butyl alcohol), 9.31 Hz (89.0 mol%), 9.04 Hz (82.2 mol%), 8.56 Hz (65.3 mol%), 7.98 Hz (48.1 mol%), 7.75 Hz (36.2 mol%), 7.20 Hz (18.5 mol%), 7.04 Hz (10.9 mol%), 6.93 Hz (0 mol%). The pooled standard error of  $J(H_2/OH)$  from all measurements is 0.04 Hz (38 measurements and 9 average observed couplings or 29 degrees of freedom). This represents the standard error for our method of measurement of  $J(H_2/OH)$ , irrespective of solvent composition.

**Curve Fitting.** The coupling constant data were curve fitted by quadratic regression on Texas Instruments calculator SR52, using program number ST1-13. The standard error of the fit of the nine average observed couplings to eq 1 is 0.10 Hz (6 degrees of freedom).

**Acknowledgment** is made to the National Institutes of Health (grant number CA 20574) for support of this work. We thank Mr. Paul Bergstein for valuable assistance.

**Registry No. 6**, 19439-32-8.

## Synthesis of Seleno and Telluro Isocoumarins: 1*H*-2-Seleno- (and -Telluro-) benzopyran-1-ones

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Although seleno<sup>1</sup> (and telluro)<sup>2</sup> chromones (4*H*-1-seleno- (and -telluro-) benzopyran-4-ones) as well as seleno<sup>3</sup> (and -telluro)<sup>4</sup> coumarins (2*H*-1-seleno- (and -telluro-) benzopyran-2-ones) have been synthesized, their isomers, iso-seleno- (and isotelluro-) coumarins **3** are still unknown. In order to investigate the chemical and physicochemical properties of compounds of the three isomeric series, we needed a synthesis of chalcogenated isocoumarins. This was accomplished in a three-step reaction pathway (Scheme I). Ethyl *o*-ethynylbenzoate **1** is readily available from ethyl *o*-acetylbenzoate by classical reaction with phosphorus pentachloride-pyridine<sup>5</sup> or from ethyl *o*-iodobenzoate by bis(triphenylphosphine)-palladium dichloride catalyzed cross-coupling reaction with acetylene.<sup>6</sup> The triple bond of this ester undergoes easily the regio-specific nucleophilic  $\beta$ -addition of the methaneselenolate (or -tellurolate) anion, affording the chalcogenated esters

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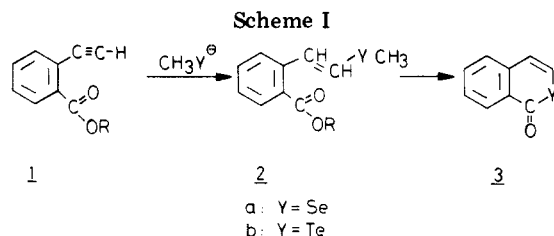
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Table I. IR and NMR Spectral Data for Isocoumarins

3	IR $\nu_{C=O}$ (CHCl <sub>3</sub> ), cm <sup>-1</sup>	AB system		$J_{H_3-H_4}$ , Hz	$H_5-H_6-H_7$ , (m)	$H_8$ (m)
		H <sub>3</sub>	H <sub>4</sub>			
Y = O <sup>10</sup>	1745	6.40	7.17 <sup>12</sup>	5.5	7.2-7.8	8.05-8.2
Y = S <sup>11</sup>	1640	6.98	7.10	9.52	7.3-7.7	8.1-8.3
3a	1643	7.46	7.26	9.8	7.2-7.7	8.1-8.2
3b	1628	7.92	7.61	10.7	7.05-7.65	7.9-8.15



2 (R = C<sub>2</sub>H<sub>5</sub>) in a mixture *Z:E* = 9:1. Saponification allows the isolation of the corresponding acids 2 (R = H). The acid chlorides are electrophilically cyclized on the Y atom of the ether group, giving rise in this way to the new isoseleno (and isotelluro) coumarins 3. The structure of these compounds is firmly established by C and H elemental analysis, IR, <sup>1</sup>H NMR (Table I), and mass spectrometry.

The assignment of H<sub>3</sub> and H<sub>4</sub> is realized on the basis of broader and smaller peaks in the AB system for the H<sub>4</sub> proton, due to long-range coupling with the aromatic protons. The mass spectra of 3a and 3b give correct molecular ions with the correct isotopic ratio for one selenium or one tellurium atom per molecule. For isoselenocoumarin (3a), the molecular ion (*m/e* 210, based on <sup>80</sup>Se, 67% of the base peak) shows a M<sup>+</sup> - CO peak at *m/e* 182 (66%, correct isotopic ratio) and a M<sup>+</sup> - CO - Se peak (*m/e* 102, base peak). The fragmentation is very similar to those of benzo[b]selenophene,<sup>7</sup> with principal peaks at *m/e* 91 (10%), 90 (8%), 89 (20%), 76 (15%), 75 (18%), 74 (15%), 63 (11%), 51 (10%), and 50 (12%). No significant loss of selenium can be seen from the molecular ion.

In contrast, the molecular ion of isotellurocoumarin (3b) (*m/e* 260 for <sup>130</sup>Te, 25% of the base peak) gives, beside the classical loss of CO (*m/e* 232, 45%), an important loss of tellurium (*m/e* 130, 36%; this peak, without isotopic distribution, does not correspond to Te<sup>+</sup>). The base peak is the same as that for 3a (*m/e* 102), and further degradations are the same as for benzo[b]tellurophene:<sup>8</sup> *m/e* 76 (27%), 75 (19%), 74 (12%), 63 (7%), 51 (10%), 50 (10%).

For comparison, the fragmentation of isothiocoumarin (M<sup>+</sup>, *m/e* 162, base peak) is the following: loss of CO (*m/e* 134, 75%) and loss of CS (*m/e* 118, 5%) from the molecular ion and an important peak for the loss of these two fragments at *m/e* 90 (16%) and 89 (23%).

Loss of CS instead of S is characteristic of the difference observed between the fragmentation of benzo[b]thiophene<sup>9a</sup> and benzo[b]selenophene. Very small peaks correspond to M<sup>+</sup> - COS (*m/e* 102, 6%) and to M<sup>+</sup> - CO - C<sub>2</sub>H<sub>2</sub> (*m/e* 108, 6%). This spectrum also displays peaks at *m/e* 69 (7%), derived from 108, and at *m/e* 67 (14%)

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[(M - CO)<sup>2+</sup>], missing in the selenium and tellurium analogues.

### Experimental Section

The physical data were obtained as follows: IR spectra on a Beckman IR 20 A; mass spectra on a Varian MAT 112 (70 eV) by VPC introduction; NMR spectra on a Varian T-60 in CDCl<sub>3</sub> solutions using HMDS as internal standard. The following abbreviations are used: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet. Melting points are uncorrected. The compounds give satisfactory elemental analyses within ±0.4% for C and H and mass spectra with the correct molecular ion and correct isotopic values for one selenium or one tellurium atom per molecule.

**Esters or Acids 2 (R = C<sub>2</sub>H<sub>5</sub> or H).** To a well stirred solution of 3.76 g (20 mmol) of dimethyl diselenide (or 5.68 g of dimethyl ditelluride) in 50 mL of ethanol is added sodium borohydride portionwise under an argon atmosphere until the reaction mixture is decolorized. Ethyl *o*-ethynylbenzoate (40 mmol) is then added and the solution is refluxed for 10 h. If the esters are needed, ethanol is evaporated. After hydrolysis (HCl, ice) and classical workup of the mixture, the esters are distilled. When the acids are required, a solution of 3 g of potassium hydroxide in 50 mL of ethanol is added and the saponification is performed by refluxing for 4 h. Solvent is evaporated and the residue is diluted with 70 mL of water. After the solution is decolorized with Norit and acidified, acids 2 (R = H) are collected by filtration, air-dried, and recrystallized in a toluene-hexane mixture. These acids are also available from pure esters by the same saponification procedure.

2a (R = C<sub>2</sub>H<sub>5</sub>): 64%; bp 130 °C (1 mm); IR (CHCl<sub>3</sub>)  $\nu_{C=O}$  1710 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.25 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.2 (s, 3 H, SeCH<sub>3</sub>, <sup>2</sup>*J*<sub>Se-CH<sub>3</sub></sub> = 11 Hz), 4.3 (q, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 6.54 and 7.44 (AB system, 2 H, H<sub>α</sub>, H<sub>β</sub>, <sup>3</sup>*J*<sub>H<sub>α</sub>-H<sub>β</sub></sub> = 10.4 Hz), 7-7.6 (m, 3 H, Ar H), 7.8-8 (m, 1 H, H<sub>6</sub>).

2b (R = C<sub>2</sub>H<sub>5</sub>): 40%; bp 165 °C (1 mm); IR (CHCl<sub>3</sub>)  $\nu_{C=O}$  1710 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.3 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.9 (s, 3 H, TeCH<sub>3</sub>, <sup>2</sup>*J*<sub>Te-CH<sub>3</sub></sub> = 22 Hz), 4.3 (q, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 6.89 and 7.89 (AB system, 2 H, H<sub>α</sub>, H<sub>β</sub>, <sup>3</sup>*J*<sub>H<sub>α</sub>-H<sub>β</sub></sub> = 10.8 Hz), 7.1-7.5 (m, 3 H, Ar H), 7.8-8 (m, 1 H, H<sub>6</sub>). Chemical shifts of the *E* isomer are not distinguishable from those of other aromatic protons.

2a (R = H): 89%; mp 114-117 °C; IR (KBr)  $\nu_{C=O}$  1690 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  2.1 (s, 3 H, SeCH<sub>3</sub>, <sup>2</sup>*J*<sub>Se-CH<sub>3</sub></sub> = 11 Hz), 6.6 and 7.5 (AB system, H<sub>α</sub>, H<sub>β</sub>, 2 H, <sup>3</sup>*J*<sub>H<sub>α</sub>-H<sub>β</sub></sub> = 10.2 Hz), 7-7.5 (m, 3 H, Ar H), 8-8.2 (m, 1 H, H<sub>6</sub>).

2b (R = H): 82%; mp 123-125 °C; IR (KBr)  $\nu_{C=O}$  1690 cm<sup>-1</sup>; NMR  $\delta$  1.9 (s, 3 H, TeCH<sub>3</sub>, <sup>2</sup>*J*<sub>Te-CH<sub>3</sub></sub> = 22 Hz), 7 and 7.85 (AB system, H<sub>α</sub>, H<sub>β</sub>, 2 H, <sup>3</sup>*J*<sub>H<sub>α</sub>-H<sub>β</sub></sub> = 10.6 Hz), 7-7.6 (m, 3 H, Ar H), 7.9-8.2 (m, 1 H, H<sub>6</sub>).

**Isocoumarins 3.** Acid 2 (R = H) (10 mmol) and 100 mg of anhydrous ZnCl<sub>2</sub> are left overnight in 10 mL of dichloromethyl methyl ether.<sup>9b</sup> The reagent is evaporated and the residual chloride is dissolved in 50 mL of dry methylene chloride. To this well stirred solution is added 1.33 g (10 mmol) of aluminum chloride at -80 °C. The temperature of the reaction mixture is allowed to reach the room temperature. After the usual workup, the residual solid is recrystallized from hexane.

3a: 58%; mp 79-80 °C. Anal. Calcd: C, 51.67; H, 2.87. Found: C, 52.0; H, 2.8.

3b: 30%; mp 83 °C. Anal. Calcd: C, 42.02; H, 2.33. Found: C, 42.1; H, 2.54.

**Acknowledgment.** We are very grateful to the "Fonds de la Recherche Fondamentale Collective" for a grant which permitted the purchase of a mass spectrometer.

**Registry No.** 1 (R = Et), 74185-31-2; 2a (R = H), 74185-32-3;

(*E*)-**2a** (R = Et), 74185-33-4; (*Z*)-**2a** (R = Et), 74185-34-5; **2b** (R = H), 74185-35-6; (*E*)-**2b** (R = Et), 74185-36-7; (*Z*)-**2b** (R = Et),

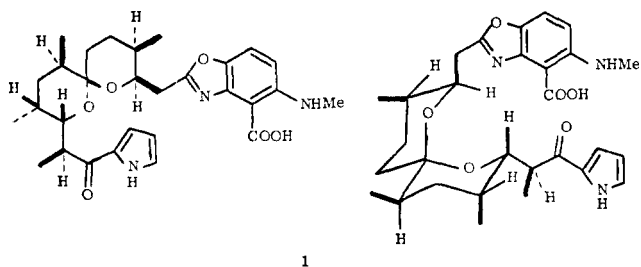
74185-37-8; **3a**, 74185-38-9; **3b**, 74185-39-0; dimethyl diselenide, 7101-31-7; dimethyl ditelluride, 20334-43-4.

## Communications

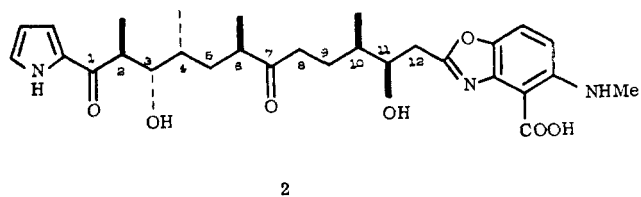
### Elaboration of the C(3)–C(12) Carbon Fragment of Calcimycin (A-23187). Formal Total Synthesis of Calcimycin

**Summary:** A formal synthesis of calcimycin is reported which features construction of the C(3)–C(12) carbon fragment **3** from bicyclo[2.2.1]heptenone **4**.

**Sir:** The structure of the unique divalent cation ionophore calcimycin (**1**; A-23187) produced from cultures of *Streptomyces chartreusensis* was recently established by Chaney and co-workers at the Lilly Research Laboratories.<sup>1</sup> The high Ca<sup>2+</sup> specificity exhibited by calcimycin coupled with its ability to transport ions across cell membranes is, in part, responsible for the extensive attention this antibiotic has received since its structure was announced in 1974.<sup>2</sup>

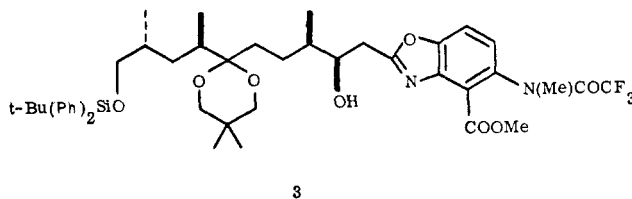


The structure of **1** reveals, in addition to a benzoxazole and an  $\alpha$ -ketopyrrole unit, a novel 1,7-dioxaspiro[5.5]undecane ring system. Analysis of **1** suggests that the acyclic keto diol **2** or its equivalent should close to the desired



dioxaspirane under thermodynamically controlled acid-catalyzed conditions. This point has recently been demonstrated by Evans and co-workers, whose endeavors have culminated in the first total synthesis of calcimycin.<sup>3</sup> Herein, we describe our efforts in this area. We detail below the synthesis of the racemic C(3)–C(12) segment **3** of calcimycin.

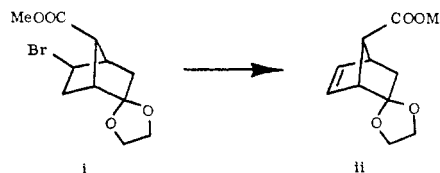
The synthetic route to **3**, which originated with the bicyclo[2.2.1]heptenone **4**<sup>4</sup> (Chart I), was performed in two



stages: (1) synthesis of the C(3)–C(9) fragment **10** (Chart I) and (2) elaboration of **10** into the C(3)–C(12) segment **3**.

Treatment of the Baeyer–Villiger oxidation product of bicyclo[2.2.1]heptenone **4**<sup>6,7</sup> with boron trifluoride etherate promoted facile rearrangement, giving rise to bicyclic lactone **5**.<sup>6,7</sup> Transformation of  $\gamma$ -lactone **5** into  $\delta$ -lactone **6**<sup>6</sup> was efficiently carried out in five steps in approximately 70% overall yield as outlined in Chart I. Alkylation of lactone **6** with methyl iodide proceeded smoothly, affording

(4) Bicyclo[2.2.1]heptenone **4** was prepared in ~45% overall yield from the known bicyclo[2.2.1]heptane derivative **i**<sup>5</sup> via a five-step sequence: (1) DBU, DMF, reflux; (2) LiAlH<sub>4</sub>, Et<sub>2</sub>O; (3) TsCl, pyridine; (4) LiEt<sub>3</sub>BH, THF; (5) HCl, THF. Note, the major product obtained during treatment of **i** with DBU is the isomerized ketal ester **ii**.



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(6) All new compounds have been fully characterized, including combustion analysis and/or high-resolution mass spectra.

(7) 4: IR (CHCl<sub>3</sub>) 1730 cm<sup>-1</sup>; NMR (250 MHz, CCl<sub>4</sub>)  $\delta$  1.00 (d, 3 H, *J* = 6.98 Hz), 1.68 (dd, 1 H, *J* = 2.25, 16.65 Hz, C(3) endo proton), 1.96 (dd, 1 H, *J* = 3.15, 16.65 Hz, C(3) exo proton), 2.53 (m, 1 H, C(7) proton), 2.64 (br s, 1 H, C(4) proton), 2.82 (br s, 1 H, C(1) proton), 6.10 (m, 1 H, C(5) proton), 6.54 (dd, 1 H, *J* = 2.70, 5.60 Hz, C(6) proton). 5: IR (CHCl<sub>3</sub>) 1770 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  1.04 (d, 3 H, *J* = 6.8 Hz), 2.36 (dd, 1 H, *J* = 1.5, 7.5 Hz) 2.94 (m, 2 H), 3.17 (dd, 1 H, *J* = 7.5, 16.0 Hz), 5.35 (br d, 1 H), 5.7–6.1 (m, 2 H, olefinic protons). 7: IR (CCl<sub>4</sub>) 1738 cm<sup>-1</sup>; NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  0.0 (s, 6 H), 0.82 (s, 9 H), 1.02 (d, 3 H, *J* = 7.3 Hz), 1.4–2.6 (m, 6 H), 3.60 (m, 2 H), 4.30 (m, 1 H). 8: IR (CCl<sub>4</sub>) 3450, 1720 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  1.02 (d, 3 H, *J* = 6.7 Hz), 1.23 (d, 3 H, *J* = 6.7 Hz), 1.5–2.2 (m, 5 H), 2.50 (m, 1 H), 3.43 (br s, 1 H, OH), 3.67 (br t, 1 H, CH<sub>2</sub>OH), 4.53 (m, 1 H). 9: IR (CCl<sub>4</sub>) 1730 cm<sup>-1</sup>; NMR (60 MHz, CCl<sub>4</sub>)  $\delta$  1.03 (d, 3 H, *J* = 7.0 Hz), 1.33 (d, 3 H, *J* = 7.0 Hz), 1.5–2.9 (m, 4 H), 4.80 (m, 1 H), 5.1–6.2 (m, 3 H, CH=CH<sub>2</sub>). 10: IR (CHCl<sub>3</sub>) 3610, 3450 cm<sup>-1</sup>; NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  0.85 (d, 6 H, *J* = 6.0 Hz), 1.20 (dd, 2 H, *J* = 6.3, 7.1 Hz), 1.4–1.9 (m, 2 H), 3.40 (br d, 2 H, *J* = 6.8 Hz), 4.00 (br t, 1 H, *J* = 4.8 Hz), 5.0–6.2 (m, 3 H, CH=CH<sub>2</sub>). 11: IR (CHCl<sub>3</sub>) 1718 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.80 (d, 3 H, *J* = 7.5 Hz), 0.82 (d, 3 H, *J* = 7.5 Hz), 1.08 (s, 9 H), 1.10 (t, 3 H, *J* = 7.0 Hz), 1.20 (m, 2 H), 1.75 (m, 2 H), 2.25 (q, 2 H, *J* = 7.0 Hz), 3.47 (d, 2 H, CH<sub>2</sub>OSi), 5.0–6.0 (m, 4 H, CH=CH<sub>2</sub>, CHOCO), 7.3–7.8 (m, 10 H). 13: IR (CCl<sub>4</sub>) 1738, 970 cm<sup>-1</sup>; NMR (600 MHz, CCl<sub>4</sub>)  $\delta$  0.89 (d, 3 H, *J* = 7.0 Hz), 0.93 (d, 3 H, *J* = 7.0 Hz), 1.05 (s, 9 H), 1.09 (d, 3 H, *J* = 7.0 Hz), 1.30 (m, 2 H), 1.63 (m, 1 H), 2.04 (m, 2 H), 2.25 (m, 1 H), 2.38 (m, 1 H), 3.38 (m, 1 H), 3.49 (m, 1 H), 3.59 (s, 3 H), 5.13 (m, 1 H), 5.28 (m, 1 H), 7.33 (m, 6 H), 7.67 (m, 4 H). 16: IR (CCl<sub>4</sub>) 1735, 1710 cm<sup>-1</sup>; NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.90 (d, 3 H, *J* = 6.5 Hz), 1.01 (d, 3 H, *J* = 6.9 Hz), 1.09 (s, 9 H), 1.15 (d, 3 H, *J* = 6.9 Hz), 1.42 (t, 2 H, *J* = 6.9 Hz), 1.6–1.9 (m, 3 H) 2.3–2.7 (m, 4 H), 3.46 (q, 2 H, *J* = 2.9 Hz), 3.66 (s, 3 H), 7.40 (m, 6 H), 7.70 (m, 4 H).

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