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Copper-Catalyzed Conjugate Addition of Trialkylaluminium to α,β-Unsaturated Carbonyl Compounds

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Abstract: The Michael-type reaction of copper-catalyzed trialkylaluminium reagents with α,β-unsaturated carbonyl compounds is a useful and simple procedure for the transfer of hydrocarbon substituents. The scope of this process and the effect of chlorotrimethylsilane as additive were investigated. Preparatively useful results were generally obtained for enones even with higher organoaluminium reagents, whereas the reaction with α,β-unsaturated aldehydes was limited to the use of trimethylaluminium.

Introduction

The 1,4-addition of hydrocarbon substituents to α,β-unsaturated carbonyl compounds is usually achieved by using organocuprate reagents[1,2]. The use of organozincates[3], organomanganese reagents[4], organotitanates[5,16] or Grignard compounds[1,6] was also reported. Attempts to transfer ligands from organoaluminium reagents to enones were successful for the insertion of vinyl[7] and alkynyl[8] groups but only gave moderate results when using trimethylaluminium (TMA)[9]. However, remarkable results were obtained by the reaction of TMA with α,β-unsaturated acetals[10].

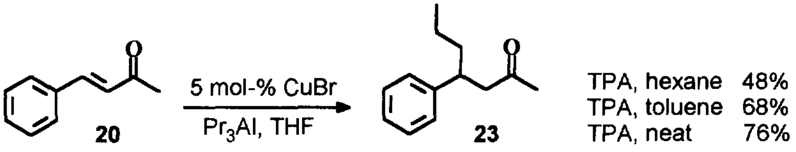
In recent communications, our group described the Cu^I-catalyzed Michael-type reaction of TMA and triethylaluminium (TEA) with enones[11,12] and α,β-unsaturated aldehydes[13] and the Ni-catalyzed conjugate addition of TMA to sterically hindered enones[14,15]. The use of $Ni(acac)_2$ as a catalyst was shown to be limited to ligands without β-hydrogen[8,14,16]. Additionally, we reported results concerning the function of chlorotrimethylsilane (TMSCl) as an additive in this type of reaction[17]. In continuation of these investigations the applicability of this procedure was expanded to the use of different commercially available trialkylaluminium compounds. The present paper describes a versatile protocol for transfering hydrocarbon substituents from trialkylaluminium to α,β-unsaturated carbonyl compounds in a catalytic process.

Results and Discussion

Previous investigations demonstrated the significance of (co-) solvents used in this type of reaction especially in view of the formation of by-products[12]. THF turned out to be the solvent of choice and CuBr was the most efficient catalyst for this method. Commercially available solutions of trialkylaluminium in *n*-hexane and toluene, respectively, were proven to be less useful in most cases. Therefore, when 4-phenylbut-3-en-2-one (**20**) was treated with tripropylaluminium (TPA, 10% solution in *n*-hexane) to insert a propyl group in the presence of catalytic amounts of CuBr (5 mol-%) in THF, 4-phenyl-2-heptanone (**23**) was isolated in only 48%.

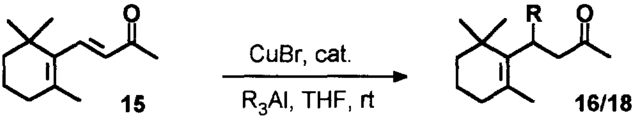
Using TPA dissolved in toluene the yield rose up to 68%. However, the reaction time decreased by using neat TPA in THF and **23** was obtained in 76% yield (Scheme 1).

Scheme 1



For higher trialkylaluminium compounds increased reaction times were observed in comparison to the reaction with TMA[12] and TEA, respectively, and 1,2-products were formed to a higher extent. For example, the reaction of TMA with β-ionone (**15**) resulted in 96% of **16** during 30 min in the presence of only 0.1 mol-% of CuBr. With TPA 83% of **18** was isolated after 5 h using 5 mol-% of CuBr under the accelerating influence of TMSCl (Scheme 2). The allylic alcohol by-product from a 1,2-attack has been detected by TLC-control along with the mainly formed silyl enol ether.

Scheme 2

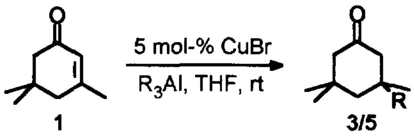


R = Me, 0.1 mol-% CuBr, 0.5 h, 96% of **16**
= Pr, 5 mol-% CuBr, TMSCl, 5 h, 83% of **18**

On systematic investigations standard conditions for the reaction of enones with trialkylaluminium compounds were established (see also ref.[12]); the results are summarized in Table 1 and 2. Therefore, the reaction of triisobutylaluminium (TIBA) dissolved in toluene with isophorone (**1**) yielded the 1,4-product **5** in 51%; 61% were obtained by the influence of TMSCl (Table 1; entries 1, 2). In both cases consumption of starting material was incomplete and polar by-products were detected by TLC. Using neat TIBA in THF as solvent the yield rose up to give **5** in 75% (entry 1.3). 82% of **5** were obtained in a very clean reaction using TMSCl as an additive (entry 1.4); the reaction rate increased and full conversion of starting material was achieved. Similar results were obtained for carvone (**6**, Table 2). Excellent yields for the transfer of an *iso*-butyl group from TIBA were obtained using TMSCl; without an additive the yield of **10** was lower (Table 2; entries 3, 4). Toluene solutions of TIBA gave less satisfying results (entries 2.1, 2.2). The reaction of **1** and **6** with triethylaluminium (TEA) led to similar results as with TIBA (Table 1; entries 5-7. Table 2; entries 5, 6).

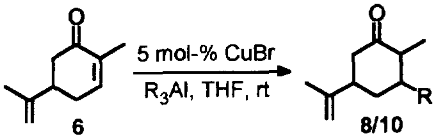
Therefore, TMSCl turned out to be an useful additive especially for the reaction of less active enones with higher trialkylaluminium reagents. Cleaner and accelerated reactions were generally observed under the influence of the silane. For standard conditions 5 mol-% of CuBr as catalyst, an extent of the neat organoaluminium compound (1.2 equiv.) and 2 equiv. of TMSCl in a 0.5 M THF solution of the carbonyl compound were used at room temperature. Advantages of the use of TMSCl were less significant for according reactions with TEA (and TMA).

Table 1. Alkylation of Isophorone (1)



Entry	R_3Al	TMSCl	Yield (product)
1	*iso*-Bu_3Al (toluene)	-	51% (5)
2	*iso*-Bu_3Al (toluene)	+	61% (5)
3	*iso*-Bu_3Al (neat)	-	75% (5)
4	*iso*-Bu_3Al (neat)	+	82% (5)
5	Et_3Al (toluene)	-	86% (3)
6	Et_3Al (neat)	-	93% (3)
7	Et_3Al (neat)	+	91% (3)

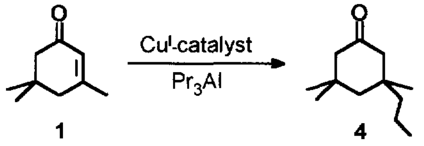
Table 2. Alkylation of Carvone (6)



Entry	R_3Al	TMSCl	Yield (product)
1	*iso*-Bu_3Al (toluene)	-	65% (10)
2	*iso*-Bu_3Al (toluene)	+	64% (10)
3	*iso*-Bu_3Al (neat)	-	73% (10)
4	*iso*-Bu_3Al (neat)	+	94% (10)
5	Et_3Al (toluene)	-	89% (8)
6	Et_3Al (neat)	-	94% (8)

Unfortunately, the reaction of the sterical hindered enone isophorone (1) with TPA under standard conditions led to an incomplete consumption of starting material (Table 3; entry 1). The influence of TMSCl (entry 3.2), higher reaction temperatures (entries 3.3, 3.4), and CuCN as catalyst (entries 3.5, 3.6) favoured this tendency. However, these problems, which are attributed to a decomposition of the organoaluminium reagent and/or of the catalyst, were circumvented by adding TPA in two portions to the mixture. Full conversion and good yields of 1,4-product were obtained (entries 3.7, 3.8).

Table 3. Propylation of Isophorone (1)

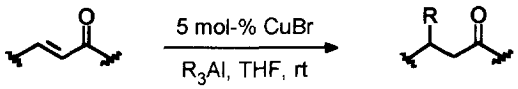


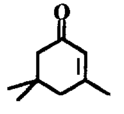
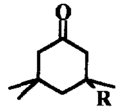
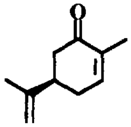
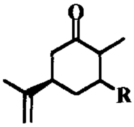
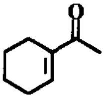
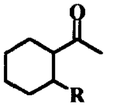
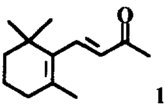
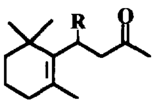
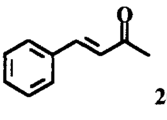
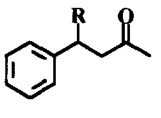
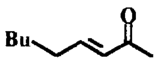
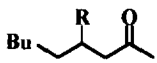
	TMSCl	Conditions	Yield[b]	GC - ratio	
				1	4
1	-	2x 5% CuBr[a], 7.5 h rt	87%	87%	9%
2	+	2x 5% CuBr[a], 7.5 h rt	91%	76%	22%
3	-	2x 5% CuBr[a], 6 h 45°C	82%	78%	14%
4	+	2x 5% CuBr[a], 6 h 45°C	82%	62%	36%
5	-	5% CuCN, 7.5 h rt	55%	64%	22%
6	+	5% CuCN, 7.5 h rt	n.d.[c]	29%	9%
7	-	5% CuBr, 6.5 h rt[d]	85%	89%	3%
8	+	5% CuBr, 6.5 h rt[d]	92%	91%	< 1%

[a] A second portion of catalyst was added after 2.5 h. [b] Yield of distillative isolated crude product. [c] 1,2-product was obtained as main product. [d] TPA was added in two portions, the second one after 2.5 h.

Table 4 summarizes the results obtained by treatment of enones with various trialkylaluminium reagents in THF. In most counts good to excellent yields of Michael-type reaction products were obtained. The use of TMSCl is of advantage especially for reactions with higher alkylaluminium reagents. As described previously[12] some typical side reactions were generally supressed by using neat TMA or TEA in THF. Unfortunately, under these conditions this effect was less significant by the use of higher trialkylaluminium compounds resulting in decreased yields of the desired 1,4-products along with high amounts of unidentified polar by-products (Table 4; entries 18, 19, 22, 23); TMSCl as an additive seemed to favour this undesired tendency (entries 4.18, 4.22).

Table 4. Michael-Addition of Trialkylaluminium to Enones

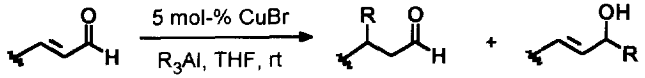


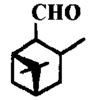
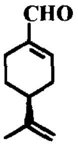
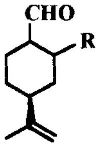
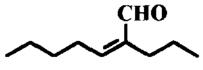
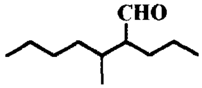
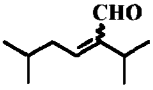
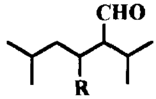
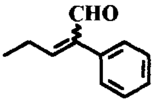
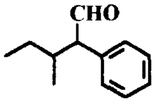
Entry	Starting material	Products	R	Product	Time, Yield (1,4-product)	
					no additive	2 equiv. TMSCl
1	 1		Me	**2**	5 h, 95%	3.5 h, 96%[b]
2			Et	**3**	2.5 h, 93%	2.5 h, 91%
3			Pr	**4**	9.5 h, 81%[a]	5.5 h, 85%[a]
4			Bu^{i}	**5**	7.5 h, 75%[c]	6.5 h, 82%[c]
5	 6		Me	**7**	0.5 h, 92%[b]	0.5 h, 96%[b]
6			Et	**8**	2.5 h, 94%	-
7			Pr	**9**	6.5 h, 76%	3.5 h, 93%
8			Bu^{i}	**10**	6.5 h, 73%	2.5 h, 94%
9	 11		Me	**12**	2 h, 81%	1.5 h, 75%[b]
10			Pr	**13**	-	3 h, 80%
11			Bu^{i}	**14**	-	2.5 h, 63%
12	 15		Me	**16**	0.5 h, 96%	-
13			Et	**17**	2.5 h, 86%	-
14			Pr	**18**	-	5 h, 83%
15			Bu^{i}	**19**	3.5 h, 37%	2.5 h, 72%
16	 20		Me	**21**	1 h, 91%[b]	0.5 h, 83%[b]
17			Et	**22**	2.5 h, 76%	0.5 h, 72%
18			Pr	**23**	4 h, 52%	5 h, 34%
19			Bu^{i}	**24**	7 h, 27%	5 h, 14%
20	 25		Me	**26**	1.5 h, 96%	0.5 h, 73%[b]
21			Et	**27**	4.5 h, 71%	-
22			Pr	**28**	4 h, 51%	4 h, 33%
23			Bu^{i}	**29**	5 h, 30%	-

[a] Pr_3Al was added in two portions of 1.15 ml (the second after 2.5 h) due to decompositon of organoaluminium reagent and/or catalyst during the long reaction time. [b] Me_3Al was used as a 10% solution in *n*-hexane. [c] A second portion of CuBr (5 mol-%) was added after 1.5 h due to reductive decomposition of the catalyst during the reaction.

Representative results for the reaction of trialkylaluminium with α,β-unsaturated aldehydes are summarized in Table 5. Using TMA good yields of the desired Michael-products were obtained in general; but 1,2-products were observed to a higher extent compared with enones (Table 5). No advantages were observed by using the neat organoaluminium compound; *n*-hexane solutions of TMA led to similar results. However, higher organoaluminium reagents gave 1,2-attack predominantly. Slightly higher yields were obtained using neat alkylalanes in this case but all in all results were unsatisfying due to the high amounts of 1,2-products (entries 5.5, 5.6, 5.12). The use of TMSCl as an additive resulted in significantly reduced yields of 1,4- and 1,2-products due to the forming of oligomeric by-products (Table 5; entries 1/2, 3/4, 11/12). Obviously, for preparatively useful reactions, this application was limited to the use of TMA.

Table 5. Michael-Addition of Trialkylaluminium to α,β-Unsaturated Aldehydes



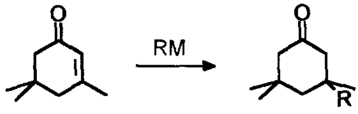
Entry	Starting material	Products	R	Product	TMSCl	Yield (1,4-/1,2-ratio)[a]
1	 30		Me	31	+	1.5 h, 87% (85 : 15)
2			Me	31	-	1.5 h, 97% (81 : 19)
3	 32		Me	33	+	1.5 h, 89% (89 : 11)
4			Me	33	-	1.5h, 95% (90 : 10)
5			Et	34	-	2.5 h, 74% (36 : 64)
6			Bu^i	35	-	1 h, 69% (25 : 75)[c]
7	 36		Me	37	-	1 h, 96% (91 : 9)
9	 38		Me	39	+	1 h, 99% (88 : 12)
10			Me	39	-	1.5 h, 98% (83 : 17)
11			Bu^i	40	+	2.5 h, -[b]
12			Bu^i	40	-	1 h, 85% (15 : 85)[d]
13	 41		Me	42	-	2 h, 98% (91 : 9)

Me_3Al was used as a 10% solution in *n*-hexane; Et_3Al and Bu^i_3Al were used in neat state. [a] 1,4-/1,2-ratio was proved by GC from isolated product mixtures. [b] Complex product mixture. [c] Bu^i_3Al in toluene: 63% (15 : 85). [d] Bu^i_3Al in toluene: Complex product mixture.

Table 6 gives an overview (not exhaustive) of results obtained for the conjugate addition of isophorone (**1**) by various organometallic reagents. In comparison with results depicted in Table 4 (entry 1 to 4) the described reaction is a useful and successful method for the conjugate alkylation of α,β-unsaturated carbonyl compounds. To obtain similar results by different methods, low temperature chemistry (entries 6.4, 6.10) and/or the use of hazardous additives (entry 6.6) is often essential.

Table 6.

Conjugate Alkylation of Isophorone by Various Methods



	RM	Conditions	R	Yield	Ref.
1	R_3Al	5% $Ni(acac)_2$, Et_2O, 0°C	Me	88%	9b
2	R_3Al	5% $Cu(acac)_2$, Et_2O, rt	Me	85%	9d
3	RLi	MAD, toluene, -78°C	Me	0%	18
4	RMgBr	5% CuCl, Et_2O, -78°C	Me	83%	1a
5	RMgBr	5% CuBr, $BF_3{*}Et_2O$, THF, -70°C	Pr	14%	6b
6	RMgBr	5% CuBr, TMSCl, HMPT, -78°C	Bu	89%	6b
7	RMnCl	5% CuCl, THF, 0°C	Bu	95%	4a
8	R_2Zn	5% $Ni(acac)_2$, Et_2O, rt	Me	90%	3b
9	R_3ZnLi	5% $Ni(acac)_2$, Et_2O, -78°C	Me	15%	3e
10	R_3Cu_2Li	$BF_3{*}Et_2O$, THF, -78°C	Bu	91%	2b

Conclusion

In summary, the Cu^I-catalyzed addition of trialkylaluminium reagents to α,β-unsaturated carbonyl compounds is an efficient and simple method of alkylation circumventing low temperature chemistry. There is no need for a titration-protocol concerning the addition of starting material, and the work-up procedure is quite simple. The process is superior to other methods concerning the ecological hazard due to the use of only catalytical amounts of transition metals and the avoidance of additives such as HMPA or TMEDA. These characteristics make the described method a useful alternative to previous methods. For enones best results were obtained using neat organoaluminium compounds; ethereal stock solutions may also be used. For α,β-unsaturated aldehydes this method seemed to be limited to the use of TMA. We have to point out, that higher trialkylalanes are very efficient reagents for the reduction of α,β-unsaturated carbonyl compounds[19]. However, under the conditions described these compounds were succesfully used as substituent shuttles.

Experimental Section

All experiments were performed under N_2. Glassware was not dried before use. Solvents and organic compounds were used without further purification in commercially available quality. Flash chromatography was performed on Merck silica gel 60 (230-400 mesh). TLC control was done with Merck TLC aluminium sheets silica gel 60 F_{254}. Distillations were performed on a kugelrohr Büchi GKR 50. The given temperatures for the products are not the expected boiling points but the chosen temperatures of the oven for isolation of analytical samples by kugelrohr distillation. For preparative isolation of substances increased ranges of oven temperatures were chosen. Yields were corrected with regard to the purity of substrate and product obtained by GC.

IR: Nicolet 20 SXB or Nicolet 710 as capillary film (neat). - MS (70 eV): Vacuum Generator TRIO 2. - NMR (^1H: 300 MHz; ^{13}C: 75 MHz): General Electric QE 300 or Bruker AM 300; $CDCl_3$ or C_6D_6 was used as solvent, tetramethylsilane as an internal standard. ^{13}C DEPT/ ATP: CH_3/ CH (+), CH_2 (-), C (∗). - GC: Perkin-Elmer Sigma 300; 50m CP Sil 8 CB (0.45/0.32), 60-260°C, 8 or 10°C/min., 135 kPa He.

Method A - General Procedure for the Reaction of Enones and α,β-Unsaturated Aldehydes with Neat Trialkylaluminium: To 20 ml of THF neat trialkylaluminium (12 mmol)* was added in one portion *via* a syringe (***Caution:*** Neat alkylaluminiums are highly pyrophoric liquids; use gastight syringes for handling!) and stirred for 30 min. CuBr (72 mg, 0.5 mmol) was added followed by the enone (10 mmol). The mixture was stirred for the given reaction time at room temperature (Table 4, 5; TLC control). Then *n*-hexane (20 ml) was added and the reaction was quenched by careful addition of 1.5 ml of a saturated aqueous NH_4Cl solution**. After recooling to room temperature 1.0 g of $MgSO_4$ was added and stirring was continued for additional 30 min. The mixture was filtered through a "Duran sintered disc filter funnel (D4)" and the residue was washed three times with 30 ml of THF each. The solvent was removed from the combined filtrates under reduced pressure and the resulting crude product was purified by kugelrohr distillation.

Method B - General Procedure for the Reaction of Enones and α,β-Unsaturated Aldehydes with Neat Trialkylaluminium/TMSCl: To 20 ml of THF neat trialkylaluminium (12 mmol)* was added in one portion *via* a syringe (***Caution:*** Neat alkylaluminiums are highly pyrophoric liquids; use gastight syringes for handling!) and stirred for 25 min. Then TMSCl (2.5 ml, 20 mmol) was added via syringe and stirring was continued for 5 min. CuBr (72 mg, 0.5 mmol) was added followed by the enone (10 mmol). The mixture was stirred for the given reaction time at room temperature (Table 4, 5; TLC control) and then worked up and isolated as described in method A (2.5 ml of NH_4Cl solution**).

Method C - General Procedure for the Reaction of Enones and α,β-Unsaturated Aldehydes with n-Hexane Solutions of TMA: To 15 ml of THF TMA (10% solution in *n*-hexane, 10.7 ml, 10 mmol) was added in one portion *via* a syringe and stirred for 30 min. CuBr (72 mg, 0.5 mmol) was added followed by the enone (10 mmol). The mixture was stirred for the given reaction time at room temperature (Table 4, 5; TLC control) and then worked up and isolated as described in method A. (Reactions involving the use of TMSCl were performed by adding the additive similar to method B.)

*Me_3Al 1.15 ml; Et_3Al 1.75 ml; Pr_3Al 2.30 ml; $^{i}Bu_3Al$ 3.05 ml. ** For distillative separation aldehydes were quenched with Na_2CO_3. During this work-up procedure the alcoholic by-products undergo an elimination reaction and the resulting hydrocarbons were generally found in the early fractions of the distillation.

3,3,5,5-Tetramethylcyclohexanone (2): Colourless liquid, 120°C/15 mbar (79°C/12 Torr[20]), 1.48 g (95%, method A). Spectroscopic data see ref.[12].

3-Ethyl-3,5,5-trimethylcyclohexanone (3): Colourless liquid, 130°C/20 mbar (224-226°C/760 Torr[21]), 1.55 g (93%, method A). - ^1H NMR ($CDCl_3$): δ = 2.15 (m, 4 H), 1.58 (d, J = 36 Hz, 1 H), 1.53 (d, J = 36 Hz, 1 H), 1.47-1.25 (m, 2 H), 1.06 (s, 3 H), 1.04 (s, 3 H), 0.99 (s, 3 H), 0.85 (t, J = 7.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, ATP): δ = 212.5 (∗), 54.2 (-), 52.7 (-), 48.6 (-), 38.8 (∗), 37.0 (-), 36.0 (∗), 32.3 (+), 30.6 (+), 26.8 (+), 8.2 (+). - MS: m/z = 168 (M^+, 9), 153 (14), 139 (50), 97 (56), 83 (100). - IR: 2960, 1715 cm^{-1}. - $C_{11}H_{20}O$: calcd. = 78.51 H = 11.98; found C = 78.08 H = 11.71.

3-Propyl-3,5,5-trimethylcyclohexanone (4): Colourless liquid, 145-150°C/15 mbar (242°C/760 Torr[21]), 1.67 g (85%, method B). - ^1H NMR ($CDCl_3$): δ = 2.15 (m, 4 H), 1.59 (d, J = 39 Hz, 1 H), 1.55 (d, J = 39 Hz, 1 H), 1.40-1.25 (m, 4 H), 1.06 (s, 6 H), 1.01 (s, 3 H), 0.90 (t, J = 7.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, ATP): δ = 211.8 (∗), 54.2 (-), 53.0 (-), 49.4 (-), 47.4 (-), 38.6 (∗), 35.8 (∗), 32.3 (+), 30.8 (+), 27.6 (+), 17.0 (-), 14.6 (+). - MS: m/z = 182 (M^+, 0.5), 167 (12), 139 (57), 97 (26), 83 (100). - IR: 2960, 1715 cm^{-1}. - $C_{12}H_{22}O$: calcd. C = 79.06 H = 12.16; found C = 78.42 H = 11.78.

3-(2'-Methylprop-1'-yl)-3,5,5-trimethylcyclohexanone[22] (5): Colourless liquid, 155-160°C/20 mbar, 1.80 g (82%, method B). - ^1H NMR ($CDCl_3$): δ = 2.15 (m, 4 H), 1.72 (m, J = 5.5 Hz, 1 H), 1.61 (d, J = 30 Hz, 1 H), 1.55 (d, J = 30 Hz, 1 H), 1.29 (dd, J = 5 Hz, J' = 25 Hz, 1 H), 1.22 (dd, J = 5 Hz, J' = 25 Hz, 1 H), 1.08 (s, 3 H), 1.05 (s, 6 H), 0.95 (d, J = 5.5 Hz, 3 H), 0.94 (d, J = 5.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 212.4 (∗), 54.4 (-), 54.1 (-), 53.3 (-), 49.9 (-), 39.5 (∗), 35.9 (∗), 33.2 (+), 30.1 (+), 27.3 (+), 25.5 (+), 25.2 (+), 24.0 (+). - MS: m/z = 196 (M^+, 0.5), 182 (7), 139 (100), 97 (22), 83 (76). - IR: 2960, 1715 cm^{-1}. - $C_{13}H_{24}O$: calcd. C = 79.53 H = 12.32; found C = 79.46 H = 12.44.

(3R)-3-Isopropenyl-5,6-dimethylcyclohexane (7): Colourless liquid, 145-150°C/12 mbar (102-103°C/11 Torr[23]), 1.60 g (96%, method B). Spectroscopic data see ref.[12].

(3R)-3-Isopropenyl-5-ethyl-6-methylcyclohexanone (8)[24]: Colourless liquid, 145-150°C/15 mbar, 1.75 g (94%, method A) as a mixture of 4 stereoisomers (6 : 5 : 3 : 1 by ^{13}C NMR). Spectral data are given for the three main isomers. - ^1H NMR ($CDCl_3$): δ = 4.76 (m, 2 H), 2.70-2.10 (m, 4 H), 2.00 (m, 1 H), 1.76 (s, 3 H), 1.78-1.20 (m, 4 H), 1.11 + 0.89 (d, J = 6.0 Hz, Σ 3 H), 1.05 + 0.95 (t, J = 7.5 Hz, Σ 3 H). - ^{13}C NMR ($CDCl_3$,

DEPT): δ = **a:** 212.8 (*), 147.7 (*), 109.5 (-), 48.8 (+), 46.6 (-), 45.4 (+), 42.5 (+), 35.7 (-), 26.2, 20.3 (+), 11.6 (+), 11.3 (+); **b:** 212.7 (*), 147.5 (*), 109.8 (-), 48.7 (+), 46.2 (-), 45.1 (+), 40.6 (+), 32.6 (-), 20.6 (+), 19.6 (-), 11.7 (+), 10.0 (+); **c:** 113.9 (*), 147.0 (*), 111.2 (-), 49.3 (+), 43.7 (-), 41.4 (+), 40.5 (+), 30.7 (-), 26.1 (-), 21.4 (+), 14.0 (+), 10.9 (+). - MS: m/z = 180 (M$^+$, 77), 151 (25), 137 (25), 109 (73), 95 (100), 83 (94). - IR: 3080, 2960, 1715, 1645 cm^{-1}. - C$_{12}$H$_{20}$O: calcd. C = 79.95 H = 11.18; found C = 79.40 H = 10.86.

(3R)-3-Isopropenyl-5-propyl-6-methylcyclohexanone (9)[24]: Colourless liquid, 165-170°C/12 mbar, 1.99 g (93%, method B) as a mixture of 4 stereoisomers (9 : 7 : 6 : 1 by ^{13}C NMR). Spectral data are given for the three main isomers. - ^{1}H NMR (CDCl$_3$): δ = 4.75 (m, 2 H), 2.70-2.07 (m, 4 H), 2.00 (m, 1 H), 1.75 (s, 3 H), 1.80-1.55 (m, 2 H), 1.50-1.20 (m, 4 H), 1.13 + 1.01 + 1.01 (d, J = 6.0 Hz, Σ 3 H), 0.92 + 0.89 (t, J = 6.0 Hz, Σ 3 H). - ^{13}C NMR (CDCl$_3$, DEPT): δ = **a:** 213.0 (*), 147.6 (*), 109.8 (-), 48.7 (+), 46.2 (-), 40.8 (+), 40.6 (+), 35.9 (-), 29.0 (-), 20.7 (+), 20.3 (-), 14.2 (+), 11.7 (+); **b:** 212.7 (*), 147.1 (*), 109.6 (-), 49.7 (+), 44.3 (+), 43.7 (-), 39.9 (+), 36.4 (-), 33.2 (-), 21.4 (+), 19.8 (-), 14.3 (+), 11.4 (+); **c:** 214.1 (*), 147.8 (*), 111.1 (-), 49.4 (+), 46.7 (-), 45.2, 36.3 (-), 31.2 (-), 30.3 (+), 20.4 (+), 19.2 (-), 14.3 (+), 14.1 (+). - MS: m/z = 194 (M$^+$, 35), 151 (17), 111 (62), 97 (100). - IR: 3080, 2960, 1710, 1640 cm^{-1}. - C$_{13}$H$_{22}$O: calcd. C = 80.36 H = 11.41; found C = 79.84 H = 10.96.

(3R)-3-Isopropenyl-5-(2'-methylprop-1'-yl)-6-methylcyclohexanone (10): Colourless liquid, 165-170°C/11 mbar, 2.02 g (94%, method B) as a mixture of 4 stereoisomers (14 : 10 : 9 : 1 by ^{13}C NMR). Spectral data are given for the three main isomers. - ^{1}H NMR (CDCl$_3$): δ = 4.75 (m, 2 H), 2.70-1.88 (m, 6 H), 1.75 (s, 3 H), 1.80-1.10 (m, 4 H), 1.15-0.80 (m, 9 H). - ^{13}C NMR (CDCl$_3$, DEPT): δ = **a:** 214.2 (*), 147.6 (*), 109.8 (-), 48.6 (+), 46.3 (-), 43.6 (-), 41.0 (+), 38.4 (+), 33.4 (-), 25.0 (+), 23.9 (+), 21.1 (+), 20.6 (+), 11.7 (+); **b:** 213.0 (*), 147.7 (*), 109.6 (-), 50.1 (+), 46.7 (-), 45.2 (+), 43.5 (-), 38.0 (+), 35.9 (-), 25.2 (+), 24.2 (+), 21.7 (+), 21.3 (+), 11.5 (+); **c:** 212.5 (*), 147.1 (*), 111.0 (-), 50.2 (+), 44.1 (-), 42.5 (+), 40.6 (+), 36.7 (-), 31.1 (-), 25.3 (+), 23.6 (+), 21.2 (+), 20.3 (+), 14.6 (+). - MS: m/z = 209 (M$^+$, 30), 137 (42), 125 (45), 111 (82), 95 (73), 81 (46), 69 (100). - IR: 3080, 2950, 1710, 1640 cm^{-1}. - C$_{14}$H$_{24}$O: calcd. C = 80.71 H = 11.61; found C = 80.35 H = 11.39.

1-Acetyl-2-methylcyclohexane (12): Colourless liquid, 130-140°C/20 mbar, 1.08 g (81%, 8 mmol scale, method A), diastereomeric mixture (2 : 1 by GC). Spectroscopic data see ref.[12].

1-Acetyl-2-propylcyclohexane (13)[25]: Colourless liquid, 140°C/15 mbar, 1.43 g (80%, method B), diastereomeric mixture (1.5 : 1 by GC). - ^{1}H NMR (CDCl$_3$): δ = 2.58 (quint, J = 4.5 Hz) + 2.16 (dq, J = 3 Hz, J'= 11 Hz) [Σ 1 H], 2.03 + 2.02 (s, Σ 3 H), 2.00 (m, 1 H), 1.84-0.90 (m, 12 H), 0.88 + 0.86 (t, J = 7.5 Hz, Σ 3 H). - ^{13}C NMR (CDCl$_3$, APT): δ = **a:** 211.3 (*), 53.9 (-), 38.3 (-), 37.2 (+), 31.0 (+), 28.8 (+), 28.8 (-), 25.8 (+), 21.9 (+), 20.9 (+), 14.2 (-); **b:** 212.7 (*), 58.0 (-), 37.2 (+), 36.6 (-), 30.9 (+), 29.8 (+), 28.8 (-), 24.5 (+), 23.9 (+), 19.6 (+), 14.1 (-). - MS: m/z = 168 (M$^+$, 5), 125 (22), 110 (21) 83 (34), 69 (55), 55 (43), 43 (100). - IR: 2925, 2860, 1710 cm^{-1}. - C$_{11}$H$_{20}$O: calcd. C = 78.51 H = 11.98; found C = 78.23 H = 11.69.

1-Acetyl-2-(2'-methylprop-1'-yl)-cyclohexane (14): Colourless liquid, 140-145°C/15 mbar, 1.33 g (63%, method B), diastereomeric mixture (3 : 1 by GC). - ^{1}H NMR (CDCl$_3$): δ = 2.58 (quint, J = 4.5 Hz) + 2.11 (m) [Σ 1 H], 2.11 + 2.05 (s, Σ 3 H), 2.10 (m, 1 H), 1.95-0.70 (m, 11 H), 0.86 (d, J = 6 Hz, 3 H), 0.88 + 0.84 (d, J = 6 Hz, Σ 3 H). - ^{13}C NMR (CDCl$_3$, DEPT): δ = **a:** 211.5 (*), 58.5 (+), 44.4 (-), 37.3 (-), 36.2 (+), 30.8 (-), 28.9 (+), 25.7 (-), 24.5 (+), 24.2 (+), 21.5 (-), 21.1 (+); **b:** 213.1 (*), 53.9 (+), 44.4 (-), 33.8 (+), 29.5 (-), 28.7

(+), 28.6 (-), 25.2 (+), 24.4 (-), 23.7 (+), 22.9 (-), 21.6 (+). - MS: m/z = 182 (M^+, 0.5), 83 (14), 67 (14), 43 (100). - IR: 2925, 2860, 1710 cm^{-1}. - $C_{12}H_{22}O$: calcd. C = 79.06 H = 12.16; found C = 78.59 H = 11.95.

4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl)-2-pentanone (16): Colourless liquid, 170-175°C/12 mbar (80°C/0.03 Torr[26]), 1.98 g (96%, method A). Spectroscopic data see ref.[12].

4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl)-2-hexanone (17): Colourless liquid, 160-165°C/11 mbar (66-67°C/0.15 Torr[27]), 2.02 g (86%, method A). - ^1H NMR ($CDCl_3$): δ = 2.79 (m, 2 H), 2.55 (dd, J = 14 Hz, J'= 21 Hz, 1 H), 2.13 (s, 3 H), 1.89 (t, J = 5.5 Hz, 2 H), 1.62 (s, 3 H), 1.55 (m, 4 H), 1.40 (quint, J = 5.5 Hz, 2 H), 1.02 (s, 3 H), 0.95 (s, 3 H), 0.82 (t, J = 7.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 208.2 (∗), 140.9 (∗), 127.9 (∗), 50.2 (-), 40.3 (-), 35.9 (∗), 35.2 (+), 34.2 (-), 30.3 (+), 28.3 (+), 28.3 (-), 28.1 (+), 21.5 (+), 19.5 (-), 13.1 (+). - MS: m/z = 223 (M^++1, 45), 222 (M^+, 42), 204 (65), 164 (71), 149 (75), 123 (42), 43 (100). - IR: 2960, 2925, 2870, 1720 cm^{-1}. - $C_{15}H_{26}O$: calcd. C = 81.02 H = 11.79; found C = 80.60 H = 11.40.

4-(2',6',6'-Trimethyl-1'-cyclohexen-1'-yl)-2-heptanone (18): Light yellow liquid, 145-150°C/0.2 mbar (78-79°C/0.2 Torr[27]), 2.1 g (83%, method B). - ^1H NMR ($CDCl_3$): δ = 2.81 (m, 2 H), 2.55 (dd, J = 14.5 Hz, J'= 20.5 Hz, 1 H), 2.12 (s, 3 H), 1.89 (t, J = 5.5 Hz, 2 H), 1.64 (s, 3 H), 1.50 (m, 4 H), 1.40 (quint, J = 5.5 Hz, 2 H), 1.20 (q, J = 7.5 Hz, 2 H), 1.01 (s, 3 H), 0.95 (s, 3 H), 0.86 (t, J = 7.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, APT): δ = 207.9 (∗), 141.7 (∗), 127.9 (∗), 50.6 (-), 40.5 (-), 38.5 (-), 36.1 (∗), 34.4 (-), 34.0 (+), 30.3 (+), 28.4 (+), 28.2 (+), 21.9 (-), 21.7 (+), 19.6 (-), 14.5 (+). - MS: m/z = 236 (M^+, 42), 218 (53), 178 (55), 163 (37), 123 (55), 109 (32), 95 (34), 43 (100). - IR: 2950, 2920, 2860, 1715 cm^{-1}. - $C_{16}H_{28}O$: calcd. C = 81.29 H = 11.94; found C = 81.15 H = 11.97.

6-Methyl-4-(2',6',6'-trimethyl-1'-cyclohexen-1'-yl)-2-heptanone (19): Light yellow liquid, 150-155°C/0.2 mbar, 2.2 g (72%, method B). - ^1H NMR ($CDCl_3$): δ = 3.00 (m, 1 H), 2.75 (dd, J = 7.5 Hz, J'= 17.5 Hz, 1 H), 2.61 (dd, J = 4.5 Hz, J'= 17.5 Hz, 1 H), 2.12 (s, 3 H), 1.89 (m, 2 H), 1.64 (s, 3 H), 1.60-1.20 (m, 7 H), 1.04 (s, 3 H), 0.96 (s, 3 H), 0.92 (d, J = 5.5 Hz, 3 H), 0.88 (d, J = 5.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, APT): δ = 207.6 (∗), 142.8 (∗), 127.8 (∗), 50.8 (-), 45.9 (-), 40.6 (-), 36.3 (∗), 34.4 (-), 31.6 (+), 30.3 (+), 28.5 (+), 28.4 (+), 26.6 (+), 24.0 (+), 22.2 (+), 21.9 (+), 19.6 (-). - MS: m/z = 250 (M^+, 16), 232 (24), 192 (50), 177 (32), 137 (27), 123 (26), 95 (22), 43 (100). - IR: 2950, 2920, 2860, 1715 cm^{-1}. - $C_{17}H_{30}O$: calcd. C = 81.54 H = 12.08; found C = 81.21 H = 11.97.

4-Phenyl-2-pentanone (21): Colourless liquid, 170°C/12 mbar (70°C/0.15 Torr[28]), 1.47 g (91%, method A). Spectroscopic data see ref.[12].

4-Phenyl-2-hexanone (22)[29]*:* Colourless liquid, 150-155°C/12 mbar, (115°C/9 Torr[30]), 1.45 g (76%, method A). - ^1H NMR ($CDCl_3$): δ = 7.33-7.12 (m, 5 H), 3.04 (m, 1 H), 2.71 (d, J = 8.0 Hz, 2 H), 2.00 (s, 3 H), 1.53-1.47 (m, 2 H), 0.77 (t, J = 8.0 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 207.9 (∗), 144.3 (∗), 128.4 (+), 127.5 (+), 126.3 (+), 50.5 (-), 42.9 (+), 30.5 (+), 29.3 (-), 11.9 (+). - MS: m/z = 176 (M^+, 7), 147 (52), 118 (94), 91 (56), 43 (100). - IR: 3030, 2940, 1715, 1600, 1495, 760, 700 cm^{-1}. - $C_{12}H_{16}O$: calcd. C = 81.77 H = 9.15; found C = 81.84 H = 9.08.

4-Phenyl-2-heptanone (23)[31]*:* Colourless liquid, 150-160°C/0.2 mbar, 1.20 g (52%, method A). - ^1H NMR ($CDCl_3$): δ = 7.31-7.12 (m, 5 H), 3.12 (quin, J = 7.5 Hz, 1 H), 2.72 (dd, J = 7.5 Hz, J'= 16.0 Hz, 1 H), 2.68 (dd, J = 7.5 Hz, J'= 16.0 Hz, 1 H), 2.00 (s, 3 H), 1.57 (m, 2 H), 1.16 (m, 2 H), 0.84 (t, J = 7.5 Hz, 3 H). -

^{13}C NMR ($CDCl_3$, DEPT): δ = 207.9 (∗), 144.5 (∗), 128.4 (+), 127.4 (+), 126.2 (+), 50.9 (-), 41.0 (+), 38.6 (-), 30.5 (+), 20.5 (-), 13.9 (+). - MS: m/z = 190 (M^+, 6), 147 (26), 132 (49), 91 (72), 43 (100). - IR: 3020, 2960, 1715, 1600, 1495, 760, 700 cm^{-1}. - $C_{13}H_{18}O$: calcd. C = 82.06 H = 9.53; found C = 81.58 H = 9.42.

6-Methyl-4-phenyl-2-heptanone (24): Colourless liquid, flash-chromatography (petroleum ether/ethyl acetate 4 : 1) 0.55 g (27%, method A). - ^{1}H NMR ($CDCl_3$): δ = 7.33-7.12 (m, 5 H), 3.22 (m, 1 H), 2.71 (dd, J = 8.0 Hz, J'= 15.0 Hz, 1 H), 2.63 (dd, J = 7.0 Hz, J'= 15.0 Hz, 1 H), 2.00 (s, 3 H), 1.57 (m, 1 H), 1.45-1.22 (m, 2 H), 0.89 (d, J = 5.5 Hz, 3 H), 0.81 (d, J = 5.5 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 207.8 (∗), 144.5 (∗), 128.4 (+), 127.4 (+), 126.3 (+), 51.4 (-), 45.6 (+), 39.1 (+), 30.6 (+), 25.3 (+), 23.4 (+), 21.6 (+). - MS: m/z = 204 (M^+, 5), 146 (38), 131 (24), 105 (20), 91 (52), 43 (100). - IR: 3030, 2950, 1715, 1600, 1490, 760, 700 cm^{-1}. - $C_{14}H_{20}O$: calcd. C = 82.30 H = 9.87; found C = 82.00 H = 9.44.

4-Methyl-2-nonanone (26): Colourless liquid, 140-150°C/20 mbar (108-112°C/39 Torr[32]), 1.42 g (96%, method A). Spectroscopic data see ref.[12].

4-Ethyl-2-nonanone (27): Colourless liquid, 130°C/20 mbar, 1.20 g (71%, method A). - ^{1}H NMR ($CDCl_3$): δ = 2.34 (d, J = 7.0 Hz, 2 H), 2.13 (s, 3 H), 1.87 (m, 1 H), 1.40-1.15 (m, 10 H), 0.90 (t, J = 7.0 Hz, 3 H), 0.88 (t, J = 7.0 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 209.3 (∗), 48.4 (-), 35.3 (+), 33.4 (-), 32.1 (-), 30.3 (+), 26.3 (-), 26.2 (-), 22.6 (-), 14.0 (+), 10.8 (+). - MS: m/z = 170 (M^+, 4), 112 (22), 70 (28), 58 (62), 43 (100). - IR: 2960, 2925, 1720 cm^{-1}. - $C_{11}H_{22}O$: calcd. C = 77.58 H = 13.02; found C = 77.12 H = 12.74.

4-Propyl-2-nonanone (28): Colourless liquid, 145-150°C/20 mbar, 1.0 g (51%, method A). - ^{1}H NMR ($CDCl_3$): δ = 2.35 (d, J = 7.5 Hz, 2 H), 2.12 (s, 3 H), 1.92 (m, 1 H), 1.25 (m, 12 H), 0.89 (t, J = 7.0 Hz, 6 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 209.3 (∗), 48.8 (-), 36.3 (-), 33.9 (-), 33.7 (+), 32.1 (-), 30.3 (+), 26.2 (-), 22.6 (-), 19.7 (-), 14.2 (+), 14.0 (+). - MS: m/z = 184 (M^+, 4), 126 (33), 113 (18), 97 (25), 71 (37), 59 (65), 43 (100). - IR: 2960, 2930, 1720 cm^{-1}. - $C_{12}H_{24}O$: calcd. C = 78.20 H = 13.12; found C = 77.81 H = 12.57.

4-(2'-Methylprop-1'-yl)-2-nonanone (29): Colourless liquid, 140°C/12 mbar, 0.96 g (30%, method A). - ^{1}H NMR ($CDCl_3$): δ = 2.34 (dd, J = 2.5 Hz, J'= 7.5 Hz, 2 H), 2.13 (s, 3 H), 1.98 (m, 1 H), 1.59 (sept, J = 6.0 Hz, 1 H), 1.28 (m, 8 H), 1.10 (ddt, J = 7.5 Hz, J'= 13.0 Hz, J''= 40.5 Hz, 2 H), 0.89 (d, J = 6.0 Hz, 3 H), 0.88 (t, J = 6.0 Hz, 3 H), 0.87 (d, J = 6.0 Hz, 3 H). - ^{13}C NMR ($CDCl_3$, DEPT): δ = 209.2 (∗), 49.1 (-), 43.9 (-), 34.2 (-), 32.1 (-), 31.7 (+), 30.4 (+), 26.1 (-), 25.3 (+), 22.8 (+), 22.7 (+), 22.6 (-), 14.0 (+). - MS: m/z = 198 (M^+, 1), 140 (10), 43 (43), 40 (100). - IR: 2950, 2920, 1715 cm^{-1}. - $C_{13}H_{26}O$: calcd. C = 78.72 H = 13.21; found C = 78.00 H = 12.89.

(1R)-Pinan-3-methyl-2-aldehyde (31): Colourless liquid, 140-155°C/20 mbar, 1.61 g (97%, method C), one major diastereomer. - ^{1}H NMR (C_6D_6): δ = 9.43 (s, 1 H), 2.47 (m, 1 H), 2.27-2.22 (m, 3 H), 2.04 (m, 1 H), 1.84 (dd, J = 2 Hz, J' = 6 Hz, 1 H), 1.70 (m, 1 H), 1.25 (m, 1 H), 1.05 (s, 3 H), 0.92 (d, J = 6 Hz, 3 H), 0.64 (s, 3 H). - ^{13}C NMR (C_6D_6, APT): δ = 203.1 (+), 70.0 (∗), 62.1 (+), 42.6 (+), 41.8 (+), 35.5 (-), 31.7 (-), 27.8 (+), 26.9 (+), 22.7 (+), 22.0 (+). - MS: m/z = 166 (M^+, 3), 136 (37), 114 (35), 96 (85), 81 (65) 69 (100). - IR: 2920, 2700, 1725 cm^{-1}.

(4S)-4-Isopropenyl-2-methyl-cyclohexane-1-aldehyde (33): Colourless liquid, 160-170°C/14 mbar, 1.58 g (95%, method C), two diastereomers (1 : 1 by GC). - ^{1}H NMR (C_6D_6): δ = 9.35 and 9.33 (s, Σ 1 H), 4.75 (br. s, 1 H), 4.69 (m, 1 H), 2.20-0.85 (m, 9 H), 1.59 and 1.56 (s, Σ 3 H), 0.82 and 0.69 (d, J = 7.5 Hz, 3 H). -

^{13}C NMR (C_6D_6, DEPT): δ = **a:** 203.3 (+), 149.9 (∗), 109.6 (-), 53.2 (+), 38.6 (+), 34.9 (-), 30.8 (-), 28.3 (+), 21.3 (+), 20.8 (-), 19.2 (+); **b:** 203.5 (+), 148.9 (∗), 108.9 (-), 53.6 (+), 38.5 (+), 38.1 (-), 28.1 (-), 27.2 (+), 20.9 (+), 20.1 (-), 13.8 (+). - MS: m/z = 166 (M^+, 40), 149 (35), 135 (40), 123 (45), 95 (98), 81 (100), 67 (97). - IR: 3080, 2940, 2710, 1725, 1640 cm^{-1}.

3-Methyl-2-propylheptanal (37): Colourless liquid, 140-150°C/20 mbar, 1.64 g (96%, method C), two diastereomers (1 : 1 by ^{13}C NMR). - ^{1}H NMR (C_6D_6): δ = 9.43 and 9.39 (d, J = 3 Hz, Σ 1 H), 1.90 (m, 1 H), 1.65-0.65 (m, 20 H). - ^{13}C NMR (C_6D_6, APT): δ = **a:** 204.0 (+), 56.7 (+), 34.0 (-), 33.9 (+), 29.8 (-), 28.6 (-), 23.2 (-), 21.5 (-), 17.0 (+), 14.3 (+), 14.3 (+); **b:** 203.8 (+), 56.7 (+), 34.4 (-), 33.0 (+), 29.9 (-), 27.2 (-), 23.1 (-), 21.3 (-), 16.3 (+), 14.4 (+), 14.3 (+). - MS: m/z = 171 (M^+ +1, 35), 170 (M^+, 27), 153 (52), 102 (45), 86 (74), 71 (81), 57 (75), 43 (100). - IR: 2960, 2700, 1725 cm^{-1}.

2-Isopropyl-3,5-dimethylhexanal (39): Colourless liquid, 140-150°C/30 mbar, 1.64 g (99%, method C), two diastereomers (1 : 1 by GC). - ^{1}H NMR (C_6D_6): δ = 9.52 and 9.51 (d, J = 3 Hz, Σ 1 H), 1.88-0.85 (m, 6 H), 0.81-0.70 (m, 15 H). - ^{13}C NMR (C_6D_6, APT): δ = **a:** 205.3 (+), 64.1 (+), 44.7 (-), 29.6 (+), 26.0 (+), 25.6 (+), 24.4 (+), 21.1 (+), 20.9 (+), 20.4 (+), 17.7 (+); **b:** 205.3 (+), 62.5 (+), 42.6 (-), 29.7 (+), 25.8 (+), 25.0 (+), 23.2 (+), 22.2 (+), 20.5 (+), 19.7 (+), 15.8 (+). - MS: m/z = 170 (37), 169 (M^+ -1, 100). - IR: 2960, 2710, 1720 cm^{-1}.

3-Methyl-2-phenylpentanal (41): Colourless liquid, 170-180°C/12 mbar, 1.65 g (98%, method C), two diastereomers (1 : 1 by ^{13}C NMR). - ^{1}H NMR (C_6D_6): δ = 9.44 and 9.42 (d, J = 4 Hz, Σ 1 H), 7.20-6.88 (m, 5 H), 3.03 and 3.00 (dd, J = 4 Hz, J′ = 10 Hz, Σ 1 H), 2.00 (m, 1 H), 1.40 and 1.15 (m, Σ 1 H), 1.00 and 0.80 (m, Σ 1 H), 0.85 and 0.57 (d, J = 6 Hz, Σ 3 H), 0.80 and 0.63 (t, J = 7 Hz, Σ 3 H). - ^{13}C NMR (C_6D_6, APT): δ = **a:** 199.6 (+), 135.8 (∗), 129.8 (+), 129.5 (+), 129.1 (+), 128.9 (+), 127.4 (+), 65.1 (+), 34.9 (+), 26.3 (-), 16.2 (+), 10.8 (+); **b:** 199.9 (+), 136.1 (∗), 129.8 (+), 129.5 (+), 129.1 (+), 128.9 (+), 127.4 (+), 65.6 (+), 35.1 (+), 27.8 (-), 17.2 (+), 11.4 (+). - MS: m/z = 177 (M^+ +1, 12), 147 (38), 120 (45), 105 (37), 91 (100). - IR: 3030, 2960, 2710, 1720, 1600, 1490, 1450, 750, 700 cm^{-1}.

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