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Acidic ionic liquid-catalyzed homologation of the polyene chain in α,β-enals (polyenals)

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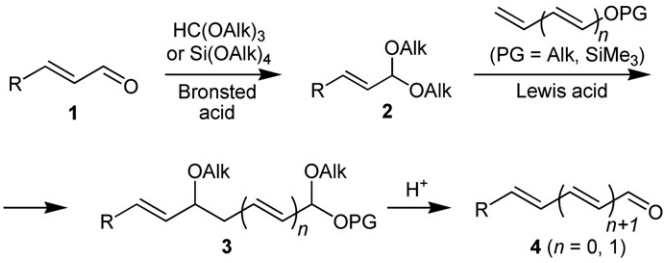
ABSTRACT

An efficient green-chemistry synthesis of conjugated polyenals from α,β-enals, orthoesters, and alkyl vinyl ethers promoted by acidic ionic liquid [emim][HSO_4] is described. The ionic liquid can be reused at least three times without any decrease in product yields.

1. Introduction

Conjugated polyene units are incorporated into a variety of natural[1] and biologically active compounds, in particular leukotrienes,[2] pheromones,[3] antibiotics,[4] and carotinoids.[5] Commonly these complex molecules are synthesized from simpler (poly)enes that contain a conjugated aldehyde group,[5d] via the aldol condensation,[5h,6,7] Peterson olefination,[8] organometallic synthesis,[9] Wittig type,[2c,3c,10–12] and some other reactions. However, these reactions often have low selectivity due to high reactivity of the enals and require preliminary introduction of protecting groups (PG).[7–9,11] In particular, a useful algorithm for the homologation of the polyene chain in α,β-enals is a sequence of acid-catalyzed reactions including the acetalization of α,β-enals **1**, condensation of acetals **2** with vinyl or 1,3-dienyl ethers, and deprotection of acetals **3** to polyenals **4** (Scheme 1).[5a–d,13–15]

However, implementation of this scheme is complicated by concurrent addition of enol (dienol) ethers to acetals **3** affording oligomeric by-products under reaction conditions.[5d,13d,16] This side process can be suppressed by carrying out the vinylogation reaction (**2**→**3**) in the presence of a mild Lewis acid ($BF_3 \cdot Et_2O$, $ZnCl_2$, $FeCl_3$),[5a,13–15] whereas the acetalization of enals **1** to acetals **2** requires Brünsted acid catalysis (H_3PO_4, TsOH, NH_4Cl, NH_4NO_3).[5a,13d] The use of different catalysts necessitates the isolation and purification of intermediates **2** and **3**, which makes the experimental procedure more difficult.



Scheme 1. Synthesis of polyenals.

We assumed that compounds **3** could be prepared from enals **1** in one-pot in the presence of an ionic liquid (IL) catalyst. Some ILs possess both Lewis[17a,b] and Brünsted acidity[17c,d,18] and find applications in various catalytic reactions.[19] For instance, they catalyze the formation of acetals from alkyl (aryl) aldehydes and alcohols[17] or triethyl orthoformate.[18] However there is no information on the synthesis of acetals from α,β-enals and on the condensation of acetals with vinyl ethers in the presence of ILs.

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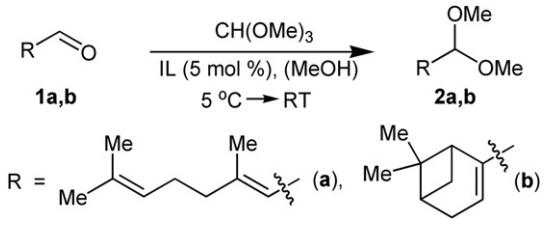
2. Results and discussion

To verify this hypothesis we compared the catalytic activities of 1-ethyl-3-methyl- (emim) and 1-butyl-3-methylimidazolium (bmim) salts with HSO_4^-, BF_4^-, PF_6^- or OTf^- anions (5 mol %) in the reaction between citral (**1a**) and trimethyl orthoformate (Scheme 2).



Scheme 2. Acetalization of α,β-enals **1a**,**b**.

Aldehyde **1a** was slowly added to IL-containing (5 mol %) orthoformate at 5 °C. It turned out that ILs with BF_4^-, PF_6^-, and OTf^- anions did not catalyze an acetalization reaction under the studied conditions (Table 1, entries 1–3). However acetal **2a** was formed in 92% yield in the presence of [emim][HSO_4] (Table 1, entry 4). The reaction proceeded faster when methanol was added to the reaction mixture (Table 1, entries 5 and 6), and a pronounced effect was detected in the presence of 5 mol % of CH_3OH. Furthermore, the addition of methanol simplified the regeneration of IL, which after the product decantation retained catalytic activity over at least two reaction cycles (Table 1, entry 6). The catalytic system [bmim][HSO_4]/MeOH (5 mol % each) exhibited similar activity (Table 1, entry 7). Acetal **2b** was obtained from myrtenal (**1b**) in 93% yield under the proposed conditions (Table 1, entry 8).

Table 1
Comparison of ILs and IL/MeOH systems in the synthesis of acetals **2**[a]

Entry	Enal	IL	MeOH (equiv)	Time (h)	Product	Yield[b] (%) [run]
1	**1a**	[bmim][BF_4]	—	15	—	0
2	**1a**	[bmim][PF_6]	—	15	—	0
3	**1a**	[bmim][OTf]	—	15	—	0
4	**1a**	[emim][HSO_4]	—	5.5	**2a**	92
5	**1a**	[emim][HSO_4]	10	3.5	**2a**	88
6	**1a**	[emim][HSO_4]	0.05	1.5	**2a**	99[1], 97[2], 98[3]
7	**1a**	[bmim][HSO_4]	0.05	1.5	**2a**	98
8	**1b**	[emim][HSO_4]	0.05	1.5	**2b**	93

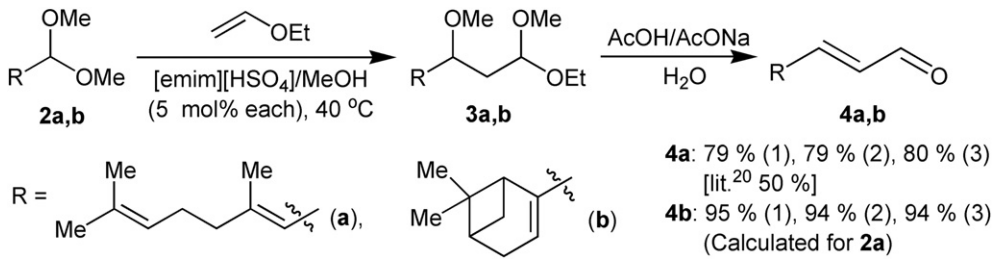
[a] Reaction mixture: **1** (10 mmol), $CH(OMe)_3$ (10 mmol), IL (0.5 mmol), and (if it is used) MeOH.
[b] The yield is given for the isolated and purified product.

Then we evaluated the catalytic properties of the system [emim][HSO_4]/MeOH (5 mol % of each) in the condensation of acetals **2a**,**b** with ethyl vinyl ether and it appeared that desired alkoxyacetals **3a**,**b** had been formed as major products (Scheme 3). We succeeded in isolation of compounds **3a**,**b**, though their purification by column chromatography led to a significant mass loss, possibly due to the hydrolysis of the acetal group. Therefore, we further hydrolyzed crude alkoxyacetals **3** to more stable dienals **4** without purification by a routine procedure (treatment with aqueous acetate buffer) and fully characterized the latter. Yields of thereby synthesized compounds **4a**,**b** (calculated for acetals **2**) were higher than those reported in literature.[20] The IL, poorly-soluble in the reaction mixture, could be easily separated and reused without a catalytic activity decrease. We attempted to carry out the homologation and hydrolysis/elimination reactions as a one-pot process by adding water directly to **3a** (or **3b**)/[emim][HSO_4]/MeOH mixtures, which formed at the C–C bond-forming stage. However, unlike reactions in the acetate buffer, these reactions led to complex mixtures of products.

On the other hand, similar conditions for the synthesis of acetals **2a**,**b** and alkoxyacetals **3a**,**b** allowed carrying out both reactions successively in the same reaction vessel. Upon completion of the first stage, ethyl vinyl ether was added directly to the reaction mass affording compounds **3a**,**b**, which were separated from the catalyst via the decantation and converted to dienals **4a**,**b** under the action of AcOH/AcONa system.[5a,13a,b] Yields of dienals **4a**,**b** in this reaction sequence (Table 2, entries 1 and 2) were comparable with those obtained in the reactions where isolated acetals **2a**,**b** had been used as starting compounds (Scheme 3).

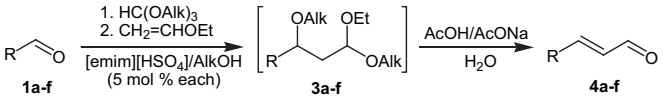
The proposed method is applicable to the synthesis of dienals **4** having various aliphatic, alicyclic or aromatic groups at the double bond. The acetalization procedure is merely different for aldehydes **1a**,**b** and **1c**–**f**. To suppress side reactions, acid-labile compounds **1a**,**b** should be slowly (drop-wise) added to orthoester at 5 °C (method A), whereas the acetalization of more stable enals **1c**–**f** proceeded efficiently at rt irrespective of the mode of mixing of components (method B). According to ^{1}H NMR data ($\delta_{CH=CH}$ 5.95–6.30 ppm, $^3J_{CH=CH}$ 15.0–16.0 Hz)[8a,11g] the double bond formed in compounds **4a**–**f** has *E*-configuration. No other available unsaturated or functional groups (e.g., in **1d** and **1f**) affect the process selectivity or efficacy.

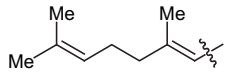
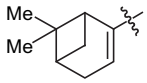
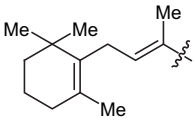
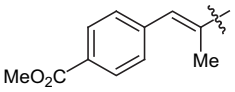
The proposed IL-based catalytic system allows further homologation of polyene chain in dienals **4**. Trienals **6a**,**c**,**e** with *E*,*E*-configurations of double bonds were synthesized from corresponding dienals **4b**,**c**,**e** and ethyl vinyl ether in the presence of this system (Table 3, entries 1, 3, and 5). Ethyl 1-propenyl ether can also serve as an alkenyl group source to afford compounds **6b**,**d**,**f** (Table 3, entries 2, 4, and 6) bearing a trisubstituted (*E*)-double bond adjacent to the aldehyde group in high yields. The *E*-configuration was assigned to the newly formed double bond by analogy with known hydrolytic reactions of β-alkoxyacetals, which afforded thermodynamically more stable *E*-isomers of corresponding enals[13,14] and based on the comparison of chemical shifts of H-atoms incorporated into the aldehyde group in compounds **6b**,**d**,**f** ($\delta_{HC=O}$ 9.40–9.53 ppm) with those reported for (*E*)-CH=C(Me)–CHO (δ 9.40–9.50 ppm)[21] and (*Z*)-CH=CH(Me)–CHO (δ 10.20–10.27 ppm)[21c,d] fragments.



Scheme 3. Condensation of acetals **2a**,**b** with ethyl vinyl ether.

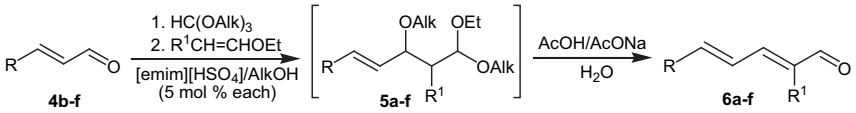
Table 2
One-pot synthesis of 2,4-dienals **4a–f**

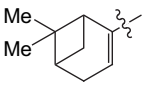
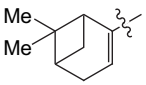
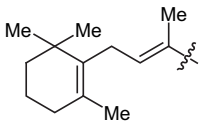
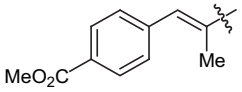


Entry	**1**	R	Alk	Method[a]	Yield of **4** (%),[b] [cycle]	Mp °C or n_D^{20}
1	**a**		Me	A	76 [1], 76 [2], 77 [3] (lit.[20] 50)	1.5380 (lit.[20] 1.5375)
2	**b**[c]		Me	A	88 [1], 87 [2], 87 [3]	1.5620
3	**c**	Me–CH=CH–	Et	B	71 (lit.[13a] 66)	1.5346 (lit.[13a] 1.5354)
4	**d**		Me	B	76 (lit.[5a] 64)	78–79 (lit.[5a] 77–78)
5	**e**	Ph–CH=CH–	Me	B	71 [1], 73 [2], 72[3] (lit.[13b] 66)	38–39 (lit.[13b] 37–38)
6	**f**		Me	B	76	110–111

[a] Method A: compound **1** (10 mmol) was added to the mixture of orthoformate (10 mmol), [emim][HSO_4] (0.5 mmol) and AlkOH (0.5 mmol) at 5 °C; method B: the mixture of **1** (10 mmol) and orthoformate (10 mmol) was added to emim][HSO_4] (0.5 mmol) and AlkOH (0.5 mmol) at rt (method B).
[b] Yield of isolated compounds **4** (purified by crystallization or via TLC) calculated for enals **1**.
[c] Compound **4b** was prepared earlier from myrtenal and *N*-methoxy-*N*-methyl-diethylphosphono-acetamide in 75% yield.[11e]

Table 3
One-pot synthesis of 2,4,6-trienals **6a–f**

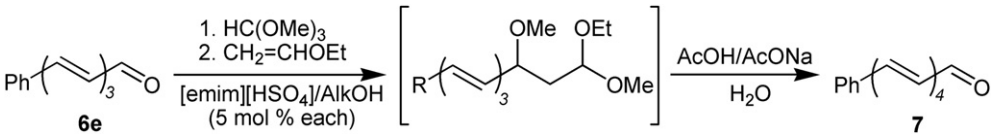


Entry	**4**	R	Alk	R^1	Method	**6**	Yield (%),[a] [cycle]	Mp °C or n_D^{20}
1	**b**		Me	H	A	**a**	81	1.6250
2	**b**		Me	Me	A	**b**	78	1.6370
3	**c**	Me–CH=CH–	Et	H	B	**c**	75 (lit.[13a] 54)	57–58 (lit.[13a] 57–58)
4	**d**		Me	Me	B	**d**	73 (lit.[5a] 62)	67–68 (lit.[5a] 66–68)[l]
5	**e**	Ph–CH=CH–	Me	H	B	**e**	81 [1], 82 [2], 80 [3] (lit.[13b] 20)	114–115 (lit.[13b] 116)
6	**f**		Me	Me	B	**f**	71.5	120–121

[a] Yield of isolated compounds **6** (purified by crystallization or via TLC) calculated for dienals **4**.

The iterative methodology could be pushed further. Trienal **6e** was readily converted to the (*E*,*E*,*E*,*E*)-tetraenal **7** in 71% overall yield under proposed conditions (Scheme 4).

The IL [emim][HSO_4] could be multiply used in the studied reactions. Upon the reaction completion, compounds **3** or **5** were separated and fresh portions of corresponding aldehydes **1** or **4**



Scheme 4. Synthesis of (*E*,*E*,*E*,*E*)-tetraenal **7**.

were added to the remaining IL. Yields of products **4** or **6** did not reduce over at least three reaction cycles (Table 2, entries 1, 2, and 5; Table 3, entry 5).

Some of the prepared compounds are analogs or intermediates for the synthesis of natural and/or biologically active compounds containing conjugated polyene units. Among them, 2,4,6-trienals **6a** and **6b** (Table 3, entries 1 and 2) are close vitamin A analogs and polyenal **6d** (Table 3, entry 4) serves as an intermediate in the industrial production of vitamin A and carotinoids.[5a–d] Polyenal **6f** (Table 3, entry 6) is a precursor to 4-(nor-polyprenyl)benzoic acid possessing anticancer activity.[22] The IL-based procedure enhances product yields and makes the synthesis of polyenals more environmentally friendly.[23]

3. Conclusion

In summary, we have developed an efficient procedure for the homologation of the polyene chain in α,β-enals (-polyenals) by means of an acidic IL-catalyzed sequence of acetalization and C–C bond-forming reactions. The method meets the requirements of environmentally friendly processes due to a one-pot methodology, neat conditions, and multiple use of the catalyst. It is of importance as an alternative to the existing procedures for the preparation of valuable polyene compounds.

4. Experimental

4.1. General

The NMR spectra were recorded with a Bruker AM-300 [300.13 MHz (^{1}H), 75.47 MHz (^{13}C)] spectrometer in $CDCl_3$ solution unless otherwise noted. ^{1}H and ^{13}C chemical shifts are given relative to Me_4Si and acetone-d_6 as reference substances, respectively. The IR spectra were recorded in KBr pellets on a Specord M-82. Microanalysis was carried out on a Perkin–Elmer 2400. The reactions were monitored by TLC [Silicagel or aluminium oxide plates from Merck KGaA; eluent: ethyl acetate/benzene (9/19) or benzene, visualization by I_2 or UV]. Ionic liquids [bmim][BF_4], [bmim][PF_6], [bmim][OTf], [emim][HSO_4], and [bmim][HSO_4] were supplied by Merck KGaA, Darmstadt, Germany. Citral, myrtenal, crotonaldehyde, cinnamaldehyde, trimethyl orthoformate, triethyl orthoformate, ethyl vinyl ether, and ethyl 1-propenyl ether were purchased from Acros and used without further purification. Compounds **1d**[24] and **1f**[25] were synthesized according to the reported methods.

4.2. General procedure for the acetalization of α,β-enals 1a and 1b

Enal **1** (10 mmol) was added drop-wise for 8–10 min to the stirred mixture of trimethyl orthoformate (1.06 g, 10 mmol), IL (0.5 mmol) and, if specified, MeOH (see Table 1) at 5 °C. The reaction mixture was left stirring for 30 min at 5–7 °C and then at rt for the time given in Table 1. The products were separated from IL by decantation and dried over K_2CO_3. Volatile impurities were removed at 40 °C (40 Torr) and the residue was passed through an Al_2O_3 pad to afford compounds **2a**,**b** (yields are specified in Table 1). Fresh portions of the reagents were added to the remaining IL and the synthesis was repeated as described above (Table 1, entry 6).

*4.2.1. 1,1-Dimethoxy-3,7-dimethylocta-2,6-diene (mixture of E- and Z-isomers 65/35, **2a**).* Compound **2a** was prepared from citral (**1a**) in 92% yield. Colorless oil, n_D^{20}=1.4550 (lit.[26] n_D^{20}=1.4548). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58–1.74 (m, 9H, 3×CH_3C=), 2.02–2.14 (m, 4H, 2×CH_2), 3.28 (s, 6H, 2×OCH_3), 4.97–5.02 [m, C*H*($OMe)_2$], 5.05–5.12, 5.20–5.26 (each m, each 1H, CH=).

*4.2.2. 2,2-Dimethoxymethyl-6,6-dimethyl-bicyclo[3.1.1]hept-2-ene (**2b**).* Compound **2b** was prepared from myrtenal (**1b**) in 93% yield. Colorless oil, n_D^{20}=1.4695. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3), 1.15 (d, *J*=8.5 Hz, 1H, CH), 1.33 (s, 3H, CH_3), 2.07–2.14, 2.28–2.45 (2m, 5H, CH, 2×CH_2), 3.27 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 4.51 (s, 1H, C*H*($OMe)_2$), 5.64 (br s, 1H, CH=) (lit.[27] NMR spectroscopic data for myrtenyl dioxolane).

4.3. General procedure for the condensation of acetals 2a or 2b with ethyl vinyl ether

Ethyl vinyl ether (0.72 g, 10 mmol) was added drop-wise for 10–15 min to the stirred mixture of acetal **2** (10 mmol), [emim][HSO_4] (0.10 g, 0.5 mmol) and MeOH (15 mg, 0.5 mmol) at the temperature ≤40–45 °C. The reaction mixture was left stirring for 6–8 h at rt, the product was separated from IL by decantation and dried over K_2CO_3. Volatile impurities were removed at 40 °C (40 Torr) for 30 min and the residue was passed through an Al_2O_3 pad (eluent: hexane) to afford alkoxyacetals **3a**,**b**.

*4.3.1. 10-Ethoxy-8,10-dimethoxy-2,6-dimethyldeca-2,6-diene (mixture of E- and Z-isomers 65/35, **3a**).* Compound **3a** was prepared from 1,1-dimethoxy-3,7-dimethylocta-2,6-diene (**2a**). Colorless oil, n_D^{20}=1.4570 (lit.[20] n_D^{20}=1.4590, data for corresponding triethyl alkoxyacetal). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13–1.24 (m, 3H, CH_3), 1.61, 1.68, 1.75 (3s, 9H, 3×CH_3C=), 1.88–2.16 (m, 6H, 3×CH_2), 3.21, 3.32 (2s, 6H, 2×OCH_3), 3.40–3.67 (m, 2H, OCH_2), 3.96–4.03 (m, 1H, C*H*–OCH_3), 4.48–4.55 (m, 1H, O–CH–O), 4.98 (d, *J*=11.0 Hz, 1H, CH=), 5.02–5.08 (m, 1H, CH=). Anal. Calcd for $C_{16}H_{30}O_3$: C 71.07, H 11.18. Found C 69.92, H 11.08.

*4.3.2. 2-(3-Ethoxy-1,3-dimethoxypropyl)-6,6-dimethyl-bicyclo[3.1.1]hept-2-ene (**3b**).* Compound **3b** was prepared from 2,2-dimethoxymethyl-6,6-dimethyl-bicyclo[3.1.1]hept-2-ene (**2b**). Colorless oil, n_D^{20}=1.4710. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (s, 3H, CH_3), 1.11 (d, *J*=8.5 Hz, 1H, CH), 1.15–1.25 (m, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.55–1.82, 2.08–2.40 (2m, 7H, CH, 3×CH_2), 3.22, 3.31 (each s, each 3H, OCH_3), 3.41–3.70 (m, 3H, OCH_2, C*H*–OCH_3), 4.50–4.65 (m, 1H, O–CH–O), 5.43 (br s, 1H, CH=). ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 21.5, 26.3, 31.3, 32.0, 37.7, 41.0, 41.5, 52.6, 53.1, 56.4, 61.8, 63.7, 101.4, 123.5, 147.5. Anal. Calcd for $C_{16}H_{28}O_3$: C 71.60, H 10.52. Found C 71.53, H 10.48.

4.4. General procedure for the one-pot synthesis of compounds 4a,b and 6a,b (method A)

Enal **1** or **4** (10 mmol) was added drop-wise for 8–10 min to the stirred mixture of orthoformate (10 mmol), [emim][HSO_4] (0.10 g,

0.5 mmol), and AlkOH (0.5 mmol) at 5 °C. The reaction mixture was left stirring for 30 min at 5–7 °C and then for 1.5 h at rt. Ethyl vinyl or ethyl 1-propenyl ether (10 mmol) was added to the reaction mixture at the temperature ≤40–45 °C and it was left stirring for 4–8 h (TLC monitoring). Crude alkoxyacetal **3** or **5** was separated from the reaction media (reused in the next run) and heated at 95 °C for 3–6 h (TLC monitoring) with the Isler mixture (6 mL; prepared from 25 g of sodium acetate, 100 mL of acetic acid and 15 mL of water). The mixture was poured onto ice and the product was extracted with diethyl ether (2×10 mL). The combined extracts were washed successively with water (10 mL), aqueous Na_2CO_3 (3×10 mL), and water (10 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, eluent: hexane; hexane/benzene 1/1; benzene) to afford compound **4** or **6**.

*4.4.1. 5,9-Dimethyldeca-2,4-8-trienal (mixture of 2E,4E- and 2E,4Z-isomers 65/35, **4a**).* Compound **4a** was prepared from citral (**1a**) in 77% yield. Colorless oil, n_D^{20}=1.5380 (lit.[20] n_D^{20}=1.5375). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58, 1.62, 1.91 (each s, each 3H, 3×CH_3C=), 2.12–2.30 (m, 4H, 2×CH_2), 5.02–5.08 (m, 1H, CH=), 6.00 (dd, *J*=16.0, 8.0 Hz, 1H, =C*H*CHO), 6.12 (d, *J*=16.0 Hz, 1H, CH=), 7.28–7.42 (m, 1H, CH=), 9.52 (dd, *J*=8.0, 1.5 Hz, 1H, CHO).

*4.4.2. (E)-3-(6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)prop-2-enal (**4b**).* Compound **4b** was prepared from myrtenal (**1b**) in 88% yield. Colorless oil, n_D^{20}=1.5620. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, 3H, CH_3), 1.12 (d, *J*=8.5 Hz, 1H, CH), 1.32 (s, 3H, CH_3), 2.10–2.15, 2.40–2.55 (2m, 5H, CH, 2CH_2), 6.02 (dd, *J*=16.0, 8.1 Hz, 1H, =C*H*CHO), 6.15 (br s, 1H, CH=), 7.07 (d, *J*=16.0 Hz, 1H, CH=), 9.52 (d, *J*=8.1 Hz, 1H, CHO) (^{1}H NMR data for **4b** were in accordance with those described in the literature[28]).

*4.4.3. (E,E)-5-(6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)penta-2,4-dienal (**6a**).* Compound **6a** was prepared from 3-(6,6-dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)prop-2-enal (**4b**) in 81% yield. Colorless oil, n_D^{20}=1.6250. IR (thin film) ν 1680 (C=O), 1616 (C=C), 1600 (C=C), 1576 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (s, 3H, CH_3), 1.16 (d, *J*=8.5 Hz, 1H, CH), 1.36 (s, 3H, CH_3); 2.10–2.20, 2.40–2.50 (2m, 4H, 2×CH_2), 2.63 (t, *J*=5.5 Hz, 1H, CH), 5.95 (br s, 1H, CH=), 6.15 (dd, *J*=16.0, 8.1 Hz, 1H, =C*H*CHO), 6.34 (dd, *J*=16.0, 11.2 Hz, 1H, CH=), 6.68 (d, *J*=16.0 Hz, 1H, CH=), 7.17 (dd, *J*=16.0, 11.2 Hz, 1H, CH=), 9.53 (d, *J*=8.1 Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 26.2, 31.2, 33.0, 37.9, 40.8, 41.5, 123.0, 124.5, 125.6, 132.6, 146.8, 153.1, 193.5. Anal. Calcd for $C_{14}H_{18}O$: C 83.12, H 8.97. Found C 83.26, H 8.81.

*4.4.4. (E,E)-5-(6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)-2-methyl-penta-2,4-dienal (**6b**).* Compound **6b** was prepared from 3-(6,6-dimethyl-bicyclo[3.1.1]hept-2-en-2-yl)prop-2-enal (**4b**) in 78% yield. Colorless oil, n_D^{20}=1.6370. IR (thin film) ν 1672 (C=O), 1616 (C=C), 1596 (C=C) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (s, 3H, CH_3), 1.15 (d, *J*=8.5 Hz, 1H, CH), 1.35 (s, 3H, CH_3), 1.85 (s, 3H, CH_3C=), 2.10–2.18, 2.41–2.51 (m, 4H, 2CH_2), 2.65 (t, *J*=5.5 Hz, 1H, CH), 5.90 (br s, 1H, CH=), 6.51 (dd, *J*=16.0, 11.2 Hz, 1H, CH=), 6.63 (d, *J*=16.0 Hz, 1H, =CH), 6.90 (d, *J*=11.2 Hz, 1H, CH=), 9.41 (s, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.7, 20.9, 26.3, 31.3, 33.0, 37.9, 40.8, 41.5, 120.2, 123.6, 125.7, 136.7, 147.0, 149.8, 194.7. Anal. Calcd for $C_{15}H_{20}O$: C 83.28, H 9.32. Found C 83.32, H 9.18.

4.5. General procedure for the one-pot synthesis of compounds 4c–f, 6c–f, and 7 (method B)

The mixture of enal **1**, **4** or **6e** (10 mmol) and orthoformate (10 mmol) was added drop-wise for 8–10 min to the stirred mixture of [emim][HSO_4] (0.10 g, 0.5 mmol) and AlkOH (0.5 mmol) at rt. The reaction mixture was left stirring for 2 h and the above described working-up procedure was used next to afford compounds **4c**–**f**, **6c**–**f**, and **7**. ^{1}H NMR data for compounds **4c**,**e**, **6c**,**e**, and **7** were in accordance with those described in the literature.[8a]

*4.5.1. (E,E)-Hexa-2,4-dienal (sorbic aldehyde) (**4c**).* Compound **4c** was prepared from *trans*-crotonaldehyde (**1c**) in 71% yield. Colorless oil, n_D^{20}=1.5346 (lit.[13a] n_D^{20}=1.5375). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (d, *J*=4.6 Hz, 3H, CH_3), 6.03 (dd, *J*=15.0, 8.0 Hz, 1H, =C*H*CHO), 6.30–6.35 (m, 2H, 2CH=), 7.10–7.14 (m, 1H, CH=), 9.51 (d, *J*=8.0 Hz, 1H, CH=O).

*4.5.2. (E,E)-4-Methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-2,4-dienal (**4d**).* Compound **4d** was prepared from 4-(2′,6′,6′-trimethylcyclohex-1′-enyl)-2-methylbut-2-enal (**1d**) in 76% yield. Mp 78–79 °C (lit.[5a] mp 78–79 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 6H, 2×CH_3), 1.51, 1.83 (each s, each 3H, CH_3CH=), 1.38–1.43, 1.48–1.60, 1.87–1.92 (each m, each 2H, CH_2), 2.90 (d, *J*=7.0 Hz, 2H, CH_2–CH=), 5.85 (t, *J*=7.0 Hz, 1H, CH=), 6.6 (dd, *J*=16.0, 8.0 Hz, 1H, =C*H*CHO), 7.08 (d, *J*=16.0 Hz, 1H, CH=), 9.50 (d, *J*=8.0 Hz, 1H, CHO).

*4.5.3. (E,E)-5-Phenylpenta-2,4-dienal (**4e**).* Compound **4e** was prepared from *trans*-cinnamaldehyde (**1e**) in 73% yield. Mp 38–39 °C (lit.[13b] mp 37–38 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 (dd, *J*=15.2, 8.0 Hz, 1H, CH=), 7.00–7.05 (m, 2H, 2CH=), 7.27 (dd, *J*=15.2, 8.0 Hz, 1H, CH=), 7.30–7.40 (m, 3H, Ph), 7.45–7.52 (m, 2H, Ph), 9.62 (d, *J*=8.0 Hz, 1H, CHO).

*4.5.4. Methyl 4-((E,E)-2-methyl-5-oxopenta-1,3-dienyl)benzoate (**4f**).* Compound **4f** was prepared from methyl 4-(2-methyl-3-oxoprop-1-enyl)benzoate (**1f**) in 76% yield. Mp 110–111 °C. IR (KBr) ν 1712 (C=O), 1668 (C=O), 1604 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H, CH_3C=), 3.91 (s, 3H, OCH_3), 6.30 (dd, *J*=16.0, 8.0 Hz, 1H, =C*H*CHO), 6.93 (s, 1H, CH=), 7.29 (d, *J*=16.0 Hz, 1H, CH=), 7.40–7.44 (m, 2H, Ar), 8.03–8.07 (m, 2H, Ar), 9.65 (d, *J*=8.0 Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 52.2, 129.1, 129.4, 129.5, 129.6, 136.2, 139.2, 140.7, 156.9, 166.5, 193.7. Anal. Calcd for $C_{14}H_{14}O_3$: C 73.02, H 6.13. Found C 72.93, H 6.05.

*4.5.5. (E,E,E)-Octa-2,4,6-trienal (**6c**).* Compound **6c** was prepared from hexa-2,4-dienal (**4c**) in 75% yield. Mp 57–58 °C (lit.[13a] mp 57–58 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (d, *J*=7.5 Hz, 3H, CH_3,), 6.01–6.05 (m, 1H, CH=), 6.12 (dd, *J*=15.2, 8.0 Hz, 1H, =C*H*CHO), 6.24–6.35 (m, 2H, 2×CH=), 6.62 (dd, *J*=15.2, 11.4 Hz, 1H, CH=), 7.12 (dd, *J*=15.2, 11.4 Hz, 1H, CH=), 9.52 (d, *J*=8.0 Hz, 1H, CHO).

*4.5.6. (E,E,E)-2,6-Dimethyl-8-(2,6,6-trimethylcyclohex-1-enyl)octa-2,4,6-trienal (**6d**).* Compound **6d** was prepared from 4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-2,4-dienal (**4d**) in 73% yield. Mp 67–68 °C (lit.[5a] mp 66–68 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 6H, 2×CH_3), 1.54, 1.88, 1.90 (3s, 9H, 3×CH_3CH=), 1.41–1.47, 1.56–1.62, 1.86–1.97 (3m, 6H, 3×CH_2), 2.92 (d, *J*=7.0 Hz, 2H, CH_2–CH=), 5.65 (t, *J*=7.0 Hz, 1H, CH=), 6.55 (dd, *J*=16.0, 11.2 Hz, 1H, CH=), 6.68 (d, *J*=16.0 Hz, 1H, =CH), 6.88 (d, *J*=11.2 Hz, 1H, CH=), 9.53 (s, 1H, CHO).

*4.5.7. (E,E,E)-7-Phenylhepta-2,4,6-trienal (**6e**).* Compound **6e** was prepared from 5-phenylpenta-2,4-dienal (**4e**) in 82% yield. Mp 114–115 °C (lit.[13b] mp 116 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, *J*=16.0, 8.0 Hz, 1H, =C*H*CHO), 6.57 (dd, *J*=14.6, 11.2 Hz, 1H, CH=), 6.81–6.93 (m, 3H, 3×CH=), 7.19 (dd, *J*=16.0, 11.2 Hz, 1H, CH=), 7.27–7.38 (m, 3H, Ph), 7.44–7.50 (m, 2H, Ph), 9.59 (d, *J*=8.0 Hz, 1H, CHO).

*4.5.8. Methyl 4-((E,E,E)-2,6-dimethyl-7-oxohepta-1,3,5-trienyl)benzoate (**6f**).* Compound **6f** was prepared from methyl 4-(2-methyl-

5-oxopenta-1,3-dienyl)benzoate (**4f**) in 76% yield. Mp 120–121 °C. IR (KBr) ν 1724 (C=O), 1680 (C=O), 1604 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (s, 3H, CH_3C=), 2.13 (s, 3H, CH_3C=), 3.91 (s, 3H, OCH_3), 6.72–6.79 (m, 2H, 2CH=), 6.81 (s, 1H, CH=), 6.97 (d, J=16.0 Hz, 1H, CH=), 7.38–7.43 (m, 2H, Ar), 7.99–8.07 (m, 2H, Ar), 9.49 (s, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 18.6, 52.0, 125.7, 126.3, 129.0, 129.4, 135.0, 136.8, 138.5, 141.2, 146.9, 167.0, 194.5. Anal. Calcd for $C_{17}H_{18}O_3$: C 75.53, H 6.71. Found C 75.67, H 6.84.

*4.5.9. (E,E,E,E)-9-Phenylnona-2,4,6,8-tetraenal (**7**).* Compound **7** was prepared from 7-phenylhepta-2,4,6-trienal (**6e**) in 71% yield. Mp 140–141 °C (lit.[8a] mp 140 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (dd, J=15.4, 8.0 Hz, 1H, =*CH*CHO), 6.48 (dd, J=14.6, 11.0 Hz, 1H, CH=), 6.64–6.78 (m, 2H, 2CH=), 6.81 (d, J=15.6 Hz, 1H, CH=), 6.90 (dd, J=14.6, 11.0 Hz, 1H, CH=), 7.17 (dd, J=15.6, 11.0 Hz, 1H, CH=), 7.35–7.40 (m, 3H, Ph), 7.42–7.52 (m, 3H, Ph, CH=), 9.58 (d, J=8.0 Hz, 1H, CHO).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.005.

References and notes

1. Thirsk, C.; Whiting, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 999–1023.
2. (a) Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammarstrom, S. *J. Am. Chem. Soc.* **1980**, *102*, 1436–1439; (b) Green, R. H.; Lambeth, P. F. *Tetrahedron* **1983**, *39*, 1687–1721; (c) Rokach, J.; Adams, J. *Acc. Chem. Res.* **1985**, *18*, 87–93; (d) Rokach, J.; Guindon, Y.; Young, R. N.; Adams, J.; Atkinson, J. G. *The Total Synthesis of Natural Products*; John Wiley and Sons: New York, NY, 1988; Vol. 7; (e) Borer, B. C.; Taylor, R. J. K. *Synlett* **1992**, 117–118; (f) Peng, Z.-H.; Li, Y.-L.; Wu, W.-L.; Liu, C.-X.; Wu, Y.-L. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1057–1065.
3. (a) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1875–1889; (b) Mori, K. *The Total Synthesis of Natural Products*; John Wiley and Sons: New York, NY, 1981; Vol. 4; (c) Hemming, K.; Taylor, R. J. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1409–1410; (d) Alvarez, R.; Herrero, M.; López, S.; de Lera, A. R. *Tetrahedron* **1998**, *54*, 6793–6810.
4. (a) Williams, J. M.; McGarvey, G. J. *Tetrahedron Lett.* **1985**, *26*, 4891–4894; (b) Nicolaou, K. C.; Chakraborty, T. K.; Daines, R. A.; Simpkins, N. S. *J. Chem. Soc., Chem. Commun.* **1986**, 413–416; (c) McGarvey, G. J.; Williams, J. M.; Hiner, R. N.; Matsubara, Y.; Oh, T. *J. Am. Chem. Soc.* **1986**, *108*, 4943–4952; (d) Schreiber, S. L.; Goulet, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 8120–8122; (e) Ohtani, T.; Kanda, H.; Misawa, K.; Urakawa, Y.; Toshima, K. *Tetrahedron Lett.* **2009**, *50*, 2270–2273; (f) Li, P.; Li, J.; Arikan, F.; Ahlbrecht, W.; Dieckmann, M.; Menche, D. *J. Org. Chem.* **2010**, *75*, 2429–2444.
5. (a) Isler, O.; Lindlar, H.; Montavon, M.; Ruegg, R.; Zeller, P. *Helv. Chim. Acta* **1956**, *39*, 249–259; (b) Isler, O.; Gutmann, H.; Lindlar, H.; Montavon, M.; Ruegg, R.; Ryser, G.; Zeller, P. *Helv. Chim. Acta* **1956**, *39*, 463–473; (c) Isler, O.; Schudel, P. *Adv. Org. Chem.* **1963**, *4*, 116–224 (Wiley Interscience Series); (d) Kienzle, F. *Pure Appl. Chem.* **1976**, *47*, 183–190; (e) Pfander, H.; Lachenmeier, A.; Hadorn, M. *Helv. Chim. Acta* **1980**, *63*, 1377–1382; (f) Dumahel, L.; Dumahel, P.; Le Gallic, Y. *Tetrahedron Lett.* **1993**, *34*, 319–322; (g) Rauchschwalbe, G.; Zellner, A.; Schlosser, M. *Eur. J. Org. Chem.* **2001**, *20*, 3903–3909; (h) Valla, A.; Valla, B.; Le Guillou, R.; Cartier, D.; Dufosse, L.; Labia, R. *Helv. Chim. Acta* **2007**, *90*, 512–520.
6. (a) Nielsen, A. T.; Houlihan, W. J. *Org. React.* **1968**, *16*, 1–438; (b) Mahata, P. K.; Barum, O.; Jla, H.; Junjappa, H. *Synlett* **2000**, 1345–1347; (c) Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. C. *J. Chem. Soc., Perkin Trans. 1* **2002**, 58–66; (d) Steen, R. O.; Nurkkala, L. J.; Angus-Dunne, S. J.; Schmitt, C. X.; Constable, E. C.; Riley, M. J.; Bernhardt, P. V.; Dunne, S. J. *Eur. J. Inorg. Chem.* **2008**, 1784–1794.
7. (a) Wittig, G.; Reiff, M. *Angew. Chem.* **1968**, *80*, 8–15; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 7–14; (b) Saito, S.; Yamamoto, H. *Chem. Commun.* **1997**, 1585–1592; (c) Saito, S.; Shiozawa, M.; Ito, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 813–814.
8. (a) Bellassoued, M.; Majidi, A. *J. Org. Chem.* **1993**, *58*, 2517–2522; (b) Bellassoued, M.; Salemkour, M. *Tetrahedron Lett.* **1993**, *34*, 5281–5284; (c) Bellassoued, M.; Reboul, E.; Salemkour, M. *Synth. Commun.* **1995**, *25*, 3097–3108; (d) Bellassoued, M.; Salemkour, M. *Tetrahedron* **1996**, *52*, 4607–4624.
9. (a) Duhamel, L.; Ple, G.; Ramondenc, Y. *Tetrahedron Lett.* **1989**, *30*, 7377–7380; (b) Contreras, B.; Duhamel, L.; Ple, G. *Synth. Commun.* **1990**, *20*, 2983–2990; (c) Duhamel, L.; Ancel, J.-E. *Tetrahedron* **1992**, *48*, 9237–9250; (d) Maeta, H.; Suzuki, K. *Tetrahedron Lett.* **1993**, *34*, 341–344; (e) Soullez, D.; Ple, G.; Duhamel, L. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1639–1645; (f) Si-Fodil, M.; Ferreira, H.; Gralak, J.; Duhamel, L. *Tetrahedron Lett.* **1998**, *39*, 8975–8978; (g) Villiers, P.; Soullez, D.; Ramondenc, Y.; Ple, G. *Tetrahedron* **1999**, *55*, 14031–14042.
10. (a) Cresp, T. M.; Sargent, M. V.; Vogel, P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 37–41; (b) Bestmann, H. J.; Vostrowsky, O.; Paulus, H.; Billmann, W.; Stransky, W. *Tetrahedron Lett.* **1977**, 121–124; (c) Rokach, J.; Young, R. N.; Kakushima, M.; Lau, C.-K.; Seguin, R.; Franette, R.; Guindon, Y. *Tetrahedron Lett.* **1981**, *22*, 979–981; (d) Bestmann, H. J.; Roth, K.; Ettlinger, M. *Chem. Ber.* **1982**, *115*, 161–171; (e) Baker, S. R.; Boot, J. R.; Morgan, S. E.; Osborn, D. J.; Ross, W. J.; Shrubsall, P. R. *Tetrahedron Lett.* **1983**, *24*, 4469–4472; (f) Ernest, I.; Main, A.; Menasse, R. *Tetrahedron Lett.* **1982**, *23*, 167–170; (g) Spangler, C. W.; McCoy, R. K. *Synth. Commun.* **1988**, *18*, 51–60; (h) Ivanova, D. I.; Eremin, S. V.; Shvets, V. I. *Tetrahedron* **1996**, *52*, 9581–9588.
11. (a) Takahashi, H.; Fujiwara, K.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1498–1500; (b) Nagata, W.; Hayase, Y. *Tetrahedron Lett.* **1968**, 4359–4362; (c) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87–89; (d) Meyers, A. J.; Tomoika, K.; Fleming, M. P. *J. Org. Chem.* **1978**, *43*, 3788–3789; (e) Nuzillard, J.-M.; Boumendjel, A.; Massiot, G. *Tetrahedron Lett.* **1989**, *30*, 3779–3780; (f) Dumahel, L.; Guillemont, J.; Le Gallic, Y.; Ple, G.; Poirier, J.-M.; Ramondenc, Y.; Chabardes, P. *Tetrahedron Lett.* **1990**, *31*, 3129–3132; (g) Kann, N.; Rein, T.; Åkermark, B.; Helquist, P. *J. Org. Chem.* **1990**, *55*, 5312–5323; (h) Mohamed-Hachi, A.; About-Jaudet, E.; Combret, J.-C.; Collignon, N. *Synthesis* **1999**, 1188–1192.
12. (a) Wang, Y.; Li, J.; Wu, Y.; Huang, Y.; Shi, L.; Yang, J. *Tetrahedron Lett.* **1986**, *27*, 4583–4584; (b) Gravier-Pelletier, C.; Dumas, J.; Le Merrer, Y.; Depezay, J. C. *Tetrahedron Lett.* **1991**, *32*, 1165–1168.
13. (a) Nazarov, I. N.; Nazarova, I. I.; Torgov, I. V. *Dokl. Akad. Nauk SSSR* **1958**, *122*, 82–85; *Chem. Abstr.* **1959**, *53*, 1123f–11224a; (b) Mikhailov, B. M.; Ter-Sarkisjan, G. S. *J. Ger. Chem. USSR* **1959**, *29*, 2560–2565 (Engl. Transl., 2525–2529); (c) Yanovskaya, L. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1638–1644; *Chem. Abstr.* **1966**, *64* 3342b–3342d; (d) Yanovskaya, L. A.; Yufit, S. S.; Kucherov, V. F. *The Chemistry of Acetals*; Nauka: Moscow, 1975; [in Russian].
14. (a) Makin, S. M. *Pure Appl. Chem.* **1976**, *47*, 173–181; (b) Reuttimann, A. Eur. Patent Appl. EP816334, 1998; (c) Reuttimann, A. Eur. Patent Appl. EP919547, 1999.
15. (a) Mukaiyama, T.; Ishida, A. *Chem. Lett.* **1975**, 319–322; (b) Mukaiyama, T.; Ishida, A. *Chem. Lett.* **1975**, 1201–1202; (c) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1161–1168; (d) Domagalska, B. W.; Syper, L.; Wilk, K. A. *Synthesis* **2001**, 2463–2469; (e) Domagalska, B. W.; Syper, L.; Wilk, K. A. *Tetrahedron* **2004**, *60*, 1931–1939.
16. (a) Hoaglin, R. I.; Hirsh, D. H. *J. Am. Chem. Soc.* **1949**, *71*, 3468–3472; (b) Brugger, U.; Lammers, R.; Mayr, H. *J. Org. Chem.* **1988**, *53*, 2920–2925.
17. (a) Li, D.; Shi, F.; Peng, J.; Guo, S.; Deng, Y. *J. Org. Chem.* **2004**, *69*, 3582–3585; (b) Wu, H.-H.; Yang, F.; Cui, P.; Tang, J.; He, M.-Y. *Tetrahedron Lett.* **2004**, *45*, 4963–4965; (c) Gupta, N.; Sonu; Kad, G. L.; Singh, J. *Catal. Commun.* **2007**, *8*, 1323–1328; (d) Wang, Y.; Jiang, D.; Dai, L. *Catal. Commun.* **2008**, *9*, 2475–2480.
18. Du, Y.; Tian, F. *Synth. Commun.* **2005**, *35*, 2703–2708.
19. (a) *Ionic Liquids in Synthesis*, 1st ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH GmbH & KGaA: Weinheim, Germany, 2008; (b) *Ionic Liquids in Synthesis*, 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH GmbH & KGaA: Weinheim, Germany, 2008; (c) Parvulescu, I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665; (d) Durand, J.; Teuma, E.; Gómez, M. *C.R. Chimie* **2007**, *10*, 152–177; (e) Šebesta, R.; Kmentová, I.; Toma, S. *Green Chem.* **2008**, *10*, 484–496.
20. Glushko, L. P.; Kryshtal, G. V.; Kogan, S. A.; Yanovskaya, L. A. *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **1977**, *26*, 869–872.
21. (a) Lee, S. Y.; Kulkarni, Y. S.; Burbaum, B. W.; Johnston, M. I.; Snider, B. B. *J. Org. Chem.* **1988**, *53*, 1848–1855; (b) Lahmar, N.; Aatar, I.; Ayed, T. B.; Amri, H.; Bellassoued, M. M. *J. Organomet. Chem.* **2006**, *691*, 3018–3026; (c) Borch, R. F.; Evans, A. J.; Wade, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 6282–6284; (d) Varelis, P.; Johnson, B. L. *Aust. J. Chem.* **1997**, *50*, 43–51.
22. (a) Yamatsu, I.; Suzuki, T.; Abe, S.; Inai, Y.; Suzuki, Y.; Tagaya, O. Ger. Offen. DE 3320544, 1983; (b) Kryshtal, G. V.; Zhdankina, G. M.; Serebryakov, E. P. *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **1993**, *42*, 2039–2041; (c) Kryshtal, G. V.; Serebryakov, E. P. *Bull. Acad. Sci. USSR. Div. Chem. Sci. (Engl. Transl.)* **1995**, *44*, 1785–1804.
23. Sasson, Y.; Rothenberg, G. In *Handbook of Green Chemistry and Technology*; Clark, J., Macquarrie, D., Eds.; Blackwell Science Ltd.: Oxford, 2002.
24. Isler, O.; Huber, W.; Konco, A.; Kofler, M. *Helv. Chim. Acta* **1947**, *30*, 1911–1927.
25. Kryshtal, G. V.; Zhdankina, G. M.; Zlotin, S. G. *Eur. J. Org. Chem.* **2005**, 2822–2827.
26. Nazarov, I. N.; Makin, S. M.; Kruptzov, V. K.; Mironov, V. A. *J. Ger. Chem. USSR* **1959**, *29*, 106–111 (Engl. Transl., 111–116).
27. Lee, A. S.-Y.; Cheng, C.-L. *Tetrahedron* **1997**, *53*, 14255–14262.
28. Salzer, A.; Schmalle, H.; Streiff, S. *J. Organomet. Chem.* **1991**, *408*, 403–424.