# An Expedient Protocol for Cyclopentenone Annulation

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This publication is dedicated to Prof. Hsing-Jang Liu on the occasion of his 60th birthday.

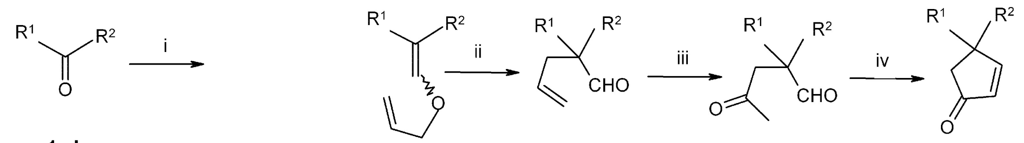
**Abstract:** A convenient and general protocol for the cyclopentenone annulation process is described.

**Key words:** cyclopentenone annulation, Wittig olefination, Claisen rearrangement, Wacker oxidation, polyquinanes

The cyclopentenone annulation process has considerable synthetic value, as one or more cyclopentane rings are part of several natural products[1–8] like the polyquinanes. The importance of this is evident by the numerous cyclopentenone annulation methodologies currently available.[9–20] In spite of this, construction of a sterically crowded cyclopentane ring is still a challenging task and inspires the development of novel approaches toward this end. In the context of our interests in the synthesis of cyclopentanoid natural products, namely (±)-α-cuparenone[19] and (±)-laurene,[19] we have developed a convenient and efficient protocol for the construction of 4-substituted and 4,4-disubstituted-2-cyclopentenones. This consists of four steps: Wittig olefination to an allyl vinyl ether;[20] Claisen rearrangement;[21–23] Wacker oxidation;[24] and finally, intramolecular aldol condensation.

Wittig olefination of aldehydes and ketones with allyloxymethylenetriphenylphosphonium chloride under reported reaction conditions[20] afforded the corresponding allyl vinyl ethers, in most cases, as an inseparable mixture of *E* and *Z* isomers[25] (Table 1). Heating these allyl vinyl ethers in refluxing xylene effected the Claisen rearrangement and gave substituted 4-pentenals in near quantitative yields. Under standard Wacker oxidation conditions, these 4-pentenals were converted smoothly to the corresponding ketoaldehydes in good yields. The aldehyde group remained unaffected under the Wacker conditions.

**Table 1**




| | $R^1$ | $R^2$ | | | | |
|---|---|---|---|---|---|---|
| **a** | Ph | $CH_3$ | 83% | 96% | 83% | 89% |
| **b** | [4-(Me)$C_6H_4$] | $CH_3$ | 81% | 93% | 84% | 90% |
| **c** | [3,4-di-(OMe)-$C_6H_3$]$CH_2CH_2$ | $CH_3$ | 81% | 97% | 83% | 86% |
| **d** | [4-(OMe)$C_6H_4$]$CH_2CH_2$ | $CH_3$ | 85% | 94% | 76% | 88% |
| **e** | $CH_3CH_2CH_2$ | $CH_3CH_2CH_2$ | 78%[31] | 89% | 71% | 83% |
| **f** | $CH_3CH_2CH_2$ | $CH_3(CH_2)_3$ | 77%[31] | 88% | 73% | 81% |
| **g** | $CH_3CH_2$ | $CH_3$ | 74%[31] | 84% | 72% | 82% |
| **h** | [3,4-di-(OMe)$C_6H_3$] | H | 86% | 95% | 76% | 87%[26] |

Reagents and Conditions:
i) $CH_2CHCH_2OCH_2Ph_3P^+Cl^-$, THF, *t*-BuO$^-$K$^+$/*t*-BuOH, 0 °C. ii) Xylene, reflux, 4–5 h. iii) $PdCl_2/CuCl_2$ (10 mol% each), $O_2$, $H_2O$–DME (1:9), r.t., 2–3 h. iv) 5% aq. methanolic KOH, r.t., 2 h.

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Intramolecular aldol condensation of the ketoaldehydes with 5% methanolic KOH afforded 2-cyclopentenones in excellent yields. The whole sequence is short enough to be executed in a single long working day.

All solvents were distilled and dried before use. 'Acme' silica gel (100–200 mesh) was used for column chromatography, and a hexane–EtOAc solvent system was used for elution. The mp and bp values are uncorrected and were obtained using a paraffin oil bath. The FT-IR spectra were recorded on a Perkin-Elmer 1600 series instrument. $^{1}H$ and $^{13}C$ NMR spectra were recorded on JEOL FX 90Q/Varian Mercury 300 instrument. Elemental analyses were obtained on a HOSLI semi-automatic C, H analyzer.

**General Procedures**[32]

To a suspension of aldehyde or ketone **1a**–**h** (5 mmol) and allyloxymethylenetriphenylphosphonium chloride (1.2 equiv) in dry THF at 0 °C was dropwise added a solution of KO*t*-Bu (1.2 equiv) in dry *t*-BuOH. After one hour, the normal aqueous extractive work up gave crude allyl vinyl ethers. Passing these crude products through a short silica gel column afforded the allyl vinyl ethers **2a**–**h** in 74–86% yield and in sufficiently pure form for the next reaction.

## Biographical Sketches


**Mukund G. Kulkarni** was born in India in 1953. He received his B.Sc. in 1973 and M.Sc. in 1975 from the University of Pune, and his doctoral degree in organic chemistry from the University of Alberta in 1985. He returned to India and was a lecturer at the University of Pune from January 1989 to December 1996 and is currently a reader at the same place. His research interests include total synthesis of natural products, newer synthetic methods, asymmetric synthesis, chemistry of carbohydrates and radical cyclisation methods in synthesis.

**Saryu I. Davawala** was born in India in 1969. She received her B.Sc. in 1990 and M.Sc. in 1992 from the University of Pune and completed her Ph. D. from the Department of Chemistry, University of Pune, in May 1999 under the guidance of Dr. M. G. Kulkarni. She worked as a postdoctoral fellow in Dr. Reddy's Research Foundation, Hyderabad from May to August, 2000. She worked as an Executive R&D in SPARC, Baroda from January to April, 2001. She was appointed as a lecturer in the Department of Chemistry, University of Pune from September 2001 to August 2002 and from November 2002 to July 2003. She is currently a Young Scientist, DST, in the same department.

**Aniruddha K. Doke** was born in India in 1976. He received his B.Sc. in 1996 and M.Sc. in 1998 from the University of Pune. He served as a research associate in Colgate-Palmolive (India) Ltd, Mumbai, India from June to December of 1998. He is currently pursuing his doctoral degree under the guidance of Dr. M. G. Kulkarni.

**Dhananjay S. Pendharkar** was born in India in 1969. He completed his B.Sc. in 1990 from Shivaji University, Kolhapur, and his M.Sc. in 1992 from the University of Pune and Ph.D. from the Department of Chemistry, University of Pune, in 1998 under the guidance of Dr. M. G. Kulkarni. He pursued postdoctoral research at the University of Kentucky from 1998 to 2000. He then joined Wockhardt, India, Aurangabad and is currently working in Aurigene Discovery Tech. Ltd., Bangalore.

A solution of the allyl vinyl ethers **2a**–**h** was heated in refluxing xylene for 4–5 h. Removal of xylene under reduced pressure gave 4-pentenals **3a**–**h** in 84–97% yield and in fairly pure form.

The 4-pentenals **3a**–**h**, $PdCl_2$ (10 mol%), and $CuCl_2$ (10 mol%) were dissolved in aqueous DME (1:9) and stirred under an oxygen atmosphere for 2–3 h. When the reaction was observed to be complete, normal aqueous extractive work-up gave the ketoaldehydes **4a**–**h** in 71–84% yield.

The crude ketoaldehydes **4a**–**4h** were dissolved in 5% aq. methanolic KOH and stirred at r.t. until the reaction was complete. Removal of methanol under reduced pressure and purification of the product on a silica gel column gave 2-cyclopentenones **5a**–**g**,**j** in 81–90% yield.

**Table 2**

| Compound | Bp/Mp [°C] (Torr) | IR [$cm^{-1}$] (neat/nujol) | $^1$H NMR ($CDCl_3$) δ *J* (Hz) | $^{13}$C NMR ($CDCl_3$) δ | Microanalysis calcd/found C | H |
|---|---|---|---|---|---|---|
| **2a** viscous liquid | – | 1645.0, 1513.4, 1434.1, 1378.7, 814.6. | 1.84, 1.96 (2 × s, 3 H, *E*,*Z* -C=C-CH$_3$), 4.30 (m, 2 H, -O-C*H*$_2$CH=), 5.32 (m, 2 H, -C=CH$_2$), 5.91 (m, 1 H, -C=CH-), 6.20, 6.48 (2 × s, 1 H, *E*,*Z* O-CH=C), 7.31 (s, 5 H, Ar-H) | 16.6, 21.4 (-C=C-*C*H$_3$), 74.6 (-O-*C*H$_2$CH), 109.4 (Ar-*C*=CH-), 117.9 (-CH=*C*H$_2$), 127.7 (C$_{arom}$*para*), 128.1 (C$_{arom}$*meta*), 129.4 (C$_{arom}$*ortho*), 133.8 (CH$_2$-*C*=CH$_2$), 135.8 (C$_{arom}$1), 138.7 (O-*C*H=C) | 82.72<br>82.92 | 8.10<br>8.28 |
| **2b** viscous liquid | – | 1654.1, 1512.8, 1434.1, 1378.6, 812.8. | 2.04, 2.12 (2 × s, 3 H, *E*,*Z* C=C-CH$_3$), 2.44 (s, 3 H, Ar-CH$_3$), 4.64 (m, 2 H, -OCH$_2$-), 5.62 (m, 2 H, C=CH$_2$), 6.24 (m, 1 H, -C=CH-), 6.48, 6.84 (2 × s, 1 H, *E*,*Z* -O-CH=C), 7.66 (m, 4 H, Ar-H) | 16.5, 21.3 (-C=C-*C*H$_3$), 21.4 (Ar-*C*H$_3$), 74.7 (-O-*C*H$_2$CH=), 109.5 (Ar-*C*=CH), 118.1 (-CH=*C*H$_2$-), 128.3 (C$_{arom}$*meta*), 129.6 (C$_{arom}$*ortho*), 133.7 (-CH$_2$-*C*=CH$_2$), 135.9 (C$_{arom}$1), 137.3 (C$_{arom}$*para*), 138.8 (-O-*C*H=C-) | 82.93<br>83.11 | 8.57<br>8.62 |
| **2c** viscous liquid | – | 1682.0, 1603.0, 1522.0, 1461.0, 820.0 | 1.57, 1.68 (2 × s, 3 H, *E*,*Z* C=C-CH$_3$), 2.15, 2.39 (t, 2 H, C=C-CH$_2$-, *J* = 7.7 Hz), 2.64 (m, 2 H, Ar-CH$_2$-), 3.84 (s, 3 H, -OCH$_3$), 3.86 (s, 3 H, -OCH$_3$), 4.12–4.17 (m, 2 H, -OCH$_2$), 5.16–5.27 (m, 2 H, -C=CH$_2$-), 5.81–5.89 (m, 1 H, CH$_2$=C*H*-), 6.70, 6.79 (2 × s, 1 H, *E*,*Z* -CH=C), 6.75–6.87 (m, 3 H, Ar-H) | 16.8, 21.2 (=C-*C*H$_3$), 32.8 (Ar-CH$_2$-*C*H$_2$-), 33.8 (Ar-CH$_2$-), 55.8, 55.9 (2 × -O-CH$_3$), 74.8 (-O-*C*H$_2$-CH=), 108.9 (CH$_3$*C*=C-O-), 113.1 (C$_{arom}$5*meta*), 114.5 (C$_{arom}$2*ortho*), 118.1 (-CH=*C*H$_2$), 121.5 (C$_{arom}$6*ortho*), 131.6 (C$_{arom}$1), 133.3 (-CH$_2$-*C*=CH$_2$), 137.9 (-O-*C*H=C), 144.1 (C$_{arom}$4*para*), 147.8 (C$_{arom}$3*meta*) | 73.25<br>73.40 | 8.45<br>8.61 |
| **2d** viscous liquid | – | 1675.0, 1621.0, 1520.0, 1445.0, 835.0. | 1.55, 1.68 (2 × s, 3 H, *E*,*Z* -C=C-CH$_3$), 2.14, 2.38 (2 × t, 2 H, *J* = 8.0 Hz, -C=C-CH$_2$-), 2.65 (m, 2 H, Ar-CH$_2$-), 3.78 (s, 3 H, -OCH$_3$), 4.12–4.18 (m, 2 H, -OCH$_2$), 5.19–5.28 (m, 2 H, -CH=C*H$_2$*-), 5.78–5.92 (m, 1 H, -C*H*=CH$_2$), 6.81, 6.83 (2 × s, 1 H, *E*,*Z* -O-CH=C), 7.07–7.15 (m, 4 H, Ar-H) | 16.4, 21.0 (=C-*C*H$_3$), 32.6 (Ar-CH$_2$-*C*H$_2$-), 33.5 (Ar-CH$_2$-), 55.8 (-O-*C*H$_3$), 74.5 (-O-*C*H$_2$-CH=), 109.5 (CH$_3$*C*=C-O-), 114.1 (C$_{arom}$*meta*), 117.9 (-CH=*C*H$_2$), 128.2 (C$_{arom}$*ortho*), 131.9 (C$_{arom}$1), 133.1 (CH$_2$-*C*=CH$_2$), 138.2 (-O-*C*H=C), 148.7 (C$_{arom}$*para*) | 77.55<br>77.66 | 8.68<br>8.49 |
| **2e** liquid | 167–169 (760) | 2933.2, 1651.3, 1464.7, 1168.2 | 0.95 (m, 6 H, 2 × -CH$_3$), 1.29 (m, 4 H, 2 × -C*H$_2$*-CH$_3$), 1.87 (m, 4 H, 2 × -C*H$_2$*-CH$_2$-CH$_3$), 4.59 (m, 2 H, -O-CH$_2$-), 5.26 (m, 2 H, -CH=C*H$_2$*), 5.96 (m, 1 H, -CH$_2$-C*H*=CH$_2$), 6.4 (s, 1 H, -O-C*H*=C-) | 13.7 (*C*H$_3$CH$_2$-), 22.4 (CH$_3$*C*H$_2$-), 30.5, 34.1 (CH$_3$CH$_2$*C*H$_2$-), 74.2 (-O*C*H$_2$-), 114.2 (-*C*=CH-O-), 118.3 (-CH$_2$CH=*C*H$_2$), 132.8 (-CH$_2$*C*H=CH$_2$), 139.7 (-O-*C*H=C-) | 78.51<br>78.42 | 11.98<br>11.79 |

**Table 2** (continued)

| Compound | Bp/Mp [°C] (Torr) | IR [$cm^{-1}$] (neat/nujol) | $^1$H NMR ($CDCl_3$) δ *J* (Hz) | $^{13}$C NMR ($CDCl_3$) δ | Microanalysis calcd/found C | H |
|---|---|---|---|---|---|---|
| **2f** liquid | 181–182 (760) | 2920.5, 1653.2, 1462.5, 1157.9 | 0.94–1.0 (m, 6 H, 2 × -$CH_3$), 1.25–1.40 (m, 6 H, -C*H*$_2$CH$_3$, -CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.86–1.93 (m, 4 H, 2 × -CH$_2$-C-), 4.58 (m, 2 H, -O-CH$_2$-), 5.21–5.40 (m, 2 H, -CH=C*H*$_2$), 5.96 (m, 1 H, -CH$_2$C*H*=CH$_2$), 6.41, 6.48 (2 × s, 1 H, *E*,*Z* -O-C*H*=C-) | 13.9 (*C*H$_3$CH$_2$-), 17.8 (CH$_3$*C*H$_2$-), 20.7, 22.5 (2 × -*C*H$_2$CH$_3$), 29.2, 29.8 (2 × -*C*H$_2$CH$_2$CH$_3$), 31.8 (-*C*H$_2$C=CH), 73.8 (-O-*C*H$_2$-), 112.2 (-*C*=CH-O-), 117.2 (-CH$_2$CH=*C*H$_2$), 133.1 (-CH$_2$*C*H=CH$_2$), 138.6 (-O-*C*H=C-) | 79.06 78.92 | 12.16 12.27 |
| **2g** liquid | 142–144 (760) | 2925.8, 1658.7, 1454.2, 1164.9 | 0.92 (m, 3 H, -CH$_2$C*H*$_3$), 1.41 (s, 3 H, -C-CH$_3$), 1.93 (m, 2 H, -C*H*$_2$CH$_3$), 4.51 (m, 2 H, -O-CH$_2$-), 5.21–5.36 (m, 2 H, -CH=C*H*$_2$), 5.94 (m, 1 H, -CH$_2$C*H*=CH$_2$), 6.42, 6.48 (2 × s, 1 H, *E*,*Z* -O-C*H*=C-) | 14.1 (*C*H$_3$CH$_2$-), 17.7, 21.6 (*E*,*Z* CH$_3$-C-), 28.4 (CH$_3$*C*H$_2$-), 73.9 (-O-*C*H$_2$-), 108.9 (-*C*=CH-O-), 118.1 (-CH$_2$CH=*C*H$_2$), 134.1 (-CH$_2$*C*H=CH$_2$), 138.3 (-O-*C*H=C-) | 76.14 75.92 | 11.18 11.31 |
| **2h** viscous liquid | – | 1681.2, 1653.6, 1601.7, 1515.6, 859.0 | 4.20 (s, 6 H, 2 × -OCH$_3$), 4.66 (m, 2 H, -O-CH$_2$C=), 5.68 (m, 2 H, -CH=CH$_2$-), 6.42 (m, 1 H, -CH$_2$CH=CH$_2$), 6.60 (d, 1 H, *J* = 8.0 Hz, -O-C*H*=CH-), 7.44 (m, 3 H, Ar-H), 7.82 (d, 1 H, *J* = 10.2 Hz, OCH=C*H*-) | 55.8, 56.1 (2 × O-CH$_3$), 73.9 (-O-CH$_2$-), 99.5 (Ar-*C*=C-), 110.7 ($C_{arom}$2*ortho*), 113.3 ($C_{arom}$5*meta*), 117.2 (-CH=*C*H$_2$), 119.6 ($C_{arom}$6*ortho*), 128.7 ($C_{arom}$1), 134.7 (-*C*=CH$_2$), 143.2 (-O-*C*H=C), 146.1 ($C_{arom}$4*para*), 148.3 ($C_{arom}$3*meta*) | 70.90 71.01 | 7.32 7.54 |
| **3a** liquid | 82 (3) | 2729.1, 1720.9, 1651.3, 1446.5, 922.0 | 1.32 (s, 3 H, -C-CH$_3$), 2.58 (d, 2 H, *J* = 7.7 Hz, -C=CHCH$_2$-), 5.24 (m, 2 H, -C=CH$_2$), 5.44 (m, 1 H, -C=CH-), 7.28 (s, 5 H, Ar-H), 9.60 (s, 1 H, -CHO) | 21.4 (C-*C*H$_3$), 39.5 (-*C*H$_2$CH=CH$_2$), 55.9 (Ar-*C*-CHO), 118.6 (-CH=*C*H$_2$), 124.7 ($C_{arom}$*ortho*), 126.3 ($C_{arom}$*para*), 128.7 ($C_{arom}$*meta*), 135.3 (-*C*H=CH$_2$), 137.6 ($C_{arom}$1), 201.1 (-CHO) | 82.72 82.63 | 8.10 7.96 |
| **3b** liquid | 91 (1.6) | 2721.0, 1724.0, 1645.0, 920.0 | 1.51 (s, 3 H, -C-CH$_3$), 2.53 (s, 3 H, Ar-CH$_3$), 2.78 (d, 2 H, *J* = 7.5 Hz, =CHC*H*$_2$-), 5.22 (m, 2 H, -CH=C*H*$_2$), 5.64 (m, 1 H, -C*H*=CH$_2$), 7.44 (s, 4 H, Ar-H), 9.93 (s, 1 H, -CHO) | 20.9 (Ar-CH$_3$), 21.3 (-C-*C*H$_3$), 39.6 (-*C*H$_2$-CH=CH$_2$), 55.8 (Ar-*C*-CHO), 118.7 (-CH=*C*H$_2$), 124.6 ($C_{arom}$*ortho*), 129.7 ($C_{arom}$*meta*), 135.2 (-*C*H=CH$_2$), 135.6 ($C_{arom}$*para*), 136.2 ($C_{arom}$1), 201.2 (-CHO) | 82.93 83.09 | 8.57 8.79 |
| **3c** liquid | 128 (1) | 2690.0, 1710.0, 1631.0, 1580.0, 1507.0, 919.0 | 1.10 (s, 3 H, -C-CH$_3$), 1.81 (m, 2 H, -C-CH$_2$-C), 2.29 (m, 2 H, -C=C-CH$_2$-), 2.45 (m, 2 H, Ar-CH$_2$-), 3.82 (s, 3 H, -OCH$_3$), 3.85 (s, 3 H, -OCH$_3$), 5.01–5.16 (m, 2 H, -C=CH$_2$), 5.71 (m, 1 H, -C*H*=CH$_2$-), 6.60–6.80 (m, 3 H, Ar-H), 9.48 (s, 1 H, -CHO) | 20.8 (-C-*C*H$_3$), 30.2 (Ar-CH$_2$-), 34.8 (Ar-CH$_2$-*C*H$_2$), 38.1 (-*C*H$_2$-CH=), 51.2 (-*C*-CHO), 55.7, 55.8 (2 × -OCH$_3$), 113.2 ($C_{arom}$5*meta*), 114.4 ($C_{arom}$2*ortho*), 118.3 (-CH=*C*H$_2$), 120.9 ($C_{arom}$6*ortho*), 133.6 ($C_{arom}$1), 138.6 (-*C*H=CH$_2$), 144.9 ($C_{arom}$4*para*), 147.7 ($C_{arom}$3*meta*), 202.5 (-CHO) | 73.25 73.45 | 8.45 8.59 |
| **3d** liquid | 148 (2) | 2705.8, 1724.8, 1639.3, 1583.5, 1512.8, 912.6 | 1.11 (s, 3 H, -C-CH$_3$), 1.76 (m, 2 H, -C-CH$_2$-C-), 2.30 (t, 2 H, *J* = 8.1 Hz, -C=CHCH$_2$-), 2.61 (m, 2 H, Ar-CH$_2$-), 3.78 (s, 3 H, -OCH$_3$), 5.13 (m, 2 H, -C=CH$_2$), 5.84 (m, 1 H, -C*H*=CH$_2$-), 6.82 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.10 (m, 2 H, Ar-H), 9.50 (s, 1 H, -CHO) | 20.7 (-C-*C*H$_3$), 30.3 (Ar-CH$_2$-), 35.1 (Ar-CH$_2$*C*H$_2$), 38.2 (-*C*H$_2$CH=), 51.3 (-*C*-CHO), 55.8 (-O-*C*H$_3$), 114.1 ($C_{arom}$*meta*), 118.4 (-CH=*C*H$_2$), 128.4 ($C_{arom}$*ortho*), 132.1 ($C_{arom}$1), 138.3 (-*C*H=CH$_2$), 149.7 ($C_{arom}$*para*), 202.6 (-CHO) | 77.55 77.46 | 8.68 8.84 |

**Table 2** (continued)

| Compound | Bp/Mp [°C] (Torr) | IR [$cm^{-1}$] (neat/nujol) | $^1H$ NMR ($CDCl_3$) δ *J* (Hz) | $^{13}C$ NMR ($CDCl_3$) δ | Microanalysis calcd/found C | H |
|---|---|---|---|---|---|---|
| **3e** liquid | 187−188 (760) | 2730.3, 1718.5, 1533.4, 1428.2 | 0.9–1.02 (m, 6 H, 2 × $CH_3$), 1.3–1.42 (m, 4 H, 2 × $CH_3$-$CH_2$-), 1.46–1.55 (m, 4 H, $CH_3CH_2CH_2$-), 2.33 (m, 2 H, -$CH_2$CH=$CH_2$), 5.02–5.16 (m, 2 H, -CH=$CH_2$), 5.72 (m, 1 H, -*C*H=$CH_2$), 9.53 (s, 1 H, -CHO) | 13.8 (-$CH_3$), 18.7 (-$CH_2CH_3$), 33.8 (-$CH_2CH_2CH_3$), 37.4 (-$CH_2$CH=), 49.1 (-*C*-CHO), 117.4 (-CH=$CH_2$), 138.2 (-*C*H=$CH_2$), 202.5 (-CHO) | 78.51 78.37 | 11.98 12.07 |
| **3f** liquid | 202–203 (760) | 2726.1, 1720.2, 1548.7, 1433.3 | 0.9–1.03 (m, 6 H, 2 × $CH_3$), 1.17–1.43 (m, 6 H, -$CH_2CH_3$, -$CH_2CH_2CH_2CH_3$), 1.49–1.58 (m, 4 H, 2 × -$CH_2$-C-), 2.31 (m, 2 H, -$CH_2$CH=$CH_2$), 5.03–5.14 (m, 2 H, -CH=$CH_2$), 5.73 (m, 1 H, -*C*H=$CH_2$), 9.57 (s, 1 H, -CHO) | 13.6, 14.1 (-$CH_3$), 18.9 (-$CH_2CH_3$), 23.2, 26.4 (-$CH_2CH_2CH_3$), 33.2, 33.7 (-$CH_2$-C-), 37.6 (-$CH_2$CH=$CH_2$), 48.7 (-*C*-CHO), 117.9 (-CH=$CH_2$), 138.7 (-*C*H=$CH_2$), 202.3 (-CHO) | 79.06 79.21 | 12.12 12.01 |
| **3g** liquid | 179–181 (760) | 2722.2, 1719.7, 1543.6, 1427.1 | 0.90–0.97 (t, 3 H, *J* = 7.0 Hz, -$CH_2CH_3$), 1.22 (s, 3 H, -C-$CH_3$), 1.54 (q, 2 H, *J* = 7.0 Hz, -$CH_2CH_3$), 2.27 (m, 2 H, -$CH_2$CH=$CH_2$), 5.05–5.20 (m, 2 H, -CH=$CH_2$), 5.74 (m, 1 H, -*C*H=$CH_2$), 9.48 (s, 1 H, -CHO) | 11.3 ($CH_3CH_2$-), 17.4 ($CH_3$C-), 22.2 ($CH_3CH_2$-), 37.3 (-$CH_2$CH=$CH_2$), 48.4 (-*C*-CHO), 116.8 (-CH=$CH_2$), 137.3 (-*C*H=$CH_2$), 202.1 (-CHO) | 76.14 76.31 | 11.18 11.05 |
| **3h** liquid | 157 (2) | 2719.3, 1722.0, 1681.2, 1590.5, 1517.5, 918.0. | 2.79 (m, 2 H, -$CH_2$CH=C), 3.68 (m, 1 H, -*CH*-CHO), 4.02 (s, 6 H, 2 × -$OCH_3$), 5.3 (m, 2 H, -C=$CH_2$), 6.00 (m, 1 H, $CH_2$=*CH*-), 6.96–7.88 (m, 3 H, Ar-H), 10.24 (d, 1 H, *J* = 2.40 Hz, -CHO) | 32.8 (-$CH_2$CH=), 55.7 (Ar-*C*-CHO), 55.9, 56.1 (2 × -$OCH_3$), 112.3 ($C_{arom}$2*ortho*), 113.7 ($C_{arom}$5*meta*), 119.6 (-CH=$CH_2$), 121.3 ($C_{arom}$6*ortho*), 130.5 ($C_{arom}$1), 136.7 (-*C*=$CH_2$), 147.1 ($C_{arom}$4*para*), 147.8 ($C_{arom}$3*meta*), 201.7 (-CHO) | 70.89 70.71 | 7.32 7.49 |
| **4a** liquid | 121 (2.5) | 2689.2, 1718.8, 1711.3. | 1.56 (s, 3 H, -C-$CH_3$), 2.04 (s, 3 H, -$COCH_3$), 3.10 (s, 2 H, -$COCH_2$-), 7.35 (s, 5 H, Ar-H), 9.66 (s, 1 H, -CHO) | 21.8 (-C-$CH_3$), 27.9 ($CH_3$-C=O), 48.9 (-$CH_2$-C=O), 53.3 (Ar-*C*-CHO), 125.8 ($C_{arom}$*ortho*), 126.9 ($C_{arom}$*para*), 128.6 ($C_{arom}$*meta*), 137.1 ($C_{arom}$1), 201.3 (-CHO), 206.7 ($CH_3$-*C*=O) | 75.76 75.94 | 7.42 7.38 |
| **4b** liquid | 123 (2.5) | 2681.0, 1722.0, 1707.0 | 1.62 (s, 3 H, -C-$CH_3$), 2.11 (s, 3 H, -$COCH_3$), 2.39 (s, 3 H, Ar-$CH_3$), 3.16 (s, 2 H, -$CH_2$-CO), 7.42 (s, 4 H, Ar-H), 9.88 (s, 1 H, -CHO) | 21.0 (Ar-$CH_3$), 21.7 (-C-$CH_3$), 27.8 ($CH_3$-C=O), 49.1 (-$CH_2$-C=O), 53.5 (Ar-*C*-CHO), 125.6 ($C_{arom}$*ortho*), 125.9 ($C_{arom}$*meta*), 133.5 ($C_{arom}$1), 135.4 ($C_{arom}$*para*), 201.1 (-CHO), 206.6 ($CH_3$-*C*=O) | 76.44 76.31 | 7.90 8.01 |
| **4c** liquid | 136 (0.6) | 2695.0, 1716.0, 1707.0. | 1.19 (s, 3 H, -C-$CH_3$), 1.83 (m, 2 H, -C-$CH_2$-), 2.12 (s, 3 H, -$COCH_3$), 2.45 (t, 2 H, *J* = 8.6 Hz, Ar-$CH_2$-), 2.69 (d, 1 H, *J* = 17.8 Hz, -CO-$CH_2$-), 2.84 (d, 1 H, *J* = 17.8 Hz, -CO-$CH_2$-), 3.82 (s, 3 H, -$OCH_3$), 3.84 (s, 3 H, -$OCH_3$), 6.55–6.85 (m, 3 H, Ar-H), 9.58 (s, 1 H, -CHO) | 20.4 (C-$CH_3$), 26.1 ($CH_3$-C=O), 30.2 (Ar-$CH_2$-), 34.4 (Ar-$CH_2CH_2$), 46.2 (-$CH_2$-C=O), 47.1 (-*C*-CHO), 55.8, 55.9 (2 × -$OCH_3$), 113.5 ($C_{arom}$5*meta*), 114.3 ($C_{arom}$2*ortho*), 120.8 ($C_{arom}$6*ortho*), 133.8 ($C_{arom}$1), 145.4 ($C_{arom}$4*para*), 147.8 ($C_{arom}$3*meta*), 204.5 (-CHO), 206.4 ($CH_3$-*C*=O) | 69.04 69.15 | 7.97 7.99 |

**Table 2** (continued)

| Compound | Bp/Mp [°C] (Torr) | IR [cm$^{-1}$] (neat/nujol) | $^1$H NMR ($CDCl_3$) δ *J* (Hz) | $^{13}$C NMR ($CDCl_3$) δ | Microanalysis calcd/found C | H |
|---|---|---|---|---|---|---|
| **4d** solid | 41–42 | 2712.1, 1718.1, 1705.6. | 1.22 (s, 3 H, -C-$CH_3$), 1.72–1.85 (m, 2 H, -C-$CH_2$-C-), 2.12 (s, 3 H, -$COCH_3$), 2.46 (t, 2 H, *J* = 8.5 Hz, Ar-$CH_2$-), 2.67 (d, 1 H, *J* = 17.7 Hz, -CO-$CH_2$-), 2.84 (d, 1 H, *J* = 17.7 Hz, -CO-$CH_2$-), 3.77 (s, 3 H, -$OCH_3$), 6.81 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.05 (d, *J* = 8.0 Hz, 2 H, Ar-H), 9.58 (s, 1 H, -CHO) | 20.5 (-C-*C*$H_3$), 26.3 (*C*$H_3$-C=O), 30.1 (Ar-$CH_2$-), 34.3 (Ar-$CH_2$*C*$H_2$), 46.3 (-*C*$H_2$-C=O), 47.2 (-*C*-CHO), 55.7 (-O*C*$H_3$), 114.3 ($C_{arom}$*meta*), 128.5 ($C_{arom}$*ortho*), 132.3 ($C_{arom}$1), 149.8 ($C_{arom}$*para*), 204.6 (-CHO) 206.7 ($CH_3$-*C*=O) | 72.55<br>72.76 | 8.12<br>8.20 |
| **4e** viscous liquid | – | 2705.6, 1718.1, 1706.2 | 0.91–1.02 (m, 6 H, 2 × $CH_3$), 1.3–1.43 (m, 4 H, 2 × $CH_3$-C*H*$_2$-), 1.5–1.6 (m, 4 H, 2 × $CH_3CH_2C$*H*$_2$), 2.11 (s, 3 H, $CH_3$-C=O), 2.69 (d, 1 H, *J* = 17.1 Hz, O=C-$CH_2$), 2.81 (d, 1 H, *J* = 17.1 Hz, O=C-$CH_2$), 9.57 (s, 1 H, -CHO) | 13.8 (-$CH_2$*C*$H_3$), 17.6 (-*C*$H_2CH_3$), 26.2 (*C*$H_3$-C=O), 33.1 (-*C*$H_2CH_2CH_3$), 44.8 (O=C-*C*$H_2$), 47.6 (-*C*-CHO), 202.3 (-CHO), 205.1 ($CH_3$-*C*=O) | 71.70 71.95 | 10.94<br>10.77 |
| **4f** viscous liquid | – | 2698.3, 1719.4, 1704.9 | 0.9–1.05 (m, 6 H, 2 × $CH_3$), 1.28–1.44 (m, 6 H, $CH_3C$*H*$_2CH_2$-C, $CH_3C$*H*$_2C$*H*$_2CH_2$-), 1.52–1.63 (m, 4 H, 2 × -C*H*$_2$-C-), 2.13 (s, 3 H, $CH_3$-C=O), 2.67 (d, 1 H, *J* = 17.3 Hz, O=C-$CH_2$), 2.79 (d, 1 H, *J* = 17.3 Hz, O=C-$CH_2$), 9.61 (s, 1 H, -CHO) | 13.9, 14.3 (*C*$H_3CH_2$-), 17.7 ($CH_3$*C*$H_2CH_2$-C-), 23.1 ($CH_3$*C*$H_2CH_2CH_2$-), 26.2 ($CH_3CH_2$*C*$H_2CH_2$), 26.4 (*C*$H_3$-C=O), 32.2 ($CH_3CH_2CH_2$*C*$H_2$-C), 33.4 ($CH_3CH_2$*C*$H_2$-C), 44.9 (O=C-*C*$H_2$), 47.8 (-*C*-CHO), 202.1 (-CHO), 205.4 ($CH_3$-*C*=O) | 72.68 72.83 | 11.18<br>11.33 |
| **4g** viscous liquid | – | 2701.2, 1717.3, 1705.8 | 0.90–0.97 (t, 3 H, *J* = 7.1 Hz, -$CH_2C$*H*$_3$), 1.21 (s, 3 H, -C-$CH_3$), 1.54 (q, 2 H, *J* = 7.1 Hz, -C*H*$_2CH_3$), 2.11 (s, 3 H, $CH_3$-C=O), 2.71 (d, 1 H, *J* = 17 Hz, O=C-$CH_2$), 2.83 (d, 1 H, *J* = 17 Hz, O=C-$CH_2$), 9.48 (s, 1 H, -CHO) | 10.2 (*C*$H_3$-$CH_2$-), 16.1 (*C*$H_3$-C-), 25.6 ($CH_3$*C*$H_2$-), 45.2 (O=C-*C*$H_2$), 47.3 (-*C*-CHO), 202.4 (-CHO), 205.7 ($CH_3$-*C*=O) | 67.57 67.39 | 9.92<br>9.84 |
| **4h** solid | 58–60 | 2685.0, 1721.0, 1698.0. | 2.17 (s, 3 H, -CO-$CH_3$), 2.62 (d, 1 H, *J* = 11.3 Hz, -$CH_2$-CO-), 3.31 (m, 1 H, -C*H*-CHO), 3.84 (s, 6 H, 2 × -$OCH_3$), 4.15 (br s, 1 H, -$CH_2$-CO-), 6.64 (s, 1 H, Ar-H), 6.69 (d, *J* = 8.1 Hz, 1 H, Ar-H), 6.82 (d, *J* = 6.0 Hz, 1 H, Ar-H), 9.63 (s, 1 H, -CHO) | 27.6 (*C*$H_3$-C=O), 43.6 (*C*$H_2$-C=O), 52.7 (Ar-*C*-CHO), 55.9, 56.2 (2 × -O*C*$H_3$), 113.1 ($C_{arom}$5*meta*), 114.2 ($C_{arom}$2*ortho*), 121.7 ($C_{arom}$6*ortho*), 130.7 ($C_{arom}$1), 147.3 ($C_{arom}$4*para*), 148.1 ($C_{arom}$3*meta*), 203.8 (-CHO), 206.5 ($CH_3$-*C*=O) | 66.08<br>65.98 | 6.83<br>6.87 |
| **5a** liquid | 110 (1.2) | 1715.2, 1587.7, 1512.9, 1454.2 | 1.60 (s, 3 H, -C-$CH_3$), 2.58 (s, 2 H, -$COCH_2$-), 6.24 (d, 1 H, *J* = 5.6 Hz, -COCH=C-), 7.32 (s, 5 H, Ar-H), 7.74 (d, 1 H, *J* = 5.6 Hz, C*H*=CH-CO-) | 22.3 (*C*$H_3$-C), 48.2 (Ar-C), 54.3 (*C*$H_2$-C=O), 124.9 ($C_{arom}$*ortho*), 125.7 ($C_{arom}$*para*), 127.9 ($C_{arom}$*meta*), 128.2 (-C=*C*-C=O), 146.5 ($C_{arom}$1), 147.6 (-*C*=C-C=O), 200.1 (-C=O) | 83.69<br>83.58 | 7.02<br>7.14 |
| **5b** liquid | 86 (0.4) | 1709.0, 1655.0, 1580.0, 1500.0 | 1.76 (s, 3 H, -C-$CH_3$), 2.51 (s, 3 H, Ar-$CH_3$), 2.69, 2.72 (2 × s, 2 H, -$COCH_2$-), 6.48 (d, 1 H, *J* = 5.9 Hz, -CO-C*H*=CH-), 7.52 (s, 4 H, Ar-H), 8.00 (d, 1 H, *J* = 5.9 Hz, -CO-CH=C*H*-) | 21.8 (Ar-$CH_3$), 22.4 (*C*$H_3$-C-), 48.3 (Ar-C-), 56.9 (-*C*$H_2$-C=O), 126.6 ($C_{arom}$*ortho*), 128.7 ($C_{arom}$*meta*), 129.5 (-C=*C*-C=O), 135.1 ($C_{arom}$*para*), 144.5 ($C_{arom}$1), 147.8 (-*C*=C-C=O), 200.2 (-C=O) | 83.83<br>83.99 | 7.58<br>7.61 |

**Table 2** (continued)

| Compound | Bp/Mp [°C] (Torr) | IR [$cm^{-1}$] (neat/nujol) | $^1$H NMR ($CDCl_3$) δ *J* (Hz) | $^{13}$C NMR ($CDCl_3$) δ | Microanalysis calcd/found C | H |
|---|---|---|---|---|---|---|
| **5c** liquid | 158 (1.5) | 1692.0, 1590.0, 1511.0, 1445.0 | 1.24 (s, 3 H, -C-$CH_3$), 1.75 (m, 2 H, -C-$CH_2$-), 2.13 (d, 1 H, *J* = 18.6 Hz, -$COCH_2$-), 2.31 (d, 1 H, *J* = 18.6 Hz, -$COCH_2$-), 2.44 (m, 2 H, Ar-$CH_2$-), 3.79 (s, 3 H, -$OCH_3$), 3.82 (s, 3 H, -$OCH_3$), 6.01 (d, 1 H, *J* = 5.5 Hz, -CO-C*H*=CH-), 6.61–6.82 (m, 3 H, Ar-H), 7.42 (d, 1 H, *J* = 5.5 Hz, -CO-CH=C*H*-) | 24.3 ($CH_3$-C-), 31.4 (Ar-$CH_2$-),39.3 (Ar-$CH_2$-$CH_2$-), 48.8 ($CH_3$-*C*-),55.6 (-$CH_2$-C=O), 55.9, 56.1 (2 × -$OCH_3$), 113.2($C_{arom}$5*meta*), 114.2 ($C_{arom}$2*ortho*), 120.7 ($C_{arom}$6*ortho*), 129.3 (-C=*C*-C=O), 133.6 ($C_{arom}$1), 145.6 ($C_{arom}$4*para*), 147.9 ($C_{arom}$3*meta*), 149.9 (-*C*=C-C=O), 200.4 (-C=O) | 73.82<br>73.70 | 7.74<br>7.71 |
| **5d** solid | 83–84 | 1705.0, 1610.0, 1581.0, 1508.0 | 1.25 (s, 3 H, -C-$CH_3$), 1.81 (m, 2 H, -C-$CH_2$-C), 2.17 (d, 1 H, *J* = 18.6 Hz, -$COCH_2$-), 2.38 (d, 1 H, *J* = 18.6 Hz, -$COCH_2$-), 2.51 (m, 2 H, Ar-$CH_2$-), 3.85 (s, 3 H, -$OCH_3$), 6.06 (d, 1 H, *J* = 5.5 Hz, -CO-C*H*=CH-), 6.81 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.05 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.44 (d, 1 H, *J* = 5.5 Hz, -CO-CH=C*H*-) | 24.1 ($CH_3$-C-), 31.5 (Ar-$CH_2CH_2$-), 39.6 (Ar-$CH_2CH_2$), 48.8 ($CH_3$-*C*-), 55.5 (-$CH_2$-C=O), 56.1 (-O-$CH_3$), 114.0 ($C_{arom}$*meta*), 128.7 ($C_{arom}$*ortho*), 129.1 (-C=*C*-C=O), 132.5 ($C_{arom}$1), 149.2 ($C_{arom}$*para*), 149.9 (-*C*=C-C=O), 200.6 (-C=O) | 78.29<br>78.10 | 7.88<br>8.04 |
| **5e** viscous liquid | – | 1704.2, 1588.3, 1471.2 | 0.89–1.03 (m, 6 H, 2 × $CH_3$), 1.2–1.46 (m, 8 H, 2 × -$CH_2$-$CH_2$-), 2.57 (s, 2 H, O=C-$CH_2$), 6.04 (d, 1 H, *J* = 5.9 Hz, CO-C*H*=CH), 7.02 (d, 1 H, *J* = 5.9 Hz, CO-CH=C*H*) | 14.1 ($CH_3CH_2$-), 18.7 ($CH_3CH_2$-), 34.5 ($CH_3CH_2$ $CH_2$-), 45.3 (-*C*-CH=C), 55.2 (O=C-$CH_2$), 128.9 (O=C-*C*H=CH-), 146.4 (O=C-CH=*C*H-), 202.2 (O=C-) | 79.46 79.61 | 10.91<br>10.74 |
| **5f** viscous liquid | – | 1701.1, 1598.4, 1482.9 | 0.92–1.05 (m, 6 H, 2 × $CH_3$), 1.21–1.48 (m, 10 H, 5 × -$CH_2$-), 2.23 (d, 1 H, *J* = 17.3 Hz, O=C-$CH_2$), 2.39 (d, 1 H, *J* = 17.3 Hz, O=C-$CH_2$), 6.08 (d, 1 H, *J* = 6.1 Hz, CO-C*H*=CH), 7.04 (d, 1 H, *J* = 6.1 Hz, CO-CH=C*H*) | 14.1, 14.5 ($CH_3CH_2$-), 18.5 ($CH_3CH_2CH_2C$), 22.8 ($CH_3CH_2CH_2CH_2C$), 28.2 ($CH_3CH_2CH_2CH_2C$), 34.7 ($CH_3CH_2CH_2C$), 35.2 ($CH_3CH_2$ $CH_2$ $CH_2C$), 45.2 (-CH=CH-*C*-), 55.6 (O=C-$CH_2$), 128.2 (O=C-*C*H=CH-), 147.4 (O=C-CH=*C*H-), 202.6 (O=C-) | 79.94 79.76 | 11.18<br>11.29 |
| **5g** viscous liquid | – | 1699.3, 1586.3, 1478.1 | 0.92–1.0 (m, 3 H, $CH_3$-$CH_2$-), 1.27 (s, 3 H, $CH_3$C-), 1.3–1.36 (m, 2 H, $CH_3CH_2$-), 2.25 (d, 1 H, *J* = 17.1 Hz, O=C-$CH_2$), 2.37 (d, 1 H, *J* = 17.1 Hz, O=C-$CH_2$), 6.03 (d, 1 H, *J* = 6.2 Hz, CO-C*H*=CH), 7.05 (d, 1 H, *J* = 6.2 Hz, CO-CH=C*H*) | 11.2 ($CH_3CH_2$-), 22.7 ($CH_3$C-), 32.8 ($CH_3CH_2$-), 43.1 (-CH=CH-*C*-), 56.3 (O=C-$CH_2$), 124.9 (O=C-*C*H=CH-), 147.6 (O=C-CH=*C*H-), 201.1 (O=C-) | 77.38 77.51 | 12.88<br>12.69 |
| **5j**[26] solid | 148–149 | 1680.0, 1595.0, 1500.0, 1446.0 | 2.53 (m, 2 H, -CO-$CH_2CH_2$), 2.99 (m, 2 H, -CO-$CH_2$-), 3.90 (s, 6 H, 2 × -$OCH_3$), 6.43 (s, 1 H, -CO-CH=C-), 6.88 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.11 (s, 1 H, Ar-H), 7.24 (d, *J* = 7.6 Hz, 1 H, Ar-H) | 30.2 (-CO-$CH_2CH_2$-), 36.8 (-$CH_2$-C=O), 55.7, 55.9 (-$OCH_3$), 114.7 ($C_{arom}$5*meta*), 115.6 ($C_{arom}$2*ortho*), 117.8 ($C_{arom}$6*ortho*), 131.1 (-C=*C*-C=O), 131.4 ($C_{arom}$1), 147.1 ($C_{arom}$4*para*), 147.4 ($C_{arom}$3*meta*), 154.9 (-*C*=C-C=O), 201.1 (-C=O) | 71.54<br>71.38 | 6.47<br>6.61 |

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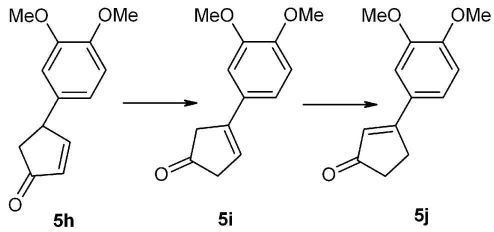
## References

(1) Tsunoda, T.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1983**, *24*, 83.
(2) Pattenden, G.; Teague, S. J. *Tetrahedron Lett.* **1982**, *23*, 5471.
(3) Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* **1983**, 935.
(4) Curran, D. P.; Chen, M.-H. *Tetrahedron Lett.* **1985**, *26*, 4991.
(5) Billington, D. C.; Kerr, W. J.; Pauson, P. L. *J. Organomet. Chem.* **1987**, *328*, 223.
(6) Sampath, V.; Lund, E. C.; Knudsen, M. J.; Olmstead, M. M.; Schore, N. E. *J. Org. Chem.* **1987**, *52*, 3595.
(7) Ramaiah, M. *Synthesis* **1984**, 529.
(8) Mehta, G.; Srikrishna, A. *Chem. Rev.* **1997**, *97*, 671.
(9) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1.
(10) Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467.
(11) Curran, D. P. *Synthesis* **1988**, 417.
(12) Curran, D. P. *Synthesis* **1988**, 489.
(13) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
(14) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1; *Angew. Chem*. **1986**, *9*, 1.
(15) Ellison, R. A. *Synthesis* **1973**, 397.
(16) Trost, B. M. *Chem. Soc. Rev.* **1982**, 141.
(17) Paquette, L. A. *Aldrichimica Acta* **1984**, *17*, 43.
(18) Negeshi, E.; Coperet, C.; Ma, S.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365.
(19) Mehta, G.; Karra, S. R. *Tetrahedron Lett.* **1991**, *32*, 3215.
(20) (a) Kulkarni, M. G.; Pendharkar, D. S. *Tetrahedron Lett.* **1997**, *53*, 3167. (b) Kulkarni, M. G.; Pendharkar, D. S. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3127.
(21) Kulkarni, M. G.; Pendharkar, D. S.; Rasne, R. M. *Tetrahedron Lett.* **1997**, *38*, 1459.
(22) (a) Claisen, L. *Chem. Ber.* **1912**, *45*, 3157. (b) Claisen, L. *Chem. Ber.* **1936**, *69*, 77.
(23) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.
(24) von Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R. *Angew. Chem.* **1959**, *71*, 176.
(25) However, in some cases[20] it was possible to separate and characterize the individual *E* and *Z* isomers.
(26) Under aldol condensation conditions product **5h** underwent isomerisation to compound **5j** through a deconjugation process[27–30] via **5i** (Scheme 1).



**5h** **5i** **5j**

**Scheme 1**

(27) Atwater, N. W. *J. Am. Chem. Soc.* **1960**, *82*, 2847.
(28) Conia, J. M.; Sandre-LeCratz, A. *Tetrahedron Lett.* **1962**, *3*, 505.
(29) Newman, M. S.; DeVries, V.; Darlak, R. *J. Org. Chem.* **1966**, *31*, 2171.
(30) Herrmann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, *26*, 2433.
(31) Calculated on the basis of recovered substrate.
(32) All the new compounds gave satisfactory analytical and spectroscopic data (Table 2).