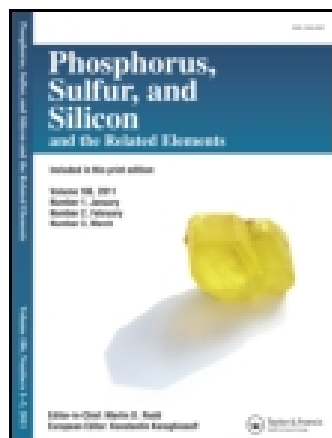


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### A Convenient Route to (E)- $\alpha,\beta$ -Unsaturated Methyl Ketones

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## A CONVENIENT ROUTE TO (*E*)- $\alpha,\beta$ -UNSATURATED METHYL KETONES

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*Aldehydes are converted into (*E*)- $\alpha,\beta$ -unsaturated methyl ketones in good yield and with a high *E* stereoselectivity using  $\alpha,\alpha$ -bis(trimethylsilyl) *N*-tert-butyl acetimine **3**. The reaction was mediated by a catalytic amount of tetrabutylammonium fluoride (TBAF) under mild conditions. The disilylated reagent **3** is easily generated from *N*-tert-butylacetimine, lithium diisopropylamide (LDA), and chlorotrimethylsilane. The mechanism of the reaction is discussed.*

**Keywords** LDA;  $\alpha$ -silylated acetimines; TBAF; *N*-tert-butylacetimine;  $\alpha,\beta$ -unsaturated methyl ketones

## INTRODUCTION

For many years, we have been interested in our laboratory in developing new approaches to retinoid synthesis using organosilicon reagents. For this purpose, we described in a previous work a new route for the (*E*)- $\alpha,\beta$ -unsaturated aldehydes synthesis using  $\alpha,\alpha$ -bis(trimethylsilyl) *N*-tert-butylaldimines.<sup>1,2</sup> We have just examined in the end of our article<sup>1</sup> the behavior of the  $\alpha,\alpha$ -bis(trimethylsilyl) *N*-tert-butylacetimine **3** with benzaldehyde leading to the benzylidene acetone **4a**. In this article, we report an account of our investigations concerning the extension of our methodology to various aldehydes and show that synthon **3** is a versatile organosilicon reagent for the direct homologation of aldehydes into (*E*)- $\alpha,\beta$ -unsaturated methyl ketones. This reagent **3** is now commercially available.

## RESULTS AND DISCUSSION

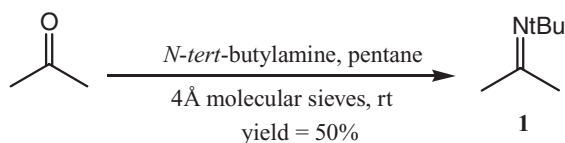
### Preparation of *N*-tert-Butylacetimine **1**

Reagent **1** was prepared from acetone and *N*-tert-butylamine in the presence of 4Å molecular sieves<sup>3</sup> at room temperature (Scheme 1). Molecular sieves serve simultaneously as a dehydrating agent and as a catalyst that can be removed at the end of the reaction by

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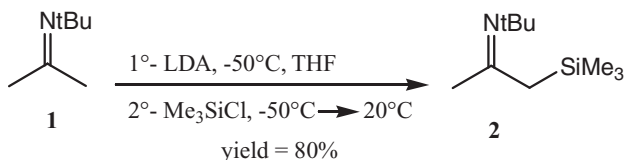
simple filtration. Since the method is so mild and so simple, it may prove preferable to the use of more vigorous catalysts such as titanium tetrachloride.<sup>4</sup>



Scheme 1

### Preparation of $\alpha$ -Trimethylsilyl *N*-*tert*-Butylacetimine **2**

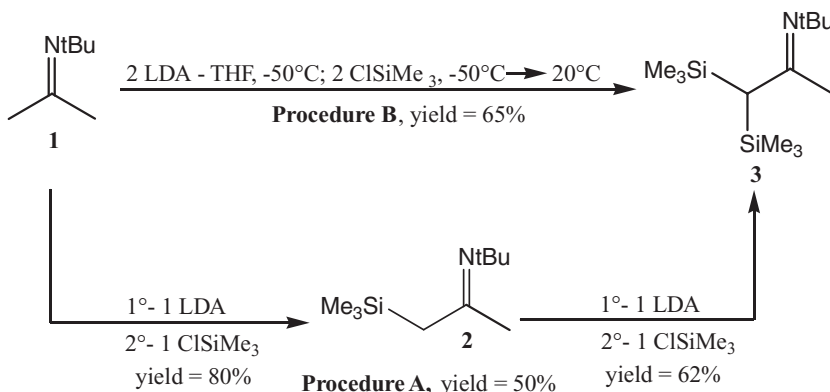
The monosilylated ketimine **2** was prepared from acetone *N*-*tert*-butylamine **1**, lithium diisopropylamide (LDA), and chlorotrimethylsilane (Scheme 2) according to a modified procedure described by Croteau and Termini.<sup>5</sup>



Scheme 2

### Preparation of $\alpha,\alpha$ -Bis(trimethylsilyl) *N*-*tert*-Butylacetimine **3**

Deprotonation of  $\alpha$ -trimethylsilyl *N*-*tert*-butyl ketimine **2** by one equivalent of LDA at -50°C followed by trimethylsilyl chloride trapping affords the disilylated ketimine **3** in 62% yield (procedure A), whereas a one-pot preparation of **3** can be achieved directly (procedure B) from *N*-*tert*-butylacetimine **1** (Scheme 3).



Scheme 3

### Reaction of the Disilylated Acetimine **3** with Benzaldehyde

The choice of the catalyst and the solvent is important in stereochemical outcomes and yields. Thus, our first investigations were focused on the reaction of **3** with benzaldehyde in the presence of several catalysts in different solvents in order to obtain the best yield associated with the highest *E* stereoselectivity. Results are reported in Table I.

The attempts carried out with Lewis acids (entries 1–6) show that zinc bromide (20%) in THF at room temperature for 24 h affords the expected enone **4a** in good yield and with very high *E* stereoselectivity (entry 3).

For the fluoride-catalyzed reaction of **3** with benzaldehyde, several sources of fluoride ion have been tested (entries 7–16). From the reported examples, CsF and TBAF in THF (entries 7–11) can be considered as the most active catalysts. However, TBAF is less hygroscopic and commercially available in THF.

On the basis of these results, TBAF in THF (entry 8) is selected as the representative catalyst and employed throughout this work.

### Stereoselective Synthesis of (*E*)- $\alpha,\beta$ -Unsaturated Methyl Ketones **4**

From the results reported in Table II, the reaction of the bis(trimethylsilyl) *N*-*tert*-butyl ketimine **3** was exceptionally effective for a large class of aldehydes. Aromatic

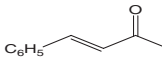
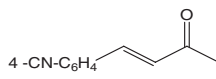
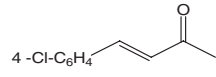
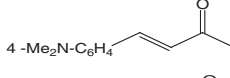
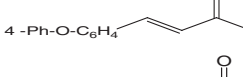
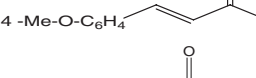
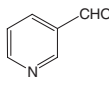
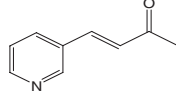
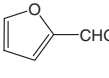
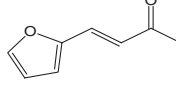
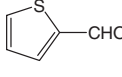
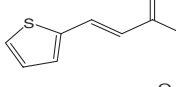
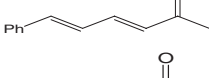

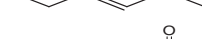
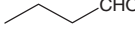
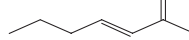
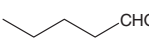

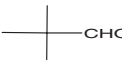
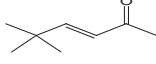
**Table I** Results of reaction of **3** with benzaldehyde in the presence of several catalysts in different solvents

Entry	Catalyst	Solvent	Reaction conditions	Yield (%) <sup>a</sup> <b>4a</b>	<i>E/Z</i> <sup>b</sup>
1	1eq. ZnBr <sub>2</sub>	THF	5 h, rt	90	100/0
2	20% ZnBr <sub>2</sub>	THF	5 h, rt	83	100/0
3	20% ZnBr <sub>2</sub>	THF	24 h, rt	95	100/0
4	10% ZnBr <sub>2</sub>	THF	24 h, rt	83	100/0
5	10% ZnBr <sub>2</sub>	Toluene	24 h, rt	80	70/30
6	10% BF <sub>3</sub>	Ether	24 h, rt	47	70/30
7	10% TBAF	THF	5 h, rt	84	87/13
8	20% TBAF	THF	5 h, rt	97	100/0
9	20% TBAF	THF	72 h, -5°C	76	80/20
10	20% TBAF	THF	72 h, -5°C then 3 h, rt	95	100/0
11	20% CsF	THF	24 h, rt	90	100/0
12	20% CsF	DMSO	24 h, rt	76	70/30
13	20% CsF	DMF	24 h, rt	88	77/23
14	20% NaF	THF	24 h, rt	82	70/30
15	20% KF	THF	72 h, rt	80	67/33
16	20% LiF	THF	72 h, rt	10	100/0

<sup>a</sup>Estimated by <sup>1</sup>H NMR on the crude reaction mixture with respect to nonreacted benzaldehyde (molar percentage).

<sup>b</sup>The stereoselectivity of the compound **4a** is determined by the <sup>1</sup>H NMR spectrum of the crude product.

**Table II** Synthesis of  $\alpha,\beta$ -unsaturated methyl ketones **4** using reagent **3**

Entry	Starting aldehydes	Time (h)	Unsaturated methyl ketones	<b>4</b>	Yield (%) <sup>a</sup>	<i>E/Z</i> <sup>b</sup>	Ref.
1	C <sub>6</sub> H <sub>5</sub> – CHO	5		<b>4a</b>	97	100/0	[6]
2	4-CNC <sub>6</sub> H <sub>4</sub> –CHO	5		<b>4b</b>	85	90/10	[7]
3	4-ClC <sub>6</sub> H <sub>4</sub> –CHO	6		<b>4c</b>	90	87/13	[8]
4	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> –CHO	6		<b>4d</b>	80	100/0	[9]
5	4-PhOC <sub>6</sub> H <sub>4</sub> –CHO	5.5		<b>4e</b>	87	94/6	[10]
6	4-MeOC <sub>6</sub> H <sub>4</sub> –CHO	5.5		<b>4f</b>	80	93/7	[11]
7		1		<b>4g</b>	86	87/13	[12]
8		5		<b>4h</b>	97	92/8	[13]
9		5		<b>4i</b>	82	94/6	[14]
10	Ph–CH=CH–CHO	3		<b>4j</b>	92	70/30	[15]
11		2		<b>4k</b>	100	100/0	[16]
12		1		<b>4l</b>	90	100/0	[16]
13		1.5		<b>4m</b>	85	100/0	[16]
14		2.5		<b>4n</b>	100	100/0	[17]

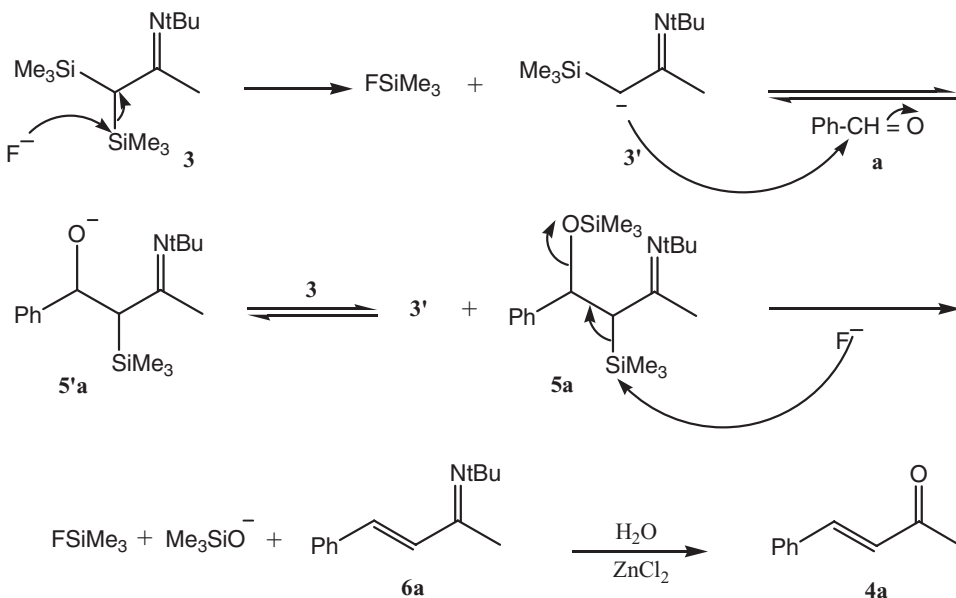
<sup>a</sup>Isolated yield.<sup>b</sup>The stereoselectivity of each compound is determined by the <sup>1</sup>H NMR spectrum of the crude product.

(entries 1–6) and heteroaromatic aldehydes (entries 7–9) were tested and gave the corresponding  $\alpha,\beta$ -ethylenic methyl ketone in good yield and with a high *E*-stereoselectivity. Saturated aldehydes (entries 11–14) undergo rapid condensation with **3** and afford only the *E* isomer. The reaction has also been performed on one  $\alpha,\beta$ -ethylenic aldehyde (entry 10), and conjugated enones, resulting from 1,2 addition, are exclusively formed in good yield.

As can be seen from the reported examples, the reaction of the disilylated reagent **3** with aldehydes exhibits high *E*-selectivity. This is not the case of the lithium derivative of the monosilylated *N*-*tert*-butylacetimine **2**.<sup>5</sup>

### Reaction Mechanism

A tentative reaction mechanism with a fluoride ion is shown in Scheme 4. It is very reasonable to assume that the reaction is initiated by a fluoride ion to generate the carbanion **3'**, which then reacts with benzaldehyde to give the alkoxide **5'a**. The reaction of the latter with **3** affords the intermediate **5a** and the regenerated carbanion **3'** in the reaction media. Further elimination of trimethylsilyl alkoxide gives the corresponding  $\alpha,\beta$ -unsaturated imine **6a**. Alternatively, the reaction could also be catalyzed by the in situ formed  $\text{Me}_3\text{SiO}^-$ . Mild acidic hydrolysis of **6a** affords the expected *E*-benzylideneacetone **4a**.



Scheme 4

Concerning the stereoselection of the reaction, in all cases, *E* isomers are formed exclusively or in majority. This result is very likely due to a thermodynamical control of the reaction (Table I, entries 8–10). Our attempts to isolate the intermediate **5a** (Scheme 4), in order to study the correlation between the elimination mechanism and the product stereochemistry, have failed. Indeed, condensation and elimination reactions must be fast, even at low temperature (Table I, entry 9). However, the unsaturated imine **6a** (Scheme 4) has been isolated and characterized.

## CONCLUSION

In conclusion and from the results obtained in this study, the disilylated acetimine **3** has proved to be a versatile organosilicon reagent for the direct homologation of aldehydes into  $\alpha,\beta$ -ethylenic methyl ketones. Indeed,  $\alpha,\alpha$ -bis(trimethylsilyl) *N*-*tert*-butyl ketimine **3** reacts with various aldehydes in the presence of a catalytic amount of TBAF at room temperature to give the desired  $\alpha,\beta$ -enones **4** with an excellent *E* stereoselectivity. This is not the case of the unsaturated methyl ketones prepared using the monosilylated acetimine **2**.<sup>5</sup>

## EXPERIMENTAL

All reactions involving water-sensitive compounds are carried out in oven-dried glassware and under nitrogen atmosphere. Unless otherwise noted, starting materials were purchased from commercial sources and used as received. All the solvents were dried and distilled prior to use. LDA was prepared in situ from diisopropylamine and *n*-butyl lithium (2.5 M solution in hexane).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 250 MHz using CDCl<sub>3</sub> or acetone-*d*<sub>6</sub> as solvent. Chemical shifts are given in ppm (*J* in Hz) relative to chloroform or acetone. Flash chromatography was done on Merck grade 60 silica gel (230–400 mesh) using mixtures of cyclohexane and ethyl acetate as eluent. Melting points were uncorrected.

### Preparation of Zinc Bromide

Zinc bromide was prepared by heating ground zinc (3.6 g, 55 mmol) and 1,2-dibromoethane (9.4 g, 50 mmol) in THF (100 mL) for 16 h at reflux. The resulting solution was allowed to cool slowly at room temperature. The remaining excess zinc was removed by filtration. Complete evaporation of the solvent under high vacuum gave pure ZnBr<sub>2</sub> as a white powder.<sup>1</sup>

### Preparation of *N*-*tert*-Butylacetimine 1

The acetimine **1** is prepared according to the procedure described by Taguchi and Westheimer<sup>3</sup> with a minor modification: To a solution of acetone (0.5 mol, 29 g), *tert*-butylamine (0.55 mol, 40 g), pyridine (2 mL), and pentane (150 mL), 40 g of molecular sieves (4Å) were added. The mixture was left at room temperature for 24 h, then the molecular sieves were filtered from the solution and washed with pentane (20 mL). The solvent and the nonreacted reagents were removed by simple distillation and the product was purified by fractionally distillation. Bp: 94°C/760 mmHg; yield = 56%.

### Preparation of $\alpha$ -(Trimethylsilyl) *N*-*tert*-Butylacetimine 2

To a cooled (–50°C) solution of LDA (50 mmol) in anhydrous THF (50 mL), a solution of *N*-*tert*-butylacetimine **1** (5.05 g, 50 mmol) in THF (5 mL) was added. The resulting mixture was stirred at –50°C for 18 h. Trimethylchlorosilane (6.5 mL, 50 mmol) was added at –50°C, and the solution was stirred for 1 h at this temperature. Then, the solution was gradually warmed to room temperature and filtered through a pad of Celite.

The solvent was removed under reduced pressure, and distillation of the remaining oil gave the monosilylated acetimine **2**.

Bp: 65°C/15 mmHg; yield = 80%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ = 0.06 (s, 9H, SiMe<sub>3</sub>), 1.26 (s, 9H, *t*Bu), 1.78 (s, 2H, CH<sub>2</sub>), 1.88 (s, 3H, CH<sub>3</sub>). Anal. Calc for C<sub>10</sub>H<sub>23</sub>NSi: C, 64.86; H, 12.43. Found: C, 64.26; H, 12.13.

### Preparation of α,α-Bis(trimethylsilyl) *N*-*tert*-Butylacetimine **3**

**Procedure A.** To a cooled (−50°C) solution of LDA (50 mmol) in anhydrous THF (50 mL), a solution of α-(trimethylsilyl)*N*-*tert*-butylacetimine **2** (8.65 g, 50 mmol) in THF (5 mL) was added. The resulting mixture was stirred at −50°C for 4 h. Trimethylchlorosilane (6.5 mL, 50 mmol) was added at −50°C, and the solution was stirred for 1 h at this temperature. The solution was then gradually warmed to room temperature and filtered through a pad of Celite. The solvent was removed under reduced pressure, and distillation of the remaining oil gave the disilylated acetimine **3**.

Bp: 106°C/12 mmHg; yield = 62%. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ = 0.07 (s, 18H, 2SiMe<sub>3</sub>), 1.25 (s, 10H, *t*Bu, CH), 1.89 (s, 3H, CH<sub>3</sub>). Anal. Calc for C<sub>13</sub>H<sub>31</sub>NSi<sub>2</sub>: C, 60.70; H, 12.06. Found: C, 60.52; H, 12.15.

**Procedure B.** The compound **3** can also be prepared directly from **1**. To a cooled (−50°C) solution of LDA (100 mmol) in anhydrous THF (50 mL), **1** (5.05 g, 50 mmol) was added dropwise at −50°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 −50°C, and the solution was stirred for 5 h at this temperature, then the second portion (6.5 mL, 50 mmol) was added, and the solution was stirred for 45 min at −50°C. 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 = 65%.

### Preparation of α,β-Unsaturated Methylketones **4a–n**

A detailed procedure for the reaction of **3** with aldehydes in THF using TBAF (20%) as catalyst is given below. All reactions are carried out in similar manner under nitrogen atmosphere.

Reaction times, yields, and the *E/Z* ratios are reported in Table II. Physical, spectral, and analytical data for the obtained unsaturated methylketones follow.

To a stirred solution of aldehyde (10 mmol) and reagent **3** (2.45 g, 10 mmol) in THF (10 mL), TBAF (2 mmol) was added dropwise at room temperature; the reaction was exothermic. The temperature was maintained at 20–25°C with a water bath. The reaction was checked using TLC until disappearance of the starting aldehyde. Then, the resulting mixture was hydrolyzed by addition of an aqueous solution of ZnCl<sub>2</sub> (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<sub>4</sub>. The solvent was removed in vacuo. The reaction crude was purified by flash chromatography to give the corresponding products **4a–n**.

**(E)-4-Phenylbut-3-en-2-one (4a).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ = 2.38 (s, 3H, CH<sub>3</sub>), 6.71 (d, 1H, *J* = 16 Hz), 7.50 (d, 1H, *J* = 16 Hz), 7.3–7.62 (m, 5H, Ar). <sup>13</sup>C NMR



(250 MHz, CDCl<sub>3</sub>)  $\delta$  = 28.4, 126.5, 129.4, 142.8, 196.0. IR (neat): 1701 cm<sup>-1</sup> (C=O), 1597 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>10</sub>H<sub>10</sub>O: C, 82.19; H, 6.85. Found: C, 82.37; H, 6.45.

**(Z)-4-Phenylbut-3-en-2-one (4a).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.17 (s, 3H, CH<sub>3</sub>), 6.30 (d, 1H, *J* = 12 Hz), 7.09 (d, 1H, *J* = 12 Hz), 7.38–7.90 (m, 5H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 31.2, 124.3, 128.1, 141.7, 192.9. IR (neat): 1670 cm<sup>-1</sup> (C=O), 1618 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>10</sub>H<sub>10</sub>O: C, 82.19; H, 6.85. Found: C, 82.52; H, 6.75.

**(E)-4-(3-Oxobut-1-enyl)benzotrile (4b).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.39 (s, 3H, CH<sub>3</sub>), 6.69 (d, 1H, *J* = 16.4 Hz), 7.43 (d, 1H, *J* = 16.4 Hz), 7.30–7.60 (m, 4H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 29.4, 126.4, 130.1, 138.4, 142.9, 197.3. IR (neat): 1681 cm<sup>-1</sup> (C=O), 1616 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>11</sub>H<sub>9</sub>NO: C, 77.19; H, 5.26. Found: C, 77.34; H, 5.32.

**(Z)-4-(3-Oxobut-1-enyl)benzotrile (4b).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.19 (s, 3H, CH<sub>3</sub>), 6.03 (d, 1H, *J* = 12.5 Hz), 6.88 (d, 1H, *J* = 12.5 Hz), 7.29–7.68 (m, 4H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 31.2, 125.9, 131.6, 139.2, 142.7, 198.5. IR (neat): 1673 cm<sup>-1</sup> (C=O), 1620 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>11</sub>H<sub>9</sub>NO: C, 77.19; H, 5.26. Found: C, 77.32; H, 5.15.

**(E)-4-(4-Chlorophenyl) but-3-en-2-one (4c).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.40 (s, 3H, CH<sub>3</sub>), 6.68 (d, 1H, *J* = 16.3 Hz), 7.41 (d, 1H, *J* = 16.3 Hz), 7.05–7.55 (m, 4H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 28.4, 126.7, 129.9, 135.4, 141.9, 198.3. IR (neat): 1675 cm<sup>-1</sup> (C=O), 1621 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>10</sub>H<sub>9</sub>ClO: C, 66.48; H, 4.99. Found: C, 66.12; H, 4.79.

**(Z)-4-(4-Chlorophenyl) but-3-en-2-one (4c).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.21 (s, 3H, CH<sub>3</sub>), 5.95 (d, 1H, *J* = 12.3 Hz), 6.68 (d, 1H, *J* = 12.3 Hz), 7.10–7.70 (m, 4H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 31.2, 125.9, 128.7, 136.5, 142.3, 197.7. IR (neat): 1665 cm<sup>-1</sup> (C=O), 1630 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>10</sub>H<sub>9</sub>ClO: C, 66.48; H, 4.99. Found: C, 66.22; H, 4.59.

**(E)-4-(4-(Dimethylamino) phenyl) but-3-en-2-one (4d).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.37 (s, 3H, CH<sub>3</sub>), 2.82 (s, 6H, 2CH<sub>3</sub>), 6.64 (d, 1H, *J* = 16.2 Hz), 6.45–7.26 (m, 4H, Ar), 7.48 (d, 1H, *J* = 16.2 Hz). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 29.2, 41.1, 114.1, 126.7, 127.8, 139.8, 144.1, 198.3. IR (neat): 1671 cm<sup>-1</sup> (C=O), 1627 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>12</sub>H<sub>15</sub>NO: C, 76.19; H, 7.94. Found: C, 76.29; H, 7.78.

**(E)-4-(4-Phenoxyphenyl) but-3-en-2-one (4e).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.25 (s, 3H, CH<sub>3</sub>), 6.55 (d, 1H, *J* = 16.27 Hz), 7.33 (d, 1H, *J* = 16.27 Hz), 6.6–7.4 (m, 9H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 27.9, 128.0, 143.2, 198.8. IR (neat): 1675 cm<sup>-1</sup> (C=O), 1616 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: C, 80.67; H, 5.88. Found: C, 80.17; H, 5.80.

**(Z)-4-(4-Phenoxyphenyl) but-3-en-2-one (4e).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.17 (s, 3H, CH<sub>3</sub>), 6.05 (d, 1H, *J* = 12.66 Hz), 6.79 (d, 1H, *J* = 12.66 Hz), 6.6–7.4 (m, 9H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 25.9, 130.0, 139.6, 192.1. IR (neat): 1664 cm<sup>-1</sup> (C=O), 1621 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: C, 80.67; H, 5.88. Found: C, 80.47; H, 5.57.

**(E)-4-(4-Methoxyphenyl) but-3-en-2-one (4f).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.33 (s, 3H, CH<sub>3</sub>), 3.78 (s, 3H, CH<sub>3</sub>O), 6.54 (d, 1H, *J* = 16.2 Hz), 7.41 (d, 1H, *J* = 16.2 Hz), 6.9–7.5 (m, 4H, Ar). <sup>13</sup>C NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 27.8, 55.7, 114.71, 125.4, 130.3, 132.2, 143.6, 162.0, 198.8. IR (neat): 1678 cm<sup>-1</sup> (C=O), 1610 cm<sup>-1</sup> (C=C). Anal. Calc for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>: C, 75.00; H, 6.81. Found: C, 75.12; H, 6.62.

**(Z)-4-(4-Methoxyphenyl) but-3-en-2-one (4f).** <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  = 2.16 (s, 3H, CH<sub>3</sub>), 3.85 (s, 3H, CH<sub>3</sub>O), 6.07 (d, 1H, *J* = 12.6 Hz), 6.91 (d, 1H, *J* = 12.6

Hz), 6.71–7.55 (m, 4H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.3, 56.0, 114.0, 127.2, 129.1, 132.3, 142.3, 160.3, 193.2. IR (neat): 1679  $\text{cm}^{-1}$  (C=O), 1618  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_{11}\text{H}_{12}\text{O}_2$ : C, 75.00; H, 6.81. Found: C, 75.18; H, 6.48.

**(E)-4-(Pyridin-3-yl) but-3-en-2-one (4g).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.39 (s, 3H,  $\text{CH}_3$ ), 5.58 (d, 1H,  $J$  = 16.24 Hz), 6.01 (d, 1H,  $J$  = 16.24 Hz), 6.8–7.75 (m, 4H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 29.4, 127.5, 129.9, 143.8, 196.8. IR (neat): 1668  $\text{cm}^{-1}$  (C=O), 1614  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_9\text{H}_9\text{NO}$ : C, 73.47; H, 6.12. Found: C, 73.97; H, 6.22.

**(Z)-4-(Pyridin-3-yl) but-3-en-2-one (4g).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.24 (s, 3H,  $\text{CH}_3$ ), 5.47 (d, 1H,  $J$  = 12.3 Hz), 6.02 (d, 1H,  $J$  = 12.3 Hz), 7.07–8.10 (m, 4H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 31.2, 126.9, 130.1, 144.2, 198.1. IR (neat): 1674  $\text{cm}^{-1}$  (C=O), 1621  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_9\text{H}_9\text{NO}$ : C, 73.47; H, 6.12. Found: C, 73.26; H, 6.15.

**(E)-4-(Furan-2-yl) but-3-en-2-one (4h).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.26 (s, 3H,  $\text{CH}_3$ ), 6.42 (d, 1H,  $J$  = 15.9 Hz), 7.33 (d, 1H,  $J$  = 15.9 Hz), 6.2–7.4 (m, 3H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 28.2, 112.9, 113.0, 124.6, 129.8, 143.2, 145.4, 198.2. IR (neat): 1690  $\text{cm}^{-1}$  (C=O), 1610  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_8\text{O}_2$ : C, 70.59; H, 5.88. Found: C, 70.18; H, 5.68.

**(Z)-4-(Furan-2-yl) but-3-en-2-one (4h).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.15 (s, 3H,  $\text{CH}_3$ ), 6.01 (d, 1H,  $J$  = 12.7 Hz), 6.85 (d, 1H,  $J$  = 12.7 Hz), 7.05–7.40 (m, 3H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 31.6, 110.6, 114.1, 123.5, 129.6, 144.9, 151.2, 198.2. IR (neat): 1681  $\text{cm}^{-1}$  (C=O), 1619  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_8\text{O}_2$ : C, 70.59; H, 5.88. Found: C, 70.71; H, 5.67.

**(E)-4-(Thiophen-2-yl) but-3-en-2-one (4i).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.29 (s, 3H,  $\text{CH}_3$ ), 6.47 (d, 1H,  $J$  = 15.9 Hz), 6.5–7.5 (m, 3H, Ar), 7.61 (d, 1H,  $J$  = 15.9 Hz).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 29.1, 127.0, 129.9, 130.1, 132.8, 134.8, 137.7, 195.8. IR (neat): 1664  $\text{cm}^{-1}$  (C=O), 1595  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_8\text{SO}$ : C, 63.16; H, 5.26. Found: C, 63.25; H, 5.15.

**(Z)-4-(Thiophen-2-yl) but-3-en-2-one (4i).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.16 (s, 3H,  $\text{CH}_3$ ), 6.07 (d, 1H,  $J$  = 12.2 Hz), 6.60 (d, 1H,  $J$  = 12.2 Hz), 6.90–7.45 (m, 3H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 23.6, 126.9, 129.6, 129.9, 130.1, 133.8, 138.2, 185.7. IR (neat): 1670  $\text{cm}^{-1}$  (C=O), 1610  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_8\text{SO}$ : C, 63.16; H, 5.26. Found: C, 63.55; H, 5.33.

**(3E, 5E)-6-Phenylhexa-3, 5-dien-2-one (4j).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.26 (s, 3H,  $\text{CH}_3$ ), 6.01 (d, 1H,  $J$  = 15.3 Hz), 6.28 (dd, 1H,  $J$  = 15.3, 10.2 Hz), 6.31 (d, 1H,  $J$  = 15.3 Hz), 6.42 (dd, 1H,  $J$  = 15.3, 10.2 Hz), 7.25–7.48 (m, 5H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 31.2, 130.1, 132.4, 134.3, 137.8, 139.5, 139.7, 143.2, 194.3. IR (neat): 1674  $\text{cm}^{-1}$  (C=O), 1612  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_{12}\text{H}_{12}\text{O}$ : C, 83.72; H, 6.97. Found: C, 83.31; H, 6.78.

**(3Z, 5E)-6-Phenylhexa-3,5-dien-2-one (4j).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.21 (s, 3H,  $\text{CH}_3$ ), 6.11 (d, 1H,  $J$  = 11.6 Hz), 6.15 (dd, 1H,  $J$  = 11.6, 7.2 Hz), 6.40 (d, 1H,  $J$  = 15.8 Hz), 6.42 (dd, 1H,  $J$  = 15.8, 7.2 Hz), 7.01–7.41 (m, 5H, Ar).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 28.1, 128.9, 130.8, 132.5, 136.1, 138.7, 139.1, 144.9, 190.1. IR (neat): 1670  $\text{cm}^{-1}$  (C=O), 1619  $\text{cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_{12}\text{H}_{12}\text{O}$ : C, 83.72; H, 6.97. Found: C, 83.47; H, 6.67.

**(E)-Hex-3-en-2-one (4k).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.89 (t, 3H,  $\text{CH}_3$ ), 1.97 (m, 2H,  $\text{CH}_2$ ), 2.35 (s, 3H,  $\text{COCH}_3$ ), 5.97 (d, 1H,  $J$  = 16.16 Hz), 6.63 (dt, 1H,

$J = 16.16$  Hz).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 10.9, 23.5, 31.3, 130.5, 145.3, 197.9$ . IR (neat):  $1687\text{ cm}^{-1}$  (C=O),  $1624\text{ cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_6\text{H}_{10}\text{O}$ : C, 73.47; H, 10.20. Found: C, 73.89; H, 10.32.

**(E)-Hept-3-en-2-one (4l).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 0.95$  (t, 3H,  $\text{CH}_3$ ), 1.75 (m, 2H,  $\text{CH}_2$ ), 2.05 (m, 2H,  $\text{CH}_2 = \text{CH}$ ), 2.37 (s, 3H,  $\text{COCH}_3$ ), 6.01 (d, 1H,  $J = 16.28$  Hz), 6.59 (dt, 1H,  $J = 16.28$  Hz).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 10.9, 23.6, 32.5, 34.5, 129.5, 146.4, 197.7$ . IR (neat):  $1697\text{ cm}^{-1}$  (C=O),  $1629\text{ cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_7\text{H}_{12}\text{O}$ : C, 75.00; H, 10.71. Found: C, 75.12; H, 10.51.

**(E)-Oct-3-en-2-one (4m).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 0.92$  (t, 3H,  $\text{CH}_3$ ), 1.15–1.84 (m, 4H, 2  $\text{CH}_2$ ), 2.25 (m, 2H,  $\text{CH}_2\text{CH} =$ ), 2.34 (s, 3H,  $\text{COCH}_3$ ), 6.03 (d, 1H,  $J = 16.26$  Hz), 6.63 (dt, 1H,  $J = 16.26$  Hz).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 11.5, 24.6, 28.9, 31.8, 32.3, 124.4, 156.3, 197$ . IR (neat):  $1695\text{ cm}^{-1}$  (C=O),  $1625\text{ cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_{14}\text{O}$ : C, 76.19; H, 11.11. Found: C, 76.79; H, 11.41.

**(E)-5,5-Dimethylhex-3-en-2-one (4n).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 1.04$  (s, 9H, *t*Bu), 2.22 (s, 3H,  $\text{COCH}_3$ ), 5.93 (d, 1H,  $J = 16.2$  Hz), 6.73 (d, 1H,  $J = 16.2$  Hz).  $^{13}\text{C}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta = 28.9, 31.8, 32.3, 124.4, 156.3, 197.6$ . IR (neat):  $1678\text{ cm}^{-1}$  (C=O),  $1622\text{ cm}^{-1}$  (C=C). Anal. Calc for  $\text{C}_8\text{H}_{14}\text{O}$ : C, 76.19; H, 11.11. Found: C, 76.68; H, 11.52.

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