Synthesis of Pentalene Systems Employing a Sequence of Pauson-Khand Reaction, Michael Reaction, and Desilylation

Armand Becheanu, Thomas Bell, Sabine Laschat, Angelika Baro, Wolfgang Frey, Nelli Steinke, and Peter Fischer

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Reprint requests to Prof. Dr. S. Laschat. E-mail: sabine.laschat@oc.uni-stuttgart.de

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The utility of cyclopentadiene (**4**) in intermolecular Pauson-Khand reactions was investigated. Subsequently, a 1,4-addition of lithium organocuprates was carried out followed by desilylation. This synthetic concept allows the preparation of β -functionalized bicyclo[3.3.0]octane derivatives **1a–c** in only three steps in total yields up to 53%.

Key words: Bicyclo[3.3.0]octanes, Cyclopentadiene, Cuprate Addition, Desilylation, Trimethylsilylacetylene

Introduction

Over the last decade the Pauson-Khand reaction, a cobalt-mediated $[2 + 2 + 1]$ cycloaddition of an alkyne, an alkene and carbon monoxide to give a cyclopentenone has been extensively investigated and many applications have been reported [1]. Bicyclo[3.3.0]octanes which are key structural motifs in many terpenoid natural products [2], may be accessible directly *via* Pauson-Khand reaction of cyclopentadiene (**4**) with a functionalized alkyne **5** (Scheme 1). The resulting enone **3** might be submitted to conjugate additions and the alkene also can be further manipulated.

Scheme 1. Retrosynthetic pathway of bicyclo[3.3.0]octane derivatives **1** and **2**.

Surprisingly, little information is available about the use of cyclopentadiene (**4**) in Pauson-Khand reactions. We anticipated that acetylene or trimethylsilylacetylene should give access to the α -unsubstituted ketones **1**. In an early paper Pauson reported the preparation of 3-alkyl-substituted pentalenones **3** ($R^1 = \text{alkyl}$) in up to 60% yield from the correspond-

ing alkyne dicobalthexacarbonyl complex and cyclopentadiene [3]. In an alternative approach Schore isolated 9% of bicyclo[3.3.0]octa-3,7-diene-2,6-dione by reacting acetylene with dicobaltoctacarbonyl in benzene [4]. In this paper we wish to disclose our exploration of a synthesis route to target bicyclo[3.3.0]octanes by using cyclopentadiene (**4**) as starting material. For comparison the corresponding derivatives containing norbornene and norbornadiene instead of cyclopentadiene were investigated as well.

Results and Discussion

The Pauson-Khand reaction of cyclopentadiene (**4**) with acetylene gave compound **3** [5] ($R^1 = H$) (Scheme 1) in only very low yield (9%). As the removal of the trimethylsilyl group in Pauson-Khand cyclization products is well documented in the literature [6], acetylene was replaced with trimethylsilylacetylene (**5**) as an alternative precursor. Alkyne **5** was treated with dicobaltoctacarbonyl in CH_2Cl_2 at room temperature [6a, b, 7] to give the cobalt-alkyne complex **6**. According to literature procedures [6a, b, 7] the latter was reacted first with norbornene (**7a**) and norbornadiene (**7b**) in the presence of NMO (Scheme 2). The corresponding TMS-substituted derivatives **8a** and **8b** [6a, b, 7, 8] were isolated in 91% and 63% yield, respectively.

Entry	Starting materials			Reaction conditions		Products	
	Enone	Reagent	Solvent	T [°C]	t [h]		Yield [%]
1	8a	TBAF	THF	20	72	9a	47
2	8a	MeSO ₃ H	MeOH	20	16	9a	40
3	8a	CsOH	DMF	−20	1	9a	7
4	8a	LiOH	DMF	20	12	9a	—
5	8a	TASF	DMF	20	12	9a	< 1
6	8a	Bu ₄ NOH	DMF	−20	1	9a	12
7	8a	Bu ₄ NOH	DMF	0	5	9a	83
8	8a	Bu ₄ NOH	DMF	20	5	9a	90
9	8a	Bu ₄ NOH	THF	20	12	9a	98
10	8b	MeSO ₃ H	Et ₂ O	20	12	9b	—
11	8b	Bu ₄ NOH	DMF	20	12	9b	68
12	8b	Bu ₄ NOH	Et ₂ O	20	12	9b	83
13	3a	MeSO ₃ H	Et ₂ O	20	5	3b	—
14	3a	Bu ₄ NOH	DMF	20	12	3b	91
15	3a	Bu ₄ NOH	Et ₂ O	20	1	3b	93

Table 1. Desilylation of α -trimethylsilylcyclopentenone derivatives **3a** and **8a, b**.Table 2. 1,4-Addition of organocuprates to α -(trimethylsilyl)cyclopentenones **3a** and **8a** and subsequent desilylation of (trimethylsilyl)ketones **2, 10** to the corresponding ketones **1** and **11**.

Entry	Conditions			TMS-ketones		Conditions		Ketones	
	Enone	T [°C]	t [min]	R =	Yield [%]	Solvent	t [h]		Yield [%]
1	8a	0	10	10a Me	84	THF	48	11a	98
2	8a	−20	15	10b Bu	92	THF	12	11b	87
3	8a	0	120	10c Ph	86	THF	1	11c	79
4	8a	−20	30	10d <i>i</i> -Pr	42	THF	12	11d	75
5	3a	0	120	2a Me	49	Et ₂ O	3	1a	63
6	3a	−20	180	2b Bu	62	Et ₂ O	12	1b	77
7	3a	0	180	2c Ph	70	Et ₂ O	3	1c	90

Scheme 2. Reaction sequence of Pauson-Khand reaction, cuprate addition and desilylation using norbornene (**7a**) and norbornadiene (**7b**).

Unfortunately, we did not succeed in clean removal of the TMS group by reacting enone **8a** in the presence of TBAF in THF following a known protocol [6a, b]. Therefore, various desilylation condi-

tions and reagents such as TASF [9], CsOH, LiOH, and MeSO₃H [10] had to be investigated (Table 1). After considerable experimentation, tetrabutylammonium hydroxide (Bu₄NOH) [11] in THF was found to be most suitable and the desilylation product **9a** was obtained in 98% yield (entry 9). Analogously norbornadiene-derived **8b** was desilylated to **9b** [11] in 83% yield (entry 12).

Although the functionalization of norbornadiene-derived **8b** by 1,4-addition of magnesiocuprate reagents was previously reported [6b], we applied the 1,4-addition of lithium dialkylcuprates to norbornene derivative **8a**. Subsequently the resulting ketones **10** were desilylated under the conditions described above (Scheme 2, Table 2). As shown in Table 2, cyclopentenone **8a** reacted cleanly with several lithium organocuprates to give the corresponding α -trimethylsilyl- β -substituted ketones **10a-d** in moderate to good yields as single *trans* diastereoisomers. Subsequent desilylation was achieved uneventfully by treatment with Bu₄NOH in THF to give products **11a-d** in 75–98% yield, thus demonstrating the possibility to remove the trimethylsilyl group even on a late stage of the synthesis.

Scheme 3. Synthesis of pentalene derivatives **1** via Pauson-Khand reaction of cyclopentadiene (**4**) with trimethylsilylacetylene (**5**), Michael reaction and desilylation.

The reaction conditions were then applied to the preparation of the desired pentalene derivatives **1** (Scheme 3). The Pauson-Khand reaction was slightly modified by cooling the cobalt-alkyne complex **6** to -20°C for 1 h prior to reaction with cyclopentadiene (**4**). A mixture of the pentalenone **3a** (46% yield) and a tricyclic *endo*-cyclopentenone derivative **12** (27% yield) was isolated (Scheme 3). The latter resulted from cocyclization of two equivalents of **5** with $\text{Co}_2(\text{CO})_8$ and subsequent Diels-Alder reaction of the intermediate 2,5-bis(trimethylsilyl)cyclopentadienone with **4**. The *endo*-configuration of **12** was confirmed by X-ray crystal structure analysis (Fig. 1). If the cobalt-alkyne complex **6** was stirred for only 20 min at -20°C prior to cyclopentadiene addition, the formation of a single isomer **3a** was observed by GC-MS and NMR, and the yield was improved to 84%.

Table 1 reveals that Et_2O turned out to be the optimal solvent for the desilylation of **3a** giving the product **3b** in 93% yield (entry 15). Thus, enone **3b** was accessible in 78% total yield via this two-step reaction. As shown in Scheme 3, even *endo*-cyclopentenone **12** was desilylated to derivative *endo*-**9b** [12] by using this system, albeit with lower yield of 42%.

Fig. 1. ORTEP view of the *endo*-configured tricyclic cyclopentane derivative **12**.

According to our retrosynthetic concept to the target compounds **1** and **2**, the α -trimethylsilyl-substituted enone **3a** was assumed to be a suitable candidate for conjugate 1,4-cuprate addition and was treated with lithium organocuprates under the reaction conditions described above (Scheme 3, Table 2). The addition proceeded cleanly to give the corresponding pentalene derivatives **2a-c**. However, the yields of the conjugate addition to pentalenone **3a** were generally somewhat lower than those of tricyclic enone **8a**. Again, the α -trimethylsilyl group could be removed at this stage of synthesis with Bu_4NOH in Et_2O to afford the functionalized target pentalene systems **1a-c**. The *endo*-compound **12** was reacted in an analogous manner to give both the bis(trimethylsilyl)-substituted methylation product **13** and the corresponding desilylation product **14** [13] in excellent yields (Scheme 3).

In conclusion, we demonstrated that cyclopentadiene (**4**) was converted with trimethylsilylacetylene (**5**) in an intermolecular Pauson-Khand reaction, leading directly to the bicyclic enone **3a** in good yield. As a by-product in the Pauson-Khand reaction an *endo*-coupled enone **12** was isolated. Functionalization of various enones was realized by 1,4-addition of organocuprates, and the desilylation of the enones **3a**, **8** or the functionalized ketones **2**, **10** could be performed under mild reaction conditions. A similar reaction se-

quence was even published for norbornadiene to give tricyclic precursors for cyclopentenone containing natural products [6b, 14], but its application in the synthesis route to functionalized bicyclo[3.3.0]octane derivatives **1** has not been reported so far. Thus, it allows the preparation of compounds **1** in only three steps in 26–53% total yield, starting with an intermolecular Pauson-Khand reaction of cyclopentadiene as the key step. The pentalenones **1–3** may be further functionalized at the alkene moiety.

Experimental Section

General information

Column chromatography was accomplished using SiO₂ 60, grain size 0.063–0.200 mm (Merck) with pentane, hexanes (b. p. 40–60 °C), EtOAc, and diethyl ether (Et₂O) as eluents. All starting materials are commercially available. The following spectroscopic and analytical instruments were used. IR: Bruker Vektor22 FTIR. – NMR: Bruker ARX 300 and Avance 500 (¹H: 300.13 MHz, 500.15 MHz, ¹³C: 75.47 MHz, 125.76 MHz). For ¹H spectra, TMS was used as internal standard. For ¹³C spectra, signal assignments are based on DEPT experiments. – Melting points: Mettler Toledo DSC 822e, m. p. are uncorrected. – Mass spectrometry: Finnigan MAT 95 and Varian MAT 711.

Pauson-Khand reaction of cyclopentadiene (**4**) with **5** to derivatives **3a** and **12**

TMS-acetylene **5** (705 μl, 5.0 mmol) was added to a solution of dicobaltoctacarbonyl (1.86 g, 5.4 mmol) in CH₂Cl₂ (25 ml) under N₂ atmosphere and the reaction mixture stirred at –20 °C for 1 h. Then **4** (700 μl, 7.7 mmol) was added dropwise, and the reaction mixture stirred for a further 20 min at –20 °C. *N*-methylmorpholin-*N*-oxide (NMO) (3.525 g, 5.0 mmol) was added portionwise and after stirring for 6 h, the reaction mixture was filtered through SiO₂ with Et₂O. The filtrate was concentrated and the residue chromatographed on SiO₂ with pentane/Et₂O (40 : 1) to give in a first fraction (*R*_f = 0.27) compound **12** (426 mg, 1.34 mmol, 27%) as a colorless solid and in a second fraction (*R*_f = 0.24) compound **3a** (444 mg, 2.31 mmol, 46%) as a colorless crystalline solid.

rac-2,7a-Bis(trimethylsilyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (**12**)

M. p. 75–78 °C. – FT-IR (ATR): ν = 3069 (w), 3025 (m), 2979 (s), 2952 (m), 1655 (vs), 1572 (s), 1294 (s), 1247 (s), 1188 (s), 988 (m) cm^{–1}. – ¹H NMR (500.15 MHz, CDCl₃): δ = 0.07 (s, 9 H, CHSi(CH₃)₃), 0.08 (s, 9 H, CSi(CH₃)₃), 1.51 (dt, *J* = 1.6 Hz, *J* = 8.3 Hz, 1 H, 10-H_b), 1.67 (d,

J = 8.3 Hz, 1 H, 10-H_a), 2.93–2.97 (m, 1 H, 1-H), 3.07–3.09 (m, 1 H, 7-H), 3.37 (dd, *J* = 3.0 Hz, *J* = 3.9 Hz, 1 H, 6-H), 5.68 (dd, *J* = 3.0 Hz, *J* = 5.4 Hz, 1 H, 9-H), 5.89 (dd, *J* = 2.8 Hz, *J* = 5.4 Hz, 1 H, 8-H), 7.54 (d, *J* = 2.7 Hz, 1 H, 5-H). – ¹³C NMR (125.76 MHz, CDCl₃): δ = –0.6 ((CH₃)₃Si), –0.9 ((CH₃)₃Si), 46.4, 48.6 (C-8, C-9), 52.6 (C-10), 55.1 (C-6), 55.6 (C-2), 132.4, 137.4 (C-8, C-9), 150.9 (C-4), 171.5 (C-5), 217.1 (C-3). – GC-MS (EI): *m/z* (%) 290.2 (17) [M⁺], 259.2 (10), 209.1 (23), 202.2 (17), 193.1 (15), 147.1 (13), 133.0 (13), 73.0 (100), 66.0 (31). – HRMS (EI): calcd. for C₁₆H₂₆OSi₂ 290.1522; found 290.1516 [M⁺].

rac-2-(Trimethylsilyl)-4,6a-dihydropentalen-1(3aH)-one (**3a**)

M. p. 37 °C. – FT-IR (ATR): ν = 3061 (w), 3033 (w), 2960 (m), 2933 (m), 2901 (m), 2848 (m), 2360 (w), 1685 (vs), 1573 (s), 1293 (s), 1277 (s), 1245 (s), 1214 (s), 1176 (s), 971 (m), 831 (s), 814 (s), 749 (s), 678 (s) cm^{–1}. – ¹H NMR (500.15 MHz, CDCl₃): δ = 0.13 (s, 9 H, Si(CH₃)₃), 2.27 (tdd, *J* = 2.6 Hz, *J* = 5.4 Hz, *J* = 17.6 Hz, 1 H, 4-H_b), 2.65–2.73 (m, 1 H, 4-H_a), 3.32–3.37 (m, 1 H, 3a-H), 3.57 (tdd, *J* = 2.8 Hz, *J* = 5.7 Hz, *J* = 11.1 Hz, 1 H, 6a-H), 5.56 (td, *J* = 2.4 Hz, *J* = 7.8 Hz, 1 H, 5-H), 5.63 (td, *J* = 2.4 Hz, *J* = 7.9 Hz, 1 H, 6-H), 7.72 (d, *J* = 2.5 Hz, 1 H, 3-H). – ¹³C NMR (125.76 MHz, CDCl₃): δ = –0.8 ((CH₃)₃Si), 37.3 (C-4), 46.6 (C-3a), 60.9 (C-6a), 130.6, 132.2 (C-5, C-6), 144.7 (C-2), 176.2 (C-3), 213.3 (C-1). – GC-MS (EI): *m/z* (%) 192.1 (64) [M⁺], 177.1 (73), 149.1 (17), 99.0 (15), 73.0 (100), 66.0 (18). – HRMS (EI): calcd. for C₁₁H₁₆OSi 192.0970; found 192.0967 [M⁺].

Preparation of **3a**

TMS-acetylene (**5**) (141 μl, 1.0 mmol) was added to a solution of dicobaltoctacarbonyl (342 mg, 1.0 mmol) in CH₂Cl₂ (5 ml) under N₂ atmosphere and the reaction mixture stirred at –20 °C for 20 min. Then **4** (90 μl, 1.0 mmol) was added dropwise, and the reaction mixture stirred for a further 20 min at –20 °C. NMO (705 g, 1.0 mmol) was added portionwise and after stirring for 6 h, the reaction mixture was filtered through SiO₂ with Et₂O. The filtrate was concentrated and the residue chromatographed on SiO₂ with pentane/Et₂O (40 : 1) to give **3a** (162 mg, 0.84 mmol, 84%).

Pauson-Khand reaction of alkenes **7a**, **b** with **5**

TMS-acetylene (**5**) was added to a solution of dicobaltoctacarbonyl (342 mg, 1.0 mmol) in CH₂Cl₂ (5 ml) under N₂ atmosphere and the reaction mixture stirred at r. t. for 20 min. Then alkene **7a** or **7b** (1.2 mmol) was added dropwise, and the reaction mixture stirred at r. t. for a further 20 min. NMO (705 mg, 6.0 mmol) was added portionwise and after stir-

ring for 30 min, the reaction mixture was filtered through SiO₂ with Et₂O. The filtrate was concentrated and the residue chromatographed on SiO₂ with pentane/Et₂O to give products **8a** or **8b**. Physical and spectroscopic data were in accordance with those in the literature [8].

General procedure for the cuprate addition

A suspension of copper(II) iodide (104 mg, 0.54 mmol) in Et₂O (5 ml) was stirred at 0 °C or –20 °C (see Table 2) for 10 min. Then the respective organolithium compound (1.08 mmol) was added dropwise and the reaction mixture stirred for a further 10 min at the given temperature. The respective enone **3a**, **12**, or **8a** (0.45 mmol) was added, the reaction mixture stirred for 10–180 min (tlc control) and then hydrolyzed with a saturated solution of NH₄Cl (5 ml). The layers were separated and the aqueous layer was extracted with Et₂O (5 × 10 ml). The combined organic layers were dried (K₂CO₃), concentrated and the crude products **2**, **10**, and **13** purified by chromatography on SiO₂ with pentane/Et₂O (20 : 1) or (10 : 1) for **10a**, **d**, **13**.

rac-3-Methyl-2-(trimethylsilyl)-3,3a,4,6a-tetrahydropentalen-1(2H)-one (**2a**)

$R_f = 0.24$. – FT-IR (ATR): $\nu = 2952$ (s), 2924 (s), 2900 (m), 2870 (m), 2848 (m), 1706 (vs), 1457 (m), 1444 (m), 1416 (w), 1377 (m), 1247 (vs), 1173 (s), 916 (s), 836 (s) cm^{–1}. – ¹H NMR (500.15 MHz, (CD₃)₂CO): $\delta = 0.03$ (s, 9 H, Si(CH₃)₃), 1.15 (d, $J = 6.8$ Hz, 3 H, CH₃), 1.64 (dd, $J = 1.7$ Hz, $J = 10.0$ Hz, 1 H, 2-H), 1.76–1.85 (m, 1 H, 3-H), 2.26–2.32 (m, 1 H, 4-H_a), 2.38 (q, $J = 7.6$ Hz, 1 H, 3a-H), 2.57–2.64 (m, 1 H, 4-H_b), 3.27–3.32 (m, 1 H, 6a-H), 5.46 (td, $J = 2.3$ Hz, $J = 7.2$ Hz, 1 H, 5-H), 5.81 (dt, $J = 2.6$ Hz, $J = 5.2$ Hz, 1 H, 6-H). – ¹³C NMR (125.76 MHz, (CD₃)₂CO): $\delta = -0.8$ (Si(CH₃)₃), 23.1 (CH₃), 41.1 (C-4), 42.3 (C-3), 49.7 (C-3a), 50.7 (C-2), 65.3 (C-6a), 129.1 (C-5), 134.1 (C-6). – MS (EI): m/z (%) 208.1 (32) [M⁺], 193.1 (100), 180.1 (6), 79.1 (14), 73.1 (75), 66.1 (9), 45.0 (8). – HRMS (EI): calcd. for C₁₂H₂₀OSi 208.1283; found 208.1291 [M⁺].

rac-3-Butyl-2-(trimethylsilyl)-3,3a,4,6a-tetrahydropentalen-1(2H)-one (**2b**)

$R_f = 0.20$. – FT-IR (ATR): $\nu = 2955$ (s), 2925 (s), 2857 (m), 1706 (vs), 1466 (m), 1378 (w), 1248 (vs), 1152 (s), 1058 (m), 1022 (m), 918 (s), 891 (m), 725 (m), 693 (s) cm^{–1}. – ¹H NMR (500.15 MHz, CDCl₃): $\delta = 0.04$ (s, 9 H, Si(CH₃)₃), 0.91 (t, $J = 7.0$ Hz, 3 H, CH₃), 1.23–1.45 (m, 5 H, 1'-H_a, 2'-H, 3'-H), 1.47–1.55 (m, 1 H, 1'-H_b), 1.72 (dd, $J = 1.9$ Hz, $J = 7.7$ Hz, 1 H, 2-H), 1.80–1.86 (m, 1 H, 3-H), 2.26 (d, $J = 17.0$ Hz, 1 H, 4-H_a), 2.51–2.56 (m, 1 H, 3a-H), 2.72 (dddd, $J = 2.6$ Hz, $J = 4.9$ Hz, $J = 7.8$ Hz,

$J = 16.7$ Hz, 1 H, 4-H_b), 3.37–3.42 (m, 1 H, 6a-H), 5.50 (td, $J = 2.3$ Hz, $J = 7.4$ Hz, 1 H, 5-H), 5.78 (dt, $J = 2.5$ Hz, $J = 5.2$ Hz, 1 H, 6-H). – ¹³C NMR (125.76 MHz, CDCl₃): $\delta = -1.8$ (Si(CH₃)₃), 14.0 (C-4'), 22.9 (C-3'), 29.4 (C-2'), 38.4 (C-1'), 41.8 (C-4), 45.2 (C-3a), 45.9 (C-3), 48.8 (C-2), 63.6 (C-6a), 127.5 (C-5), 132.5 (C-6). – GC-MS (EI): m/z (%) 250.4 (4) [M⁺], 193.2 (100), 183.2 (15), 73.1 (61), 55.1 (6). – HRMS (CI, CH₄): calcd. for C₁₅H₂₅OSi 249.1674; found 249.1666 [M-H]⁺.

rac-3-Phenyl-2-(trimethylsilyl)-3,3a,4,6a-tetrahydropentalen-1(2H)-one (**2c**)

$R_f = 0.27$. – M. p. 102 °C. – FT-IR (ATR): $\nu = 3059$ (m), 3026 (w), 2950 (s), 2922 (s), 2891 (s), 2852 (m), 1699 (vs), 1599 (s), 1491 (s), 1452 (s), 1443 (s), 1360 (w), 1263 (s), 1247 (vs), 1224 (s), 1175 (s), 1159 (s), 1143 (s), 1074 (s), 1037 (m), 1029 (w), 946 (s), 924 (s), 910 (s) cm^{–1}. – ¹H NMR (500.15 MHz, (CD₃)₂CO): $\delta = -0.11$ (s, 9 H, Si(CH₃)₃), 2.35 (dd, $J = 1.8$ Hz, $J = 11.3$ Hz, 1 H, 2-H), 2.37–2.43 (m, 1 H, 4-H_a), 2.43–2.49 (m, 1 H, 4-H_b), 2.79–2.84 (m, 1 H, 3a-H), 2.89 (dd, $J = 8.6$ Hz, $J = 11.2$ Hz, 1 H, 3-H), 3.46–3.51 (m, 1 H, 6a-H), 5.55 (td, $J = 2.2$ Hz, $J = 7.2$ Hz, 1 H, 5-H), 5.87 (dt, $J = 2.6$ Hz, $J = 5.3$ Hz, 1 H, 6-H), 7.21–7.25 (m, 1 H, 4'-H), 7.31–7.43 (m, 4 H, 2'-H, 3'-H, 5'-H, 6'-H). – ¹³C NMR (125.76 MHz, (CD₃)₂CO): $\delta = -0.9$ (Si(CH₃)₃), 40.0 (C-4), 50.7 (C-2), 51.5 (C-3a), 53.8 (C-3), 65.0 (C-6a), 128.2 (C-4'), 128.9 (C-5), 129.7, 130.3 (C-2', C-3', C-5', C-6'), 133.9 (C-6), 147.4 (C-1'), 219.1 (C-1). – GC-MS (EI): m/z (%) 270.2 (72) [M⁺], 255.2 (10), 242.2 (19), 229.2 (8), 193.2 (9), 179.2 (32), 165.2 (21), 153.2 (10), 115.1 (12), 103.0 (22), 73.0 (100), 66.1 (12), 50.9 (7). – HRMS (EI): calcd. for C₁₇H₂₂OSi 270.1440; found 270.1441 [M⁺].

rac-3-Methyl-2-(trimethylsilyl)octahydro-1H-4,7-methaninden-1-one (**10a**)

$R_f = 0.35$. – FT-IR (ATR): $\nu = 2949$ (s), 2911 (m), 2871 (m), 1708 (vs), 1475 (m), 1375 (w), 1288 (w), 1246 (s), 1207 (s), 1168 (s), 1134 (s), 1101 (s), 1017 (m), 981 (m) cm^{–1}. – ¹H NMR (300.13 MHz, CDCl₃): $\delta = 0.08$ (s, 9 H, Si(CH₃)₃), 0.93–1.05 (m, 2 H, 10-H), 1.11 (d, $J = 1.9$ Hz, 1 H, 8-H_a), 1.14 (d, $J = 1.9$ Hz, 1 H, 9-H_a), 1.17 (d, $J = 6.4$ Hz, 3 H, CH₃), 1.41–1.57 (m, 3 H, 6-H, 8-H_b, 9-H_b), 1.67–1.77 (m, 2 H, 2-H, 5-H), 2.14–2.22 (m, 2 H, 1-H, 4-H), 2.47–2.51 (m, 1 H, 7-H). – ¹³C NMR (75.47 MHz, CDCl₃): $\delta = -1.6$ (Si(CH₃)₃), 23.9 (CH₃), 28.0, 28.6 (C-8, C-9), 34.7 (C-10), 38.2 (C-5), 40.4 (C-7), 42.6 (C-1), 49.4 (C-6), 53.5 (C-2), 58.8 (C-4). – GC-MS (EI): m/z (%) 236 (10) [M⁺], 221 (100), 169 (5), 155 (4), 91 (7), 73 (78), 67 (12), 45 (17). HRMS (EI): calcd. for C₁₄H₂₄OSi 236.1596; found 236.1596 [M⁺].

rac-3-Butyl-2-(trimethylsilyl)octahydro-1*H*-4,7-methanoinden-1-one (**10b**)

$R_f = 0.30$. – FT-IR (ATR): $\nu = 2951$ (s), 2926 (s), 2871 (m), 1708 (vs), 1457 (m), 1378 (w), 1246 (s), 1200 (s), 1184 (m), 1167 (s), 1130 (s), 1102 (s), 1050 (w), 1005 (w), 936 (m) cm^{-1} . – ^1H NMR (500.15 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 0.08$ (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.93 (t, $J = 6.7$ Hz, 3 H, 4'-H), 0.98–1.05 (m, 2 H, 10-H), 1.11–1.16 (m, 1 H, 8-H_a), 1.18–1.24 (m, 1 H, 9-H_a), 1.29–1.43 (m, 4 H, 1'-H_a, 2'-H_a, 3'-H), 1.45–1.52 (m, 3 H, 2'-H_b, 8-H_b, 9-H_b), 1.60–1.72 (m, 3 H, 1'-H_b, 5-H, 6-H), 1.86 (dd, $J = 5.1$ Hz, $J = 8.9$ Hz, 1 H, 2-H), 2.15 (d, $J = 9.5$ Hz, 1 H, 4-H), 2.16–2.19 (m, 1 H, 1-H), 2.38–2.42 (m, 1 H, 7-H). – ^{13}C NMR (125.76 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -0.4$ ($\text{Si}(\text{CH}_3)_3$), 15.4 (C-4'), 24.5 (C-3'), 29.7, 30.0 (C-8, C-9), 31.4 (C-2'), 36.0 (C-10), 40.2 (C-1'), 42.1 (C-7), 44.9 (C-5), 45.7 (C-1), 49.1 (C-6), 53.1 (C-2), 60.1 (C-4). – GC-MS (EI): m/z (%) 278 (2) [M^+], 263 (4), 221 (100), 73 (44), 67 (7), 45 (9). – $\text{C}_{17}\text{H}_{30}\text{OSi}$ (278.5): calcd. C 73.31, H 10.86; found C 73.31, H 10.82.

rac-3-Phenyl-2-(trimethylsilyl)octahydro-1*H*-4,7-methanoinden-1-one (**10c**)

$R_f = 0.37$. – FT-IR (ATR): $\nu = 3063$ (w), 2948 (s), 2940 (s), 2876 (m), 2847 (m), 1704 (vs), 1598 (m), 1492 (m), 1451 (m), 1240 (s), 1197 (s), 1178 (s), 1132 (m), 1121 (m), 1099 (s), 1028 (m), 1015 (m) cm^{-1} . – ^1H NMR (500.15 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -0.09$ (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.00–1.19 (m, 4 H, 8-H_a, 9-H_a, 10-H), 1.48–1.52 (m, 2 H, 8-H_b, 9-H_b), 2.12 (dd, $J = 6.8$ Hz, $J = 9.2$ Hz, 1 H, 6-H), 2.29–2.33 (m, 2 H, 4-H, 7-H), 2.37 (d, $J = 9.5$ Hz, 1 H, 2-H), 2.48–2.51 (m, 1 H, 1-H), 2.83 (dd, $J = 9.2$ Hz, $J = 21.2$ Hz, 1 H, 5-H), 7.18–7.23 (m, 1 H, 4'-H), 7.30–7.42 (m, 4 H, 2'-H, 3'-H, 5'-H, 6'-H). – ^{13}C NMR (125.76 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -0.7$ ($\text{Si}(\text{CH}_3)_3$), 29.5, 29.9 (C-8, C-9), 36.0 (C-10), 41.9 (C-1), 43.7 (C-7), 49.8 (C-4), 51.7 (C-5), 56.9 (C-6), 59.8 (C-2), 128.0 (C-4'), 129.3, 130.3 (C-2', C-3', C-5', C-6'), 149.1 (C-1'). – MS (EI): m/z (%) 298.2 (80) [M^+], 297.2 (100), 257.2 (8), 231.1 (49), 203.1 (6), 161.1 (9), 135.1 (7), 91.0 (8), 73.1 (67), 59.1 (6), 45.0 (5). – HRMS (EI): calcd. for $\text{C}_{19}\text{H}_{26}\text{OSi}$ 298.1753; found 298.1737 [M^+].

rac-3-Isopropyl-2-(trimethylsilyl)octahydro-1*H*-4,7-methanoinden-1-one (**10d**)

$R_f = 0.50$. – FT-IR (ATR): $\nu = 2951$ (s), 2871 (s), 1706 (vs), 1464 (m), 1409 (m), 1246 (s), 1205 (s), 1170 (s), 1138 (s), 1123 (s), 1103 (m), 1060 (m), 1038 (w), 1014 (w), 998 (m) cm^{-1} . – ^1H NMR (500.15 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 0.09$ (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.88 (d, $J = 6.5$ Hz, 3 H, CH_3), 1.01 (d, $J = 6.8$ Hz, 3 H, CH_3), 1.02–1.07 (m, 2 H, 10-H), 1.12–1.28 (m, 2 H, 8-H_a, 9-H_a), 1.44–1.54 (m, 2 H, 8-H_b,

9-H_b), 1.77–1.84 (m, 3 H, 2-H, 6-H, $\text{CH}(\text{CH}_3)_2$), 1.96 (d, $J = 9.1$ Hz, 1 H, 5-H), 2.04–2.09 (m, 1 H, 4-H), 2.10–2.13 (m, 1 H, 1-H), 2.37–2.40 (m, 1 H, 7-H). – ^{13}C NMR (125.76 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -0.1$ ($\text{Si}(\text{CH}_3)_3$), 17.2 (CH_3), 22.8 (CH_3), 29.8, 29.9 (C-8, C-9), 33.1 ($\text{CH}(\text{CH}_3)_2$), 36.1 (C-10), 42.5 (C-7), 46.4, 46.5, 46.6 (C-1, C-5, C-6), 50.9 (C-2), 60.3 (C-4). – MS (EI): m/z (%) 264.2 (4) [M^+], 249.1 (3), 221.1 (100), 73.0 (12). – HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{28}\text{OSi}$ 264.1909; found 264.1899 [M^+].

rac-3-Methyl-2,7a-bis(trimethylsilyl)-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-1-one (**13**)

$R_f = 0.65$. – FT-IR (ATR): $\nu = 2952$ (s), 2896 (m), 1685 (vs), 1454 (m), 1407 (m), 1374 (w), 1245 (vs), 1205 (m), 1183 (m), 1149 (vs), 1070 (m), 1043 (m), 915 (m), 832 (s), 735 (s), 688 (s), 618 (s) cm^{-1} . – ^1H NMR (500.15 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 0.02$ (s, 9 H, 7a-Si(CH_3)₃), 0.12 (s, 9 H, 2-Si(CH_3)₃), 1.15 (d, $J = 6.8$ Hz, 3 H, CH_3), 1.32 (td, $J = 1.7$ Hz, $J = 8.3$ Hz, 1 H, 10-H_a), 1.48 (d, $J = 9.7$ Hz, 1 H, 4-H), 1.49–1.51 (m, 1 H, 10-H_b), 1.83 (m, 1 H, 5-H), 2.55 (t, $J = 4.0$ Hz, 1 H, 6-H), 3.03 (m, 1 H, 1-H), 3.07 (m, 1 H, 7-H), 6.08 (dd, $J = 3.0$ Hz, $J = 5.5$ Hz, 1 H, 8-H), 6.20 (dd, $J = 2.7$ Hz, $J = 5.5$ Hz, 1 H, 9-H). – ^{13}C NMR (125.76 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -0.9$ (7a-Si(CH_3)₃), 0.0 (2-Si(CH_3)₃), 25.4 (CH_3), 35.9 (C-5), 49.1 (C-7), 50.0 (C-1), 52.4 (C-10), 54.6 (C-4), 56.3 (C-6), 136.2 (C-8), 142.5 (C-9). – GC-MS (EI): m/z (%) 306.5 (2) [M^+], 291.3 (2), 240.4 (35), 233.3 (30), 147.2 (9), 133.1 (23), 73.0 (100), 66.1 (20). – HRMS (EI): calcd. for $\text{C}_{17}\text{H}_{30}\text{OSi}_2$ 306.1835; found 306.1839 [M^+].

General procedure for the desilylation

The respective desilylation agent (1.5 equiv.) was added to a solution of the appropriate enone **2**, **3a**, **8a**, **b**, **10**, **12**, or **13** (1.0 equiv.) in the respective solvent given in Tables 1, 2, and the reaction mixture stirred at the given temperature and times (Tables 1, 2) (tlc control). Then the reaction mixture was filtered through SiO_2 with Et_2O and the filtrate was concentrated. The conversion was estimated by GC. The novel products were purified by chromatography on SiO_2 with pentane/ Et_2O (15 : 1) for **1** or pentane/ Et_2O (10 : 1) for **11**. Physical and spectroscopic data of compounds **11a** and **14** were in accordance with those in the literature [13, 15].

rac-3-Methyl-3,3a,4,6a-tetrahydropentalen-1(2*H*)-one (**1a**)

$R_f = 0.21$. – FT-IR (ATR): $\nu = 3061$ (m), 2953 (s), 2923 (s), 2870 (m), 2848 (m), 1733 (vs), 1457 (m), 1410 (m), 1378 (m), 1344 (m), 1286 (w), 1213 (s), 1172 (s), 909 (m), 772 (m) cm^{-1} . – ^1H NMR (500.15 MHz, CDCl_3): $\delta = 1.13$ (d, $J = 6.7$ Hz, 3 H, CH_3), 1.72–1.83 (m, 1 H, 3-H), 1.95 (ddd, $J = 1.4$ Hz, $J = 11.1$ Hz, $J = 17.0$ Hz, 1 H, 2-H_a), 2.24 (dd, $J = 7.0$ Hz, $J = 17.0$ Hz, 1 H, 2-H_b), 2.26–2.32

(m, 1 H, 4-H_a), 2.48 (dq, $J = 1.3$ Hz, $J = 6.7$ Hz, 1 H, 3a-H), 2.64 (dddd, $J = 2.7$ Hz, $J = 5.1$ Hz, $J = 8.0$ Hz, $J = 16.9$ Hz, 1 H, 4-H_b), 3.30–3.35 (m, 1 H, 6a-H), 5.54 (td, $J = 2.4$ Hz, $J = 7.6$ Hz, 1 H, 5-H), 5.75 (dt, $J = 2.4$ Hz, $J = 7.6$ Hz, 1 H, 6-H). – ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 20.8$ (CH₃), 38.5 (C-3), 40.1 (C-4), 47.9 (C-2), 48.0 (C-3a), 62.3 (C-6a), 129.3 (C-5), 133.6 (C-6), 217.2 (C-2). – GC-MS (EI): m/z (%) 136.1 (56) [M^+], 107.1 (10), 94.1 (44), 79.0 (32), 66.0 (100). – HRMS (EI): calcd. for $\text{C}_9\text{H}_{12}\text{O}$ 136.0888; found 136.0888 [M^+].

rac-3-Butyl-3,3a,4,6a-tetrahydropentalen-1(2H)-one (**1b**)

$R_f = 0.26$. – FT-IR (ATR): $\nu = 3062$ (m), 2956 (s), 2920 (s), 2872 (m), 2852 (s), 1733 (vs), 1465 (m), 1410 (m), 1379 (w), 1344 (w), 1287 (w), 1230 (m), 1213 (m), 1168 (s), 1116 (m), 910 (s), 732 (s), 689 (vs) cm^{-1} . – ^1H NMR (500.15 MHz, CDCl_3): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3 H, 4'-H), 1.24–1.39 (m, 5 H, 1'-H_a, 2'-H, 3'-H), 1.56–1.64 (m, 1 H, 1'-H_b), 1.70–1.79 (m, 1 H, 3-H), 1.94 (ddd, $J = 1.5$ Hz, $J = 11.0$ Hz, $J = 17.6$ Hz, 1 H, 2-H_a), 2.26–2.32 (m, 1 H, 4-H_a), 2.39 (dd, $J = 7.2$ Hz, $J = 17.4$ Hz, 1 H, 2-H_b), 2.52 (dq, $J = 0.9$ Hz, $J = 8.0$ Hz, 1 H, 3a-H), 2.64–2.72 (m, 1 H, 4-H_b), 3.37–3.42 (m, 1 H, 6a-H), 5.61 (td, $J = 2.3$ Hz, $J = 7.7$ Hz, 1 H, 5-H) 5.76 (dt, $J = 2.4$ Hz, $J = 5.0$ Hz, 1 H, 6-H). – ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 13.9$ (C-4'), 22.8 (C-3'), 30.2 (C-2'), 35.4 (C-1'), 39.4 (C-4), 42.1 (C-3), 44.7, 44.9 (C-2, C-3a), 60.7 (C-6a), 127.3 (C-5), 132.1 (C-6), 217.9 (C-2). – GC-MS (EI): m/z (%) 178.3 (36) [M^+], 149.2 (7), 136.2 (28), 121.2 (25), 111.1 (30), 107.1 (15), 92.1 (44), 79.1 (37), 66.1 (100), 55.1 (26). – HRMS (EI): calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$ 178.1358; found 178.1358 [M^+].

rac-3-Phenyl-3,3a,4,6a-tetrahydropentalen-1(2H)-one (**1c**)

$R_f = 0.11$. – FT-IR (ATR): $\nu = 3062$ (m), 3028 (m), 2899 (s), 2847 (s), 1732 (vs), 1601 (m), 1494 (s), 1453 (s), 1407 (m), 1342 (w), 1261 (m), 1211 (m), 1186 (s), 1168 (s), 1114 (m), 909 (s), 832 (m), 759 (s), 686 (vs) cm^{-1} . – ^1H NMR (500.15 MHz, CDCl_3): $\delta = 2.32$ –2.38 (m, 1 H, 4-H_a), 2.47 (dd, $J = 7.3$ Hz, $J = 17.1$ Hz, 1 H, 2-H_a), 2.58–2.63 (m, 2 H, 2-H_b, 4-H_b), 2.87–2.94 (m, 1 H, 3-H), 3.05 (q, $J = 8.4$ Hz, 1 H, 3a-H), 3.50–3.55 (m, 1 H, 6a-H), 5.63 (dt, $J = 2.4$ Hz, $J = 7.4$ Hz, 1 H, 5-H), 5.82 (dt, $J = 2.6$ Hz, $J = 5.2$ Hz, 1 H, 6-H). – ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 39.8$ (C-4), 48.2, 48.4 (C-2, C-3a), 49.5 (C-3), 62.5 (C-6a), 128.4, 129.1, 129.3, 130.4, 133.4 (C-5, C-6, C-2', C-3', C-4', C-5', C-6'), 145.2 (C-4'), 216.2 (C-2). – GC-MS (EI): m/z (%) 198.2 (42) [M^+], 155.1 (20), 133.1 (18), 115.1 (12), 104.1 (100), 91.0 (23), 66.1 (59). – HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{14}\text{O}$ 198.1045; found 198.1037 [M^+].

rac-3-Butyloctahydro-1H-4,7-methanoinden-1-one (**11b**)

$R_f = 0.35$. – FT-IR (ATR): $\nu = 2952$ (s), 2919 (s), 2871 (s), 1731 (vs), 1457 (m), 1411 (w), 1378 (w), 1311 (w),

1297 (w), 1250 (m), 1198 (s), 1183 (s), 1168 (s), 1119 (w), 1097 (w), 968 (w), 951 (w), 917 (w) cm^{-1} . – ^1H NMR (500.15 MHz, CDCl_3): $\delta = 0.91$ (t, $J = 7.0$ Hz, 3 H, 4'-H), 1.02–1.08 (m, 2 H, 10-H), 1.11–1.21 (m, 2 H, 8-H_a, 9-H_a), 1.30–1.39 (m, 4 H, 2'-H, 3'-H), 1.44–1.66 (m, 5 H, 1'-H, 5-H, 8-H_b, 9-H_b), 1.86 (dd, $J = 6.7$ Hz, $J = 8.9$ Hz, 1 H, 6-H), 1.95 (ddd, $J = 1.6$ Hz, $J = 11.4$ Hz, $J = 17.2$ Hz, 1 H, 4-H_a), 2.12–2.19 (m, 3 H, 2-H, 4-H_b, 7-H), 2.41–2.43 (m, 1 H, 1-H). – ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 15.3$ (C-4'), 24.5 (C-3'), 29.7, 29.8 (C-8, C-9), 32.1 (C-2'), 36.0 (C-10), 38.9 (C-1'), 40.8 (C-1), 41.0 (C-5), 44.1 (C-7), 47.1 (C-4), 52.6 (C-6), 57.5 (C-2). – MS (EI): m/z (%) 206.2 (41) [M^+], 177.1 (8), 149.1 (100), 139.0 (30), 121.1 (19), 111.0 (59), 95.0 (20), 79.0 (21), 66.0 (43), 55.0 (14). – HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$ 206.1671; found 206.1671 [M^+].

rac-3-Phenyloctahydro-1H-4,7-methanoinden-1-one (**11c**)

$R_f = 0.32$. – FT-IR (ATR): $\nu = 3061$ (w), 3027 (m), 2949 (s), 2871 (s), 1732 (vs), 1693 (s), 1601 (m), 1494 (s), 1452 (s), 1410 (m), 1384 (m), 1297 (m), 1268 (m), 1198 (s), 1180 (s), 1117 (m), 1092 (m), 944 (w), 914 (m) cm^{-1} . – ^1H NMR (500.15 MHz, CDCl_3): $\delta = 1.09$ –1.15 (m, 2 H, 9-H_a, 10-H_a), 1.15–1.20 (m, 1 H, 9-H_b), 1.23–1.27 (m, 1 H, 10-H_b), 1.48–1.56 (m, 2 H, 8-H), 2.26–2.33 (m, 2 H, 6-H, 7-H), 2.36–2.42 (m, 2 H, 2-H, 4-H_a), 2.51–2.54 (m, 1 H, 1-H), 2.58 (ddd, $J = 1.7$ Hz, $J = 12.6$ Hz, $J = 16.7$ Hz, 1 H, 4-H_b), 2.87 (td, $J = 7.6$ Hz, $J = 12.5$ Hz, 1 H, 5-H), 7.20–7.39 (m, 5 H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H). – ^{13}C NMR (125.76 MHz, CDCl_3): $\delta = 29.6$, 29.7 (C-8, C-9), 35.9 (C-10), 40.8 (C-1), 43.4 (C-6), 46.8 (C-5), 48.5 (C-4), 54.8 (C-7), 57.7 (C-2), 128.1 (C-4'), 129.0 (C-3', C-5'), 130.4 (C-2', C-6'), 147.4 (C-1'), 219.0 (C-3). – GC-MS (EI): m/z (%) 226 (68) [M^+], 130 (13), 115 (8), 104 (100), 91 (14), 78 (28), 66 (42), 51 (16). – HRMS (EI): calcd. for $\text{C}_{16}\text{H}_{18}\text{O}$ 226.1358; found 226.1354 [M^+].

rac-3-Isopropyloctahydro-1H-4,7-methanoinden-1-one (**11d**)

$R_f = 0.35$. – FT-IR (ATR): $\nu = 2953$ (s), 2871 (s), 1731 (vs), 1652 (w), 1601 (m), 1469 (m), 1410 (w), 1385 (m), 1368 (m), 1201 (m), 1172 (m), 1095 (w), 864 (w) cm^{-1} . – ^1H NMR (300.13 MHz, CDCl_3): $\delta = 0.90$ (d, $J = 6.6$ Hz, 3 H, CH₃), 1.00 (d, $J = 6.6$ Hz, 3 H, CH₃), 1.02–1.05 (m, 2 H, 10-H), 1.10–1.51 (m, 5 H, 5-H, 8-H, 9-H), 1.59 (sept, $J = 6.6$ Hz, 2 H, CH(CH₃)₂), 1.90–2.20 (m, 4 H, 2-H, 4-H, 6-H, 7-H), 2.40–2.42 (m, 1 H, 1-H). – ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 22.1$ (CH₃), 22.2 (CH₃), 29.6, 29.7 (C-8, C-9), 35.9 (C-10), 36.5 (CH(CH₃)₂), 40.9 (C-1), 44.9 (C-7), 45.4 (C-4), 48.2 (C-5), 50.6 (C-6), 57.9 (C-2), 220.1 (C-3). – MS (EI): m/z (%) 192.2 (63) [M^+], 149.1 (100), 121.1 (22), 97.1 (14), 79.1 (12), 66.1 (19), 41.0 (6). – HRMS (EI): calcd. for $\text{C}_{13}\text{H}_{20}\text{O}$ 192.1514; found 192.1518 [M^+].

Crystal structure determination of **12**

Suitable single crystals were obtained by crystallization from Et₂O. Data were collected on a Siemens P4 diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178$ Å) at 293 K. The structures were solved by direct methods and refined against F^2 for all observed reflections. *Crystal data*: C₁₆H₂₆OSi₂, $M = 290.6$, orthorhombic, space group $P2_12_12_1$; $a = 6.6924(4)$, $b = 14.4241(8)$, $c = 18.4173(14)$ Å, $\alpha = \beta = \gamma = 90^\circ$; $V = 1777.9(2)$ Å³, $Z = 4$; $D_c = 1.086$ g cm⁻³. *Data collection*: crystal size $0.3 \times 0.25 \times 0.20$ mm, 3177 reflections in the range $\theta = 3.89\text{--}67.48^\circ$, 2726 unique reflections. *Structure refinement*: 2726 reflection data ($I > 2\sigma(I)$), 173 parameters; the final R indices were $R = 0.0670$, $R_w = 0.0898$; residual electron density between 0.344 and -0.227 eÅ⁻³.

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC-290468. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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- [1] a) L. V. R. Bonaga, M. E. Krafft, *Tetrahedron* **60**, 9795 (2004); b) S. E. Gibson, A. Stevenazzi, *Angew. Chem.* **115**, 1844 (2003); *Angew. Chem. Int. Ed.* **42**, 1800 (2003); c) B. E. Hanson, *Comments Inorg. Chem.* **23**, 289 (2002); d) K. M. Brummond, J. L. Kent, *Tetrahedron* **56**, 3263 (2000); e) A. J. Fletcher, S. D. R. Christie, *J. Chem. Soc. Perkin Trans. 1* 1657 (2000); f) Y. K. Chung, *Coord. Chem. Rev.* **188**, 297 (1999).
- [2] Recent examples of alternative pentalenone synthesis: a) J. Yang, Y. O. Lang, L. A. Paquette, *J. Am. Chem. Soc.* **125**, 1567 (2003); b) A. N. M. M. Rahman, R. Bishop, D. C. Craig, M. L. Scudder, *Eur. J. Org. Chem.* 72 (2003); c) A. Wroblewski, K. Saha-srabudhe, J. Aubé, *J. Am. Chem. Soc.* **124**, 9974 (2002); d) H. Hashimoto, Y. Abe, Y. Mayuzumi, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett.* **43**, 265 (2002); e) J. Barluenga, S. Martinez, A. L. Suárez-Sobrino, M. Tomás, *J. Am. Chem. Soc.* **124**, 5948 (2002); f) G. Mehta, K. Sreenivas, *Tetrahedron Lett.* **43**, 3319 (2002); g) S. Kotha, R. Sivakumar, L. Damodharan, V. Pattabhi, *Tetrahedron Lett.* **43**, 4523 (2002); h) L. A. Paquette, J. Yang, Y. O. Long, *J. Am. Chem. Soc.* **124**, 6542 (2002); i) H.-P. Wu, R. Aumann, R. Fröhlich, E. Wegelius, *Organometallics* **20**, 2183 (2001); j) G. Mehta, K. Srinivas, *Tetrahedron Lett.* **42**, 2855 (2001); k) D. M. Hodgson, I. D. Cameron, M. Christlieb, R. Green, G. P. Lee, L. A. Robinson, *J. Chem. Soc. Perkin Trans. 1* 2161 (2001); l) E. Piers, A. Orellana, *Synthesis* 2138 (2001); m) R. Muto, K. Ogasawara, *Tetrahedron Lett.* **42**, 4143 (2001).
- [3] I. U. Khand, P. L. Pauson, M. J. A. Habib, *J. Chem. Res. (S)* 348 (1978).
- [4] N. E. Schore, B. E. La Belle, M. J. Knudsen, H. Hope, X.-J. Xu, *J. Organomet. Chem.* **272**, 435 (1984).
- [5] K. E. B. Parkes, G. Pattenden, *J. Chem. Soc. Perkin Trans. 1* 1119 (1988).
- [6] a) X. Verdager, A. Lledó, C. Lopez-Mosquera, M. A. Maestro, M. A. Pericas, A. Riera, *J. Org. Chem.* **69**, 8053 (2004); b) J. Castro, A. Moyano, M. A. Pericas, A. Riera, A. Alvarez-Larena, J. F. Piniella, *J. Am. Chem. Soc.* **122**, 7944 (2000); c) P. Magnus, L. M. Principe, M. J. Slater, *J. Org. Chem.* **52**, 1483 (1987); d) E. Carceller, V. Centellas, A. Moyano, M. A. Pericas, F. Serratos, *Tetrahedron Lett.* **26**, 2475 (1985); e) C. Exon, P. Magnus, *J. Am. Chem. Soc.* **105**, 2477 (1983).
- [7] X. Verdager, A. Moyano, M. A. Pericas, A. Riera, M. A. Maestro, J. Mahia, *J. Am. Chem. Soc.* **122**, 10242 (2000).
- [8] a) W. J. Kerr, D. M. Lindsay, M. McLaughlin, P. L. Pauson, *Chem. Commun.* 1467 (2000); b) M. Iqbal, Y. Li, P. Evans, *Tetrahedron* **60**, 2531 (2004).
- [9] J. L. Loebach, D. M. Bennett, R. L. Danheiser, *J. Am. Chem. Soc.* **120**, 9690 (1998).
- [10] R. Ducray, N. Cramer, M. A. Ciufolini, *Tetrahedron Lett.* **42**, 9175 (2001).
- [11] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, M. I. Foreman, *J. Chem. Soc. Perkin Trans. 1* 977 (1973).
- [12] J.-B. Wiel, F. Rouessac, *J. Chem. Soc. Chem. Commun.* 446 (1976).
- [13] a) T. Sakan, K. Abe, *Tetrahedron Lett.* 2471 (1968); b) P. P. M. A. Dols, M. M. H. Verstappen, A. J. H. Klunder, B. Zwanenburg, *Tetrahedron* **49**, 11353 (1993).
- [14] M. Iqbal, P. Evans, A. Lledó, X. Verdager, M. A. Pericas, A. Riera, C. Loeffler, A. K. Sinha, M. J. Mueller, *ChemBioChem* **6**, 276 (2005).
- [15] L. N. Ivanova, T. A. Severina, G. A. Kogan, V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1438 (1963); *Chem. Abstr.* **59**, 13838b (1963).