A Simple and Highly Stereoselective Route to E-α,β-Unsaturated Aldehydes

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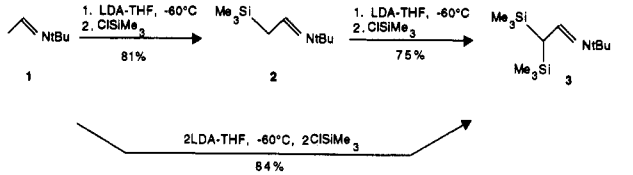
Zinc bromide mediated reaction of α,α-bis(trimethylsilyl)-*tert*-butylacetaldimine (3) with a wide range of aldehydes takes place under mild conditions and affords the corresponding α,β-unsaturated aldehydes in good yields and with very high *E* stereoselectivity (>98%). This procedure is successfully applied to the preparation of intermediates for retinoid and natural product synthesis.

Introduction and Background

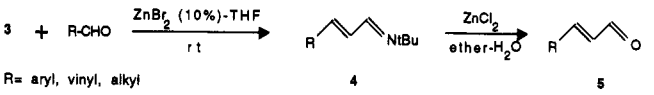
Homologation of an aldehyde into an α,β-unsaturated aldehyde with the introduction of two additional carbon atoms in the resulting chain is an important reaction in organic synthesis, especially in the area of natural products.[1] A number of reagents and processes are currently available for effecting such chain extensions. These include (1) aldol condensation and its variations,[2] (2) Wittig reaction[3] or one of its variants,[4] (3) Lewis acid catalyzed acetal–vinyl ether condensation,[5] (4) acetylide[6,7] or vinyl metallic[8] addition followed by carbinol rearrangement, and (5) Peterson olefination by means of monosilylated reagents.[9,10] These techniques possess variable degrees of utility but in all of them α,β-unsaturated aldehydes having the *E* configuration are obtained. However, small quantities of the *Z* isomer usually contaminate the main product.

The goal of our program has been to develop a new approach to retinoid synthesis using organosilicon derivatives. In preliminary work[11] we proposed a new method for the preparation of *E*-α,β-unsaturated aldehydes by two-carbon elongation. In this paper we generalize the method and show that this new route offers special advantages including very high stereoselectivity in favor of the *E* isomer, high efficiency, procedural simplicity, and mildness of reaction conditions.

Scheme I



Scheme II



Results and Discussion

Preparation of α,α-Disilylated Aldimine 3. Deprotonation of *N*-*tert*-butylacetaldimine (1) by an equivalent of LDA at −60 °C followed by trimethylsilyl chloride trapping affords monosilylated aldimine 2 which is then subjected to a similar treatment to give α,α-bis(trimethylsilyl)-*tert*-butylacetaldimine (3) in 61% overall yield (procedure A). However, a one-step preparation of 3 turned out to be more advantageous: 84% yield (procedure B). The ^{1}H NMR spectrum of 3 excludes an enamine structure (Scheme I).

Reaction with Aldehydes. Condensation of 3 with a variety of aromatic, vinylic, and aliphatic aldehydes provides the expected α,β-enals as illustrated in Scheme II.

Nucleophilic addition of 3 to benzaldehyde in the presence of catalytic amounts of $ZnBr_2$ (10%) in anhydrous THF and at room temperature affords cinnamaldehyde in 86% yield (Table I, entry a). No signals—characteristic of the *Z* isomer—were present in the ^{1}H NMR spectrum of the crude product indicating the complete *E* stereoselection of the reaction. The tetrabutylammonium fluoride (TBAF) catalyzed reaction leads to an equimolecular mixture of *E* and *Z* isomers. Preliminary results[11] showed that the choice of Lewis acid was important in stereochemical outcomes and yields. On the basis of these results, $ZnBr_2$ was selected as the representative catalyst and employed throughout our work. All reactions are carried out in anhydrous tetrahydrofuran as solvent.

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(10) Duhamel, L.; Gralak, J.; Ngono, B. *J. Organomet. Chem.* **1989**, *363*. C4. For additional bibliography see: Clive, D. L. J.; Farina, V.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 2572 and references cited therein.

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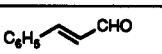
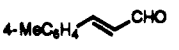
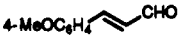
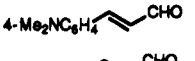
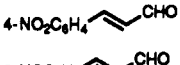
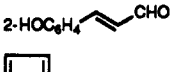
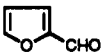
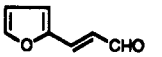
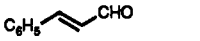
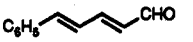
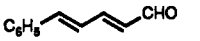
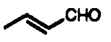
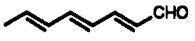
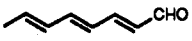
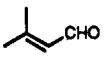
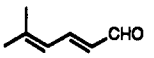
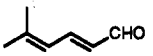
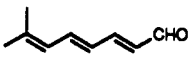
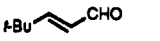
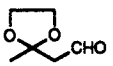
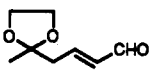
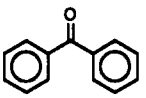
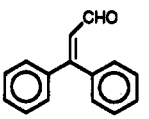
0022-3263/93/1958-2517$04.00/0

Table I. Synthesis of Unsaturated Aldehydes Using Reagent 3

entry	starting carbonyl compound	reactn time (h)	unsaturated aldehydes 5	yield (%)[a]	refs
a	C_6H_5CHO	2		86	15a
b	$4\text{-}MeC_6H_4CHO$	4		83	16
c	$4\text{-}MeOC_6H_4CHO$	6		90	16
d	$4\text{-}Me_2NC_6H_4CHO$	7(3)[b]		57 (94)[b]	15b
e	$4\text{-}NO_2C_6H_4CHO$	2.5(24)[c]		96 (65)[c]	17
f	$2\text{-}Me_3SiOC_6H_4CHO$	3[b]		98[b]	18
g		5		97	19
h		3		92	20
i		4		84	21
j		4		83	22
k		2[b]		65[b]	23
l		3		63	15c
m		4.5		82	12
n		4.5		80	12
o		3		74	24
p		2		82	21
q	*t*-BuCHO	3		66	25
r	$C_5H_{11}CHO$	6		65	26
s	$C_7H_{15}CHO$	4.5		60	25
t		6		85	27
u		4		97	28

[a] Isolated yield. [b] One equivalent of $ZnBr_2$ was used. [c] No catalyst was employed.

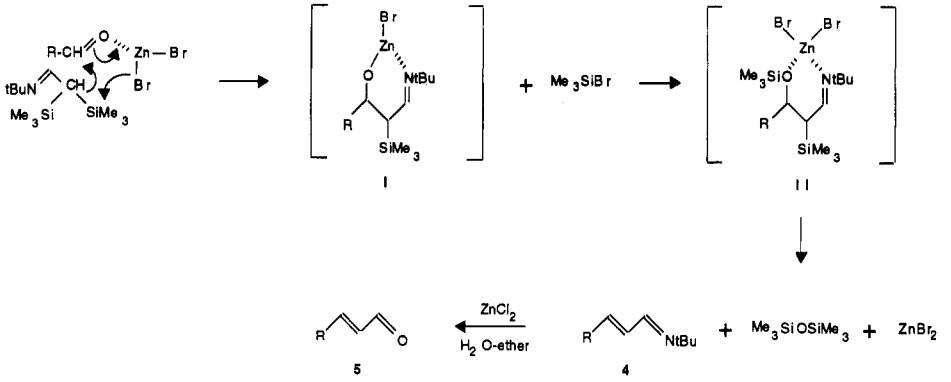
As can be seen from the data (Table I), the sense of stereoselectivity does not change with 4- and 2-substituted aromatic aldehydes; different groups of steric and electronic nature are used as substituents (entries b–f). Homologation of unsaturated aromatic aldehydes into their vinylogues is achieved efficiently (entries h–k); no double-bond migration nor any conjugate addition takes place. We thus managed the construction of two, three, and four (a retinal analogue) contiguous *E* double bonds (entries h–j) from cinnamaldehyde. The high *E* stereoselectivity of each addition is confirmed by the ^1H NMR spectrum of the crude product.

To determine the scope and limitations of our method, the reaction has also been performed on a number of aliphatic unsaturated (entries l–p) and saturated aldehydes (entries q–t). Several trends may be pointed out in examining these results: this class of aldehydes undergoes neat condensation with **3** under mild conditions in good yields; a bulky substituent adjacent to the carbonyl function does not seem to affect the reaction pathway (entry q); conjugated aldehydes (entries l–p) exhibit high levels of regio- and stereoselectivity. This methodology is successfully applied to the synthesis of 2,4,6,8-decatetraenal (entry n), an intermediate in the total synthesis of fuligorubin A.[12]

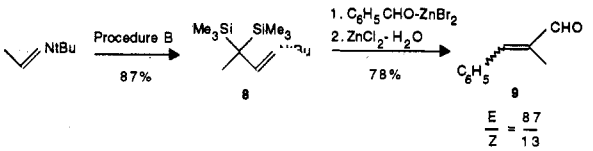
We next investigated the action of **3** on a number of ketones. The Lewis acid mediated reaction of **3** with enolizable ketones affords, in all cases, the corresponding trimethylsilyl enol ether. Treatment with TBAF gives,

(12) Ley, S. V.; Smith, S. C.; Woodward, P. R. *Tetrahedron* **1992**, *48*, 1145.

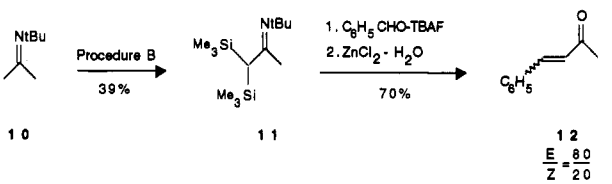
Scheme III



Scheme IV



Scheme V



after hydrolysis, the starting ketone. Only benzophenone reacts with **3**, in the presence of catalytic amounts of TBAF in anhydrous THF, providing the desired α,β-enal **5u** (entry u) with a 97% yield. Nevertheless, 4 h, of which 2 at reflux, are required for the complete conversion.

Reaction Mechanism. In spite of the fact that reaction mechanism is not clear at present, we presume that the reaction is initiated by $ZnBr_2$ complexation of C=O and subsequent reaction of **3** with the carbonyl compound to give the corresponding silyl zinc chelate I. Further Peterson-type elimination of II affords aldimine **4** with regeneration of the catalyst. Mild acidic hydrolysis of **4** gives exclusively the *E*-α,β-unsaturated aldehyde **5** (Scheme III).

Concerning the stereoselection of the reaction, in all cases only *E* isomers are observed. Our attempts to isolate the intermediate II, in order to study the correlation between the elimination mechanism and the product stereochemistry, have failed. However, the imines **4** have been isolated and characterized by ^1H NMR.

Extension to Other α,α-Disilylated Imines. With the aim of extending our methodology to other disilylated imines, we next examined the behavior of α,α-bis(trimethylsilyl)-*tert*-butylpropionaldimine (**8**) and α,α-bis(trimethylsilyl)-*tert*-butyl ketimine **11** with benzaldehyde. The deprotonation of *N*-*tert*-butylpropionaldimine (**7**) and the interception of the intermediate by Me_3SiCl gives **8** in 87% yield (procedure B).

The reaction between **8** and benzaldehyde in the presence of $ZnBr_2$ (10%) at room temperature gives a mixture of *E* and *Z* α-methyl α,β-enals **9** in 78% yield (Scheme IV). Under these conditions, the major product is the *E* isomer (*E*/*Z* = 87/13). However, this ratio can be inverted under TBAF catalysis (*E*/*Z* = 26/74).

Finally, in connection with an approach to the synthesis of α,β-unsaturated ketones, we tested the potential of **11**, as a methyl ketone aldol equivalent. For this purpose, **11** is prepared by proton extraction and $ClSiMe_3$ trapping of acetone *tert*-butylimine **10** in 39% yield (procedure B) and then TBAF (5%) catalyzed condensation with benzaldehyde at room temperature. As expected, the corresponding α,β-unsaturated methyl ketone **12** is obtained in 70% yield as a mixture of *E* and *Z* isomers in a 80/20 ratio, respectively (Scheme V). This work is now in progress and will be published in a future paper.

Conclusion

From the results reported here, it is clear that α,α-disilylated *tert*-butylacetaldimine **3** is a versatile reagent for the two-carbon homologation of aldehydes into the corresponding α,β-enals. The simplicity of the procedure, the mildness of the reaction conditions, and the very high stereoselectivity obtained make this new route a promising methodology. Furthermore, this method avoids the strong basic conditions associated with the Wittig-type reactions and thus can be applied to base-sensitive aldehydes. The mechanism of this reaction is not yet clear but the presumed intermediate—α-silyl β-siloxy *tert*-butyl imine **11**—could play a key role in the formation of the *E* carbon–carbon double bond.

Experimental Section

Reactions requiring anhydrous conditions are performed in flame-dried glassware under a nitrogen atmosphere. Unless otherwise noted, commercially available compounds are used in this work without further purification. Trimethylchlorosilane is distilled over magnesium. Diisopropylamine is distilled from CaH_2 and stored over molecular sieves. Tetrahydrofuran and diethyl ether are distilled over sodium and benzophenone. LDA is prepared in situ from diisopropylamine and *n*-butyllithium (1.6 M solution in hexane) at −20 °C. Tetrabutylammonium fluoride (1.0 M solution in THF) is purchased from Aldrich.

Proton nuclear magnetic resonance spectra are recorded at 60 MHz (Perkin Elmer R12), 200 MHz (Bruker AC 200), or 500 MHz (Bruker AM 500). All chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Infrared spectra are recorded on a Philips PU 9706 spectrophotometer. Melting points are determined on a Büchi 535 instrument and are uncorrected. Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh) with a mixture of cyclohexane/acetone as eluant. Some imines are isolated and purified by a simple workup. 2-(2-Methyl-2-dioxolanyl)acetaldehyde, the starting material for **5t**, is prepared according to the described method.[13]

(13) Kelly, T. R.; Anathasubramanian, A.; Borah, K.; Gillard, J. W.; Goerner, R. N., Jr.; King, P. F.; Lyding, J. M.; Tsang, W.-G.; Vaya, J. *Tetrahedron* **1984**, *40*, 4569.

Preparation of Zinc Bromide. $ZnBr_2$ is prepared by heating ground zinc (3.6 g, 55 mmol) and 1,2-dibromoethane (9.5 g, 50 mmol) in THF (100 mL) for 16 h at reflux. The resulting solution is allowed to cool slowly to room temperature. The remaining excess zinc is removed by filtration. Complete evaporation of the solvent under high vacuum gives pure $ZnBr_2$ as a white powder.

***N-tert*-Butyl Imines 1, 7, and 10.** The starting imines are easily prepared from the corresponding carbonyl compounds and *tert*-butylamine in pentane.[14] *N-tert*-Butylacetaldimine (1): bp 25–28 °C (95 mmHg). *N-tert*-Butylpropionaldimine (7): bp 47–49 °C (95 mmHg). *N-tert*-Butyl ketimine (10): bp 45–47 °C (80 mmHg).

Preparation of α,α-Bis(trimethylsilyl)-*tert*-butylacetaldimine (3). Procedure A. α-(Trimethylsilyl)-*tert*-butylacetaldimine (2). A solution of *N-tert*-butylacetaldimine (1) (4.95 g, 50 mmol) in THF (5 mL) was added dropwise to a stirred mixture of LDA (50 mmol) in THF (30 mL) at −60 °C. After the solution was stirred for 20 h at this temperature, chlorotrimethylsilane (6.5 mL, 50 mmol) was added to the reaction mixture. The resulting solution was stirred for another 2 h at −60 °C and was gradually warmed to room temperature over 1 h. The mixture was filtered through a pad of Celite. The solvent was removed and the product was distilled: bp 51–52 °C (12 mmHg); yield 6.92 g (81%); ^{1}H NMR (60 MHz, CCl_4) δ 0.04 (s, 9 H, $SiMe_3$), 1.06 (s, 9 H, tBu), 1.74 (d, 2 H, J = 8.0 Hz, CH_2), 7.53 (t, 1 H, J = 8.0 Hz, CH=N). Anal. Calcd for $C_9H_{21}NSi$: C, 63.21; H, 12.38; N, 8.19. Found: C, 63.17; H, 12.33; N, 8.16.

To a cooled (−60 °C) solution of LDA (50 mmol) in THF (30 mL) was added a solution of **2** (8.55 g, 50 mmol) in THF (5 mL). The resulting mixture was stirred at −60 °C for 5 h and then quenched by addition of chlorotrimethylsilane (6.5 mL, 50 mmol). After being stirred at the same temperature for 45 min, the solution was gradually warmed to room temperature and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was distilled: bp: 93–94 °C (12 mmHg); yield 9.10 g (75%); ^{1}H NMR (60 MHz, CCl_4) δ 0.02 (s, 18 H, 2 $SiMe_3$), 1.12 (s, 9 H, tBu), 1.56 (d, 1 H, J = 10.0 Hz, CH), 7.47 (d, 1 H, J = 10.0 Hz, CH=N). Anal. Calcd for $C_{12}H_{29}NSi_2$: C, 59.31; H, 12.03; N, 5.76. Found: C, 59.27; 11.98; N, 5.74.

Procedure B. **3** can also be prepared directly from **1**. To a stirred solution of LDA (100 mmol) in anhydrous THF (50 mL) was added **1** (4.95 g, 50 mmol) dropwise at −60 °C. The mixture was stirred at this temperature for 18 h. Trimethylchlorosilane was added in two portions: the first portion of TMSCl (6.5 mL, 50 mmol) was added at −60 °C and the solution was stirred for 5 h at this temperature; the second portion (6.5 mL, 50 mmol) was added and the solution was stirred for 45 min. Slow warming to room temperature of the resulting mixture was followed by filtration through a pad of Celite and evaporation of solvents at reduced pressure. The distillation of the remaining oil gave **3**: yield 10.21 g (84%).

α,α-Bis(trimethylsilyl)-*tert*-butylpropionaldimine (8). **8** was prepared according to procedure B. The detailed procedure is given above. Only the quantities of reactants, the volumes of THF, reaction times, and temperatures are presented. To a solution of LDA (100 mmol) in THF (50 mL) at −60 °C was added **7** (5.65 g, 50 mmol) dropwise, with stirring for 18 h at −60 °C; TMSCl (6.5 mL, 50 mmol) was added at −60 °C, with stirring for 5 h; and TMSCl (6.5 mL, 50 mmol) was added at the same temperature, with stirring for 45 min. **8**: bp 105–106 °C (13 mmHg); yield 11.17 g (87%); ^{1}H NMR (60 MHz, CCl_4) δ 0.02 (s, 18 H, 2 $SiMe_3$), 1.13 (s, 9 H, tBu), 1.23 (s, 3 H, CH_3), 7.67 (s, 1 H, CH=N). Anal. Calcd for $C_{13}H_{31}NSi_2$: C, 60.75; H, 12.16; N, 5.45. Found: C, 60.71; H, 12.10; N, 5.43.

α,α-Bis(trimethylsilyl)-*tert*-butyl Ketimine 11. **11** was prepared in one step according to procedure B. To a solution of LDA (100 mmol) in THF (50 mL) at −60 °C was added **10** (5.65 g, 50 mmol) dropwise, with stirring at −60 °C for 18 h; TMSCl (6.5 mL, 50 mmol) was added at −60 °C, with stirring for 4 h; and TMSCl (6.5 mL, 50 mmol) was added at −60 °C, with stirring for 45 min. **11**: bp 105–106 °C (13 mmHg); yield 5.01 g (39%); ^{1}H NMR (60 MHz, CCl_4) δ 0.04 (s, 18 H, 2 $SiMe_3$), 1.21 (s, 10 H, tBu and CH), 1.85 (s, 3 H, CH_3). Anal. Calcd for $C_{13}H_{31}NSi_2$: C, 60.75; H, 12.16; N, 5.45. Found: C, 60.64; H, 12.13; N, 5.46.

Preparation of Aldehydes 5a–t. General Procedure. A detailed procedure for the reaction of **3** with aldehydes is given below. All reactions are conducted in a similar manner, unless otherwise specified. Reaction times and yields are reported in Table I. Physical, spectral, and analytical data follow.

To a solution of the corresponding aldehyde (10 mmol) and $ZnBr_2$ (1 mmol) in THF (10 mL) was added a solution of **3** (11 mmol) in THF (5 mL) dropwise at room temperature. After being stirred at the same temperature, the resulting mixture was hydrolyzed by addition of an aqueous solution of $ZnCl_2$ (2 g in 20 mL of water) and ether (25 mL), and the solution was stirred for 1 h at room temperature. The precipitate was filtered through a pad of Celite. The aqueous layer was extracted with ether (2 × 25 mL), and the combined organic extracts were washed with water (10 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The reaction crude was purified by flash chromatography (silica gel, cyclohexane/acetone) to give the corresponding products **5a–t**.

Cinnamaldehyde (5a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.65 (dd, 1 H, J = 16.0, 8.0 Hz, =CHCO), 7.40 (d, 1 H, J = 16.0 Hz, PhCH=), 7.35–7.52 (m, 5 H, Ar), 9.64 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1685 (C=O). Anal. Calcd for C_9H_8O: C, 81.89; H, 6.11. Found: C, 81.58; H, 6.13.

(*Z*)-3-Phenyl-2-propenal. A mixture of benzaldehyde (1.06 g, 10 mmol) and **3** (2.67 g, 11 mmol) in THF (10 mL) was added dropwise to TBAF (0.5 mL, 0.5 mmol) in THF (5 mL). The reaction is exothermic; the temperature was maintained at 20–25 °C with a water bath. After 30 min of stirring at room temperature, the mixture was hydrolyzed at 10 °C with an aqueous solution of $ZnCl_2$ (2 g in 15 mL of water) and ether (20 mL). The resulting solution was stirred for another 30 min at 10 °C. The precipitate was filtered on a pad of Celite. The aqueous layer was extracted with ether (2 × 25 mL). The combined organic layers were washed with a solution of H_2SO_4 (0.5 g in 15 mL of water) and then with water (2 × 25 mL). The solvent was removed in vacuo. The crude product was subjected to ^{1}H NMR analysis; an equimolecular mixture of *E* and *Z* isomers of 3-phenyl-2-propenal was formed in 88% yield: ^{1}H NMR[29] (200 MHz, $CDCl_3$) δ 6.20 (dd, 1 H, J = 11.6, 8.3 Hz, =CHCO), 7.50 (m, 6 H, Ar and PhCH=), 9.94 (d, 1 H, J = 8.1 Hz, CHO).

4-Methylcinnamaldehyde (5b): mp = 40.2 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3 H, Me), 6.67 (dd, 1 H, J = 16.0, 8.0 Hz, =CHCO), 7.23 (d, 2 H, J = 8.0 Hz, Ar), 7.44 (d, 1 H, J = 16.0 Hz, PhCH=), 7.46 (d, 2 H, J = 8.0 Hz, Ar), 9.67 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1690 (C=O). Anal. Calcd for $C_{10}H_{10}O$: C, 82.26; H, 6.90. Found: C, 81.97; H, 6.93.

4-Methoxycinnamaldehyde (5c): mp = 58.8 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 3 H, OMe), 6.58 (dd, 1 H, J = 16.0, 7.5 Hz, =CHCO), 6.93 (m, 2 H, Ar), 7.40 (d, 1 H, J = 16.0 Hz, PhCH=), 7.50 (m, 2 H, Ar), 9.63 (d, 1 H, J = 7.5 Hz, CHO); IR (KBr) 1690 (C=O). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.14; H, 6.22. Found: C, 73.96; H, 6.21.

4-(Dimethylamino)cinnamaldehyde (5d): mp = 134.7 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.02 (s, 6 H, 2 Me), 6.52 (dd, 1 H, J = 15.6, 7.9 Hz, =CHCO), 6.66 (m, 2 H, Ar), 7.35 (d, 1 H, J = 15.6 Hz, PhCH=), 7.40–7.48 (m, 2 H, Ar), 9.56 (d, 1 H, J = 7.9 Hz, CHO); IR (KBr) 1688 (C=O). Anal. Calcd for $C_{11}H_{13}ON$: C, 75.49; H, 7.49; N, 8.00. Found: C, 75.53; H, 7.52; N, 7.98.

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4-Nitrocinnamaldehyde (5e): mp = 142.0 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 6.95 (dd, 1 H, J = 16.1, 7.5 Hz, =CHCO), 7.83 (d, 1 H, J = 16.1 Hz, PhCH=), 8.02 (m, 2 H, Ar), 8.31 (m, 2 H, Ar), 9.79 (d, 1 H, J = 7.5 Hz, CHO); IR (KBr) 1695 (C=O). Anal. Calcd for $C_9H_7NO_3$: C, 61.07; H, 3.99; N, 7.91. Found: C, 61.00; H, 3.97; N, 7.88.

2-Hydroxycinnamaldehyde (5f). The OH group was protected in this reaction with TMSCl. The 2-siloxy benzaldehyde was readily prepared by heating at reflux (using a water bath) a solution of salicylaldehyde (10 g, 82 mmol) and chlorotrimethylsilane (12 mL, 90 mmol) in anhydrous ether (90 mL). Pyridine (6.5 g, 82 mmol) was added dropwise to this solution. The mixture was heated for 5 h. After the solution was gradually cooled to room temperature, the solution was filtered through a pad of Celite, the solvent was removed under reduced pressure, and the residue was distilled; bp 85–89 °C (5 mmHg). **5f**: mp = 122.0 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 6.83 (dd, 1 H, J = 16.1, 7.8 Hz, =CHCO), 6.86 (td, 1 H J = 8.0, 1.0 Hz, H-5 Ar), 7.10 (dd, 1 H, J = 8.0, 1.0 Hz, H-3 Ar), 7.25 (td, 1 H, J = 8.0, 1.7 Hz, H-4 Ar), 7.62 (dd, 1 H, J = 7.8, 2.0 Hz, H-6 Ar), 7.86 (d, 1 H, J = 16.1 Hz, PhCH=), 9.50 (d, 1 H, J = 7.8 Hz, CHO), 9.40 (br, D_2O exchangeable, OH); IR (KBr) 1685 (C=O). Anal. Calcd for $C_9H_8O_2$: C, 73.03; H, 5.45. Found: C, 73.23; H, 5.47.

2-Furyl-β-acrolein (5g): mp = 49 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 6.48 (dd, 1 H, J = 15.6, 8.0 Hz, =CHCO), 6.65 (dd, 1 H, J = 3.5, 1.8 Hz, H-4 Ar), 7.00 (d, 1 H, J = 3.5 Hz, H-3 Ar), 7.49 (d, 1 H, J = 15.7 Hz, ArCH=), 7.79 (m, 1 H, H-5 Ar), 9.66 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1687 (C=O). Anal. Calcd for $C_7H_6O_2$: C, 68.91; H, 4.96. Found: C, 68.71; H, 4.95.

(*E,E*)-5-Phenyl-2,4-pentadienal (5h). The corresponding imine has been isolated and characterized: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (s, 9 H, tBu), 6.46 (dd, 1 H, J = 15.1, 8.7 Hz, H-2), 6.68 (d, 1 H, J = 15.8 Hz, H-5), 6.72 (dd, 1 H, J = 15.0, 9.5 Hz, H-3), 6.89 (dd, 1 H, J = 15.6, 9.5 Hz, H-4), 7.19–7.44 (m, 5 H, Ar), 7.93 (d, 1 H, J = 8.7 Hz, H-1). Anal. Calcd for $C_{15}H_{19}N$: C, 84.58; H, 8.99; N, 6.58. Found: C, 84.51; H, 8.98; N, 6.57.

5h: mp = 39.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (dd, 1 H, J = 16.0, 8.0 Hz, H-2), 6.96 (dd, 1 H, J = 16.1, 7.8 Hz, H-4), 6.98 (d, 1 H, J = 16.1 Hz, H-5), 7.21 (dd, 1 H, J = 16.0, 7.8 Hz, H-3), 7.32–7.50 (m, 5 H, Ar), 9.57 (d, 1 H, J = 8.0 Hz, H-1); IR (KBr) 1690 (C=O). Anal. Calcd for $C_{11}H_{10}O$: C, 83.61; H, 6.38. Found: C, 83.45; H, 6.35.

(*E,E,E*)-7-Phenyl-2,4,6-heptatrienal (5i). Flash column chromatography was done with a mixture of cyclohexane/CH_2Cl_2 as eluant. **5i**: mp = 113.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (dd, 1 H, J = 16.0, 8.0 Hz, H-2), 6.53 (dd, 1 H, J = 14.6, 12.0 Hz, H-4), 6.79 (d, 1 H, J = 15.3 Hz, H-7), 6.81 (dd, 1 H, J = 14.6, 10.9 Hz, H-5), 6.87 (dd, 1 H, J = 15.3, 10.9 Hz, H-6), 7.15 (dd, 1 H, J = 16.0, 12.0 Hz, H-3), 7.28–7.48 (m, 5 H, Ar), 9.57 (d, 1H, J = 8.0 Hz, CHO); IR (KBr) 1685. Anal. Calcd for $C_{13}H_{12}O$: C, 84.85; H, 6.57. Found: C, 84.86; H, 6.55.

(*E,E,E,E*)-9-Phenyl-2,4,6,8-nonatetraenal (5j): mp = 140.0 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.20 (dd, 1 H, J = 15.1, 8.0 Hz, H-2), 6.59 (dd, 1 H, J = 14.6, 11.2 Hz, H-6), 6.64 (dd, 1 H, J = 14.8, 11.3 Hz, H-4), 6.78 (dd, 1 H, J = 14.6, 11.0 Hz, H-7), 6.81 (d, 1 H, J = 15.6 Hz, H-9), 6.95 (dd, 1 H, J = 14.7, 11.2 Hz, H-5), 7.09 (dd, 1 H, J = 15.5, 11.0 Hz, H-8), 7.27 (t, 1 H, J = 7.3 Hz, Ar), 7.36 (t, 2 H, J = 7.8 Hz, Ar), 7.40 (dd, 1 H, J = 15.1, 11.3 Hz, H-3), 7.52 (d, 2 H, J = 7.4 Hz, Ar), 9.54 (d, 1 H, J = 8.1 Hz, CHO); IR (KBr) 1680 (C=O). Anal. Calcd for $C_{15}H_{14}O$: C, 85.79; H, 6.72. Found: C, 85.65; H, 6.69.

(*E,E*)-5-(4-(Dimethylamino)phenyl)-2,4-pentadienal (5k): mp = 137.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.02 (s, 6 H, 2 Me), 6.17 (dd, 1 H, J = 15.0, 8.1 Hz, H-2), 6.67 (d, 2 H, J = 8.9 Hz, Ar), 6.80 (dd, 1 H, J = 15.3, 10.3 Hz, H-4), 6.96 (d, 1 H, J = 15.3 Hz, H-5), 7.25 (dd, 1 H, J = 15.0, 10.3 Hz, H-3), 7.40 (d, 2 H, J = 8.9 Hz, Ar), 9.55 (d, 1 H, J = 8.1 Hz, CHO); IR (KBr) 1684 (C=O). Anal. Calcd for $C_{13}H_{15}NO$: C, 77.68; H, 7.52; N, 6.97. Found: C, 77.61; H, 7.50; N, 7.00.

(*E,E*)-2,4-Hexadienal (5l). The corresponding imine was isolated and characterized: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14 (s, 9 H, tBu), 1.74 (d, 3 H, J = 9.0 Hz, Me), 5.84 (m, 1 H, H-5), 6.12 (dd, 1 H, J = 15.2, 10.5 Hz, H-4), 6.18 (dd, 1 H, J = 15.2, 9.0 Hz, H-2), 6.50 (dd, 1 H, J = 15.2, 10.3 Hz, H-3), 7.79 (d, 1 H, J = 8.9 Hz, H-1). Anal. Calcd for $C_{10}H_{17}N$: C, 79.54; H, 11.35; N, 9.28. Found: C, 79.60; H, 11.40; N, 9.30.

5l: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.88 (d, 3 H, J = 4.6 Hz, Me), 6.04 (dd, 1 H, J = 15.0, 8.0 Hz, H-2), 6.42 (m, 2 H, H-4 and H-5), 7.22 (m, 1 H, H-3), 9.54 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1682. Anal. Calcd for C_6H_8O: C, 75.06; H, 8.40. Found: C, 75.23; H, 8.39.

(*E,E,E*)-2,4,6-Octatrienal (5m): mp = 57.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77 (d, 3 H, J = 7.5 Hz, Me), 5.95 (m, 1 H, H-7), 6.04 (dd, 1 H, J = 15.0, 7.5 Hz, H-2), 6.12 (m, 1 H, J = 15.0, 10.0 Hz, H-6), 6.24 (dd, 1 H, J = 15.0, 11.2 Hz, H-4), 6.57 (dd, 1 H, J = 15.0, 11.2 Hz, H-5), 7.04 (dd, 1 H, J = 15.0, 11.2 Hz, H-3), 9.46 (d, 1 H, J = 7.5 Hz, CHO); IR (KBr) 1680 (C=O). Anal. Calcd for $C_8H_{10}O$: C, 78.75; H, 8.26. Found: C, 78.60; H, 8.27.

(*E,E,E,E*)-2,4,6,8-Decatetraenal (5n): mp = 105.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.78 (d, 3 H, J = 7.5 Hz, Me), 5.95 (m, 1 H, H-9), 6.14 (dd, 1 H, J = 15.0, 7.5 Hz, H-2), 6.21 (m, 1 H, J = 15.0, 10.0 Hz, H-8), 6.31 (dd, 1 H, J = 15.0, 11.2 Hz, H-6), 6.54 (dd, 1 H, J = 15.0, 10.0 Hz, H-7), 6.55 (dd, 1 H, J = 15.0, 11.2 Hz, H-4), 6.84 (dd, 1 H, J = 15.0, 11.2 Hz, H-5), 7.35 (dd, 1 H, J = 15.0, 11.2 Hz, H-3), 9.51 (d, 1 H, J = 7.5 Hz, CHO); IR (KBr) 1680 (C=O). Anal. Calcd for $C_{10}H_{12}O$: C, 81.15; H, 8.17. Found: C, 80.99; H, 8.18.

(*E,E*)-5-Methyl-2,4-hexadienal (5o). The corresponding imine has been isolated and characterized: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14 (s, 9 H, tBu), 1.76 (s, 6 H, 2 Me), 5.92 (d, 1 H, J = 11.2 Hz, H-4), 6.18 (dd, 1 H, J = 15.1, 9.0 Hz, H-2), 6.76 (dd, 1 H, J = 15.1, 11.2 Hz, H-3), 7.85 (d, 1 H, J = 9.0 Hz, H-1). Anal. Calcd for $C_{11}H_{19}N$: C, 80.07; H, 11.61; N, 8.49. Found: C, 80.23; H, 11.65; N, 8.51.

5o: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.87 (s, 6 H, 2 Me), 5.98 (dd, 1 H, J = 15.0, 8.1 Hz, H-2), 6.08 (d, 1 H, J = 12.0 Hz, H-4), 7.32 (dd, 1 H, J = 15.0, 12.0 Hz, H-3), 9.50 (dd, 1 H, J = 8.1, 1.3 Hz, CHO); IR (KBr) 1684 (C=O). Anal. Calcd for $C_7H_{10}O$: C, 76.43; H, 9.16. Found: C, 76.51; H, 9.19.

(*E,E,E*)-7-Methyl-2,4,6-octatrienal (5p): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.79 (s, 6 H, 2 Me), 5.92 (d, 1 H, J = 11.0, H-6), 6.04 (dd, 1 H, J = 15.1, 8.0 Hz, H-2), 6.25 (dd, 1 H, J = 14.6, 11.2 Hz, H-4), 6.84 (dd, 1 H, J = 14.6, 11.0 Hz, H-5), 7.12 (dd, 1 H, J = 15.1, 11.2 Hz, H-3), 9.46 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1680 (C=O). Anal. Calcd for $C_9H_{12}O$: C, 79.48; H, 8.89. Found: C, 79.41; H, 8.85.

(*E*)-4,4-Dimethyl-2-pentenal (5q). The corresponding imine has been isolated and characterized: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99 (s, 9 H, tBu), 1.12 (s, 9 H, tBu), 6.09 (m, 2 H, H-2 and H-3), 7.76 (m, 1 H, H-1). Anal. Calcd for $C_{11}H_{21}N$: C, 79.11; H, 12.68; N, 8.39. Found: C, 78.97; H, 12.64; N, 8.36.

5q: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 (s, 9 H, tBu), 6.01 (dd, 1 H, J = 15.8, 7.8 Hz, =CHCO), 6.78 (d, 1 H, J = 15.8 Hz, CH=), 9.48 (d, 1 H, J = 7.8 Hz, CHO); IR (KBr) 1690 (C=O). Anal. Calcd for $C_7H_{12}O$: C, 75.06; H, 10.80. Found: C, 75.35; H, 10.76.

(*E*)-2-Octenal (5r). Column flash chromatography was done using a mixture of cyclohexane/CH_2Cl_2 as eluant. **5r**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (m, 11 H, C_5H_{11}), 6.08 (ddt, 1 H, J = 14.1, 8.0, 2.0 Hz, =CHCO), 6.87 (td, 1 H, J = 14.1, 7.0 Hz, CH=), 9.48 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1687 (C=O). Anal. Calcd for $C_8H_{14}O$: C, 76.25; H, 11.20. Found: C, 76.49; H, 11.15.

(*E*)-2-Decenal (5s). Column flash chromatography was done using cyclohexane/CH_2Cl_2 as eluant. **5s**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (m, 15 H, C_7H_{15}), 6.06 (ddt, 1 H, J = 16.0, 8.0, 2.0 Hz, =CHCO), 6.81 (td, 1 H, J = 16.0, 8.0 Hz, CH=), 9.42 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1690. Anal. Calcd for $C_{10}H_{18}O$: C, 77.99; H, 11.78. Found: C, 77.73; H, 11.74.

(*E*)-4-(2-Methyl-2-dioxolanyl)-2-butenal (5t): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (s, 3 H, Me), 2.61 (dd, 2 H, J = 8.1, 2.0 Hz, H-4), 3.90 (s, 4 H, OCH_2CH_2O), 6.09 (ddt, 1 H, J = 15.9, 7.9, 2.0 Hz, H-2), 6.78 (td, 1 H, J = 15.9, 7.9 Hz, H-3), 9.44 (d, 1 H, J = 8.0 Hz, CHO); IR (KBr) 1695 (C=O). Anal. Calcd for $C_8H_{12}O_3$: C, 61.59; H, 7.75. Found: 61.44; H, 7.78.

3,3-Diphenyl-2-propenal (5u). A solution of benzophenone (10 mmol) and **3** (11.0 mmol) in THF (5 mL) was added dropwise to TBAF (1 mL, 10 mmol) in THF (10 mL) at room temperature. The resulting mixture was stirred for 2 h at room temperature and then for 2 h at reflux. Hydrolysis was carried out at room temperature with an aqueous solution of $ZnCl_2$ (2 g in 20 mL of water) and ether (25 mL) and the mixture was then stirred for 1 h at the same temperature. The precipitate was filtered on a pad of Celite. The aqueous phase was extracted with ether (2

× 25 mL), and the combined organic layers were washed with water (10 mL) and dried over $MgSO_4$. Purification of the reaction crude was done with a mixture of cyclohexane/acetone. **5u**: ^1H NMR (200 MHz, $CDCl_3$)[28] δ 6.61 (d, 1 H, J = 8.0 Hz, =CHCO), 7.32–7.48 (m, 10 H, Ar), 9.54 (d, 1 H J = 8.0 Hz CHO); IR (KBr) 1680 (C=O). Anal. Calcd for $C_{15}H_{12}O$: C, 86.61; H, 5.82. Found: C, 86.58; H, 5.80.

α-Methylcinnamaldehyde (9). To a mixture of benzaldehyde (1.06 g, 10 mmol) and $ZnBr_2$ (0.22 g, 11 mmol) in THF (10 mL) was added 8 (2.83 g, 11 mmol) in THF (5 mL), and the mixture was then stirred for 2 h at room temperature. The reaction was hydrolyzed by addition of $ZnCl_2$ (3 g in 20 mL of water) and ether (30 mL). The solution was stirred for 18 h. The precipitate was filtered through a pad of Celite, the water layer was extracted with ether (2 × 25 mL), the combined extracts were washed with water (10 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude oil was subjected to ^1H NMR analysis; a mixture of E and Z isomers of **9** (E/Z = 87/13) was formed in 78% yield. Column flash chromatography cyclohexane/acetone gave a pure mixture of isomers. Anal. Calcd for $C_{10}H_{10}O$: C, 82.26; H, 6.90. Found: C, 82.15; H, 6.87.

(*E*)-α-Methylcinnamaldehyde: ^1H NMR[30] (200 MHz, $CDCl_3$) δ 2.06 (d, 3 H, J = 1.3 Hz, CH_3), 7.24 (d, 1 H, J = 1.3 Hz, CH=), 7.40–7.51 (m, 5 H, Ar), 9.57 (s, 1 H, CHO).

(*Z*)-α-Methylcinnamaldehyde: ^1H NMR[30] (200 MHz, $CDCl_3$) δ 1.94 (d, 3 H, J = 1.5 Hz, CH_3), 7.30–7.48 (m, 6 H, Ar and CH=), 9.87 (s, 1 H, CHO).

4-Phenyl-3-buten-2-one (12). A mixture of 11 (2.83 g, 11 mmol) and benzaldehyde (1.06 g, 10 mmol) in THF (10 mL) was added dropwise at 0 °C to a solution of TBAF (0.5 mL, 0.5 mmol) in THF (5 mL). The resulting mixture was stirred for 2 h at 3 °C before being hydrolyzed by a solution of $ZnCl_2$ (2 g in 20 mL of water) and ether (25 mL) for 1 h at room temperature. The water layer was extracted with ether (2 × 25 mL), and the organic layer was washed with water (10 mL), dried over $MgSO_4$, and concentrated. The crude product was subjected to ^1H NMR analysis; a mixture of E and Z isomers of 12 (E/Z = 80/20) was formed in 70% yield. Flash chromatography of the crude afforded a pure mixture of the corresponding isomers. Anal. Calcd for $C_{10}H_{10}O$: C, 82.26; H, 6.90. Found: C, 82.19; H, 6.97.

(*E*)-4-Phenyl-3-buten-2-one: ^1H NMR[31] (200 MHz, $CDCl_3$) δ 2.37 (s, 3 H, CH_3), 6.70 (d, 1 H, J = 16.3 Hz, =CHCO), 7.42 (d, 1 H, J = 16.3 Hz, PhCH=), 7.36–7.54 (m, 5 H, Ar).

(*Z*)-4-Phenyl-3-buten-2-one: ^1H NMR[31] (200 MHz, $CDCl_3$) δ 2.15 (s, 3 H, CH_3), 6.30 (d, 1 H, J = 12.7 Hz, =CHCO), 7.02 (d, 1 H, J = 12.7 Hz, PhCH=), 7.40–7.89 (m, 5 H, Ar).

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