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

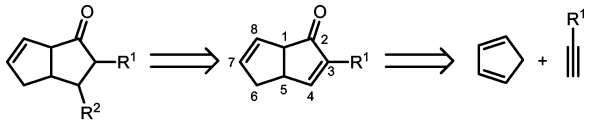
Z. Naturforsch. **61b,** 589 – 596 (2006); received January 17, 2006

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 $[2+2+1]$cocyclization 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.



1 (R^1 = H)
2 (R^1 = $SiMe_3$)
3 **4** **5**

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 = alkyl) in up to 60% yield from the corresponding 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

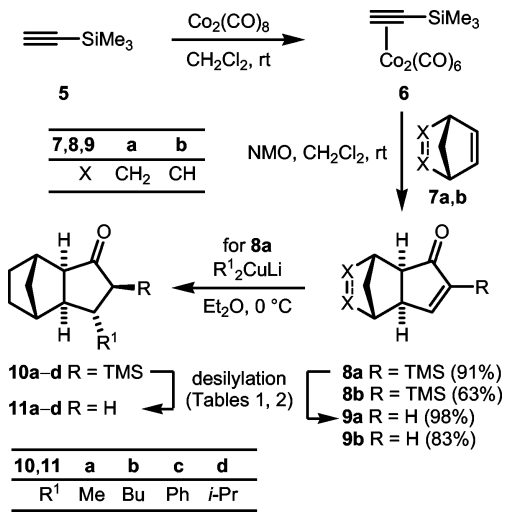
The Pauson-Khand reaction of cyclopentadiene (**4**) with acetylene gave compound **3** [5] (R^1 = H) (Scheme 1) in only very low yield (9%). As the removal of the trimethylsilyl group in Pauson-Khand cyclization products is well documented in the literature [6], acetylene was replaced with trimethylsilylacetylene (**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.

Table 1. Desilylation of α-trimethylsilylcyclopentenone derivatives **3a** and **8a**, **b**.

	Starting materials			Reaction conditions		Products	
Entry	Enone	Reagent	Solvent	T [°C]	*t* [h]		Yield [%]
1	**8a**	TBAF	THF	20	72	**9a**	47
2	**8a**	$MeSO_3H$	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_4NOH	DMF	−20	1	**9a**	12
7	**8a**	Bu_4NOH	DMF	0	5	**9a**	83
8	**8a**	Bu_4NOH	DMF	20	5	**9a**	90
9	**8a**	Bu_4NOH	THF	20	12	**9a**	98
10	**8b**	$MeSO_3H$	Et_2O	20	12	**9b**	–
11	**8b**	Bu_4NOH	DMF	20	12	**9b**	68
12	**8b**	Bu_4NOH	Et_2O	20	12	**9b**	83
13	**3a**	$MeSO_3H$	Et_2O	20	5	**3b**	–
14	**3a**	Bu_4NOH	DMF	20	12	**3b**	91
15	**3a**	Bu_4NOH	Et_2O	20	1	**3b**	93

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**.

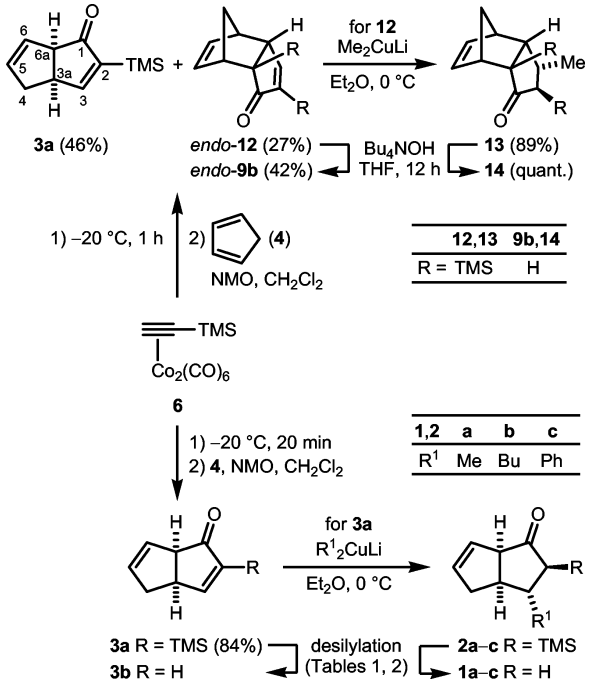
		Conditions		TMS-ketones			Conditions		Ketones	
Entry		T [°C]	*t* [min]		R =	Yield [%]	Solvent	*t* [h]		Yield [%]
1	**8a**	0	10	**10a**	Me	84	THF	48	**11a**	98
2	**8a**	−20	15	**10b**	Bu	92	THF	12	**11b**	87
3	**8a**	0	120	**10c**	Ph	86	THF	1	**11c**	79
4	**8a**	−20	30	**10d**	*i*-Pr	42	THF	12	**11d**	75
5	**3a**	0	120	**2a**	Me	49	Et_2O	3	**1a**	63
6	**3a**	−20	180	**2b**	Bu	62	Et_2O	12	**1b**	77
7	**3a**	0	180	**2c**	Ph	70	Et_2O	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 conditions and reagents such as TASF [9], CsOH, LiOH, and $MeSO_3H$ [10] had to be investigated (Table 1). After considerable experimentation, tetrabutylammonium hydroxide (Bu_4NOH) [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 Bu_4NOH 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 $Co_2(CO)_8$ 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%.

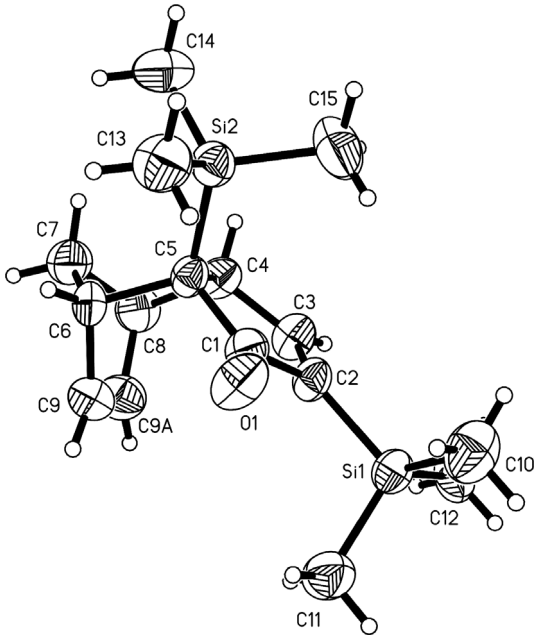


Fig. 1. ORTEP view of the *endo*-configured tricyclic cyclopentane derivative **12**.

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 SiO_2 60, grain size 0.063–0.200 mm (Merck) with pentane, hexanes (b. p. 40–60 °C), EtOAc, and diethyl ether (Et_2O) 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 (^{1}H: 300.13 MHz, 500.15 MHz, ^{13}C: 75.47 MHz, 125.76 MHz). For ^{1}H spectra, TMS was used as internal standard. For ^{13}C 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 CH_2Cl_2 (25 ml) under N_2 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 SiO_2 with Et_2O. The filtrate was concentrated and the residue chromatographed on SiO_2 with pentane/Et_2O (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): $\nu = 3069$ (w), 3025 (m), 2979 (s), 2952 (m), 1655 (vs), 1572 (s), 1294 (s), 1247 (s), 1188 (s), 988 (m) cm^{-1}. – ^{1}H NMR (500.15 MHz, $CDCl_3$): $\delta = 0.07$ (s, 9 H, $CHSi(CH_3)_3$), 0.08 (s, 9 H, $CSi(CH_3)_3$), 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). – ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = -0.6$ ($(CH_3)_3Si$), −0.9 ($(CH_3)_3Si$), 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 $C_{16}H_{26}OSi_2$ 290.1522; found 290.1516 [M$^+$].

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

M. p. 37 °C. – FT-IR (ATR): $\nu = 3061$ (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}. – ^{1}H NMR (500.15 MHz, $CDCl_3$): $\delta = 0.13$ (s, 9 H, $Si(CH_3)_3$), 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). – ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = -0.8$ ($(CH_3)_3Si$), 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 $C_{11}H_{16}OSi$ 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 CH_2Cl_2 (5 ml) under N_2 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 SiO_2 with Et_2O. The filtrate was concentrated and the residue chromatographed on SiO_2 with pentane/Et_2O (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 CH_2Cl_2 (5 ml) under N_2 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 SiO_2 with Et_2O. The filtrate was concentrated and the residue chromatographed on SiO_2 with pentane/Et_2O 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 Et_2O (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 NH_4Cl (5 ml). The layers were separated and the aqueous layer was extracted with Et_2O (5 × 10 ml). The combined organic layers were dried (K_2CO_3), concentrated and the crude products **2**, **10**, and **13** purified by chromatography on SiO_2 with pentane/Et_2O (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): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = 0.03 (s, 9 H, Si(CH_3)$_3$), 1.15 (d, J = 6.8 Hz, 3 H, CH_3), 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). – ^{13}C NMR (125.76 MHz, $(CD_3)_2CO$): δ = −0.8 (Si(CH_3)$_3$), 23.1 (CH_3), 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 $C_{12}H_{20}OSi$ 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): ν = 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}. – ^{1}H NMR (500.15 MHz, $CDCl_3$): δ = 0.04 (s, 9 H, Si(CH_3)$_3$), 0.91 (t, J = 7.0 Hz, 3 H, CH_3), 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). – ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = −1.8 (Si(CH_3)$_3$), 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, CH_4): calcd. for $C_{15}H_{25}OSi$ 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): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = −0.11 (s, 9 H, Si(CH_3)$_3$), 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). – ^{13}C NMR (125.76 MHz, $(CD_3)_2CO$): δ = −0.9 (Si(CH_3)$_3$), 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 $C_{17}H_{22}OSi$ 270.1440; found 270.1441 [M^+].

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

R_f = 0.35. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.08 (s, 9 H, Si(CH_3)$_3$), 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, CH_3), 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). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = −1.6 (Si(CH_3)$_3$), 23.9 (CH_3), 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 $C_{14}H_{24}OSi$ 236.1596, found 236.1596 [M^+].

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

R_f = 0.30. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = 0.08 (s, 9 H, Si(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, $(CD_3)_2CO$): δ = −0.4 (Si(*C*H$_3$)$_3$), 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). – $C_{17}H_{30}OSi$ (278.5): calcd. C 73.31, H 10.86; found C 73.31, H 10.82.

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

R_f = 0.37. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = −0.09 (s, 9 H, Si(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, $(CD_3)_2CO$): δ = −0.7 (Si(*C*H$_3$)$_3$), 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 $C_{19}H_{26}OSi$ 298.1753; found 298.1737 [M$^+$].

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

R_f = 0.50. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = 0.09 (s, 9 H, Si(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, C*H*(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, $(CD_3)_2CO$): δ = −0.1 (Si(*C*H$_3$)$_3$), 17.2 (CH$_3$), 22.8 (CH$_3$), 29.8, 29.9 (C-8, C-9), 33.1 (*C*H(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 $C_{16}H_{28}OSi$ 264.1909; found 264.1899 [M$^+$].

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

R_f = 0.65. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (500.15 MHz, $(CD_3)_2CO$): δ = 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, $(CD_3)_2CO$): δ = −0.9 (7a-Si(*C*H$_3$)$_3$), 0.0 (2-Si(*C*H$_3$)$_3$), 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 $C_{17}H_{30}OSi_2$ 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(2H)-one (***1a***)*

R_f = 0.21. – FT-IR (ATR): ν = 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}. – ^{1}H NMR (500.15 MHz, $CDCl_3$): δ = 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, $CDCl_3$): $\delta = 20.8$ (*C*H_3), 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 $C_9H_{12}O$ 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}. – ^{1}H 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 $C_{12}H_{18}O$ 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}. – ^{1}H 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-5,0 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 $C_{14}H_{14}O$ 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}. – ^{1}H 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 $C_{14}H_{22}O$ 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}. – ^{1}H 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 $C_{16}H_{18}O$ 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}. – ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 0.90$ (d, $J = 6.6$ Hz, 3 H, CH_3), 1.00 (d, $J = 6.6$ Hz, 3 H, CH_3), 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, C*H*(CH_3)$_2$), 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, $CDCl_3$): $\delta = 22.1$ (CH_3), 22.2 (CH_3), 29.6, 29.7 (C-8, C-9), 35.9 (C-10), 36.5 (*C*H(CH_3)$_2$), 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 $C_{13}H_{20}O$ 192.1514; found 192.1518 [M^+].

Crystal structure determination of **12**

Suitable single crystals were obtained by crystallization from Et_2O. 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*: $C_{16}H_{26}OSi_2$, $M = 290.6$, orthorhombic, space group $P2_12_12_1$; $a = 6.6924(4)$, $b = 14.4241(8)$, $c = 18.4173(14)$ Å, $\alpha = \beta = \gamma = 90°$; $V = 1777.9(2)$ Å^3, $Z = 4$; $D_c = 1.086$ g cm^{-3}. *Data collection*: crystal size $0.3 \times 0.25 \times 0.20$ mm, 3177 reflections in the range $\theta = 3.89 - 67.48°$, 2726 unique reflections. *Structure refinement*: 2726 reflection data ($I > 2\sigma(I)$), 173 parameters; the final R indices were $R = 0.0670$, $Rw = 0.0898$; 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).

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg is gratefully acknowledged. A. Becheanu thanks the Deutsche Akademische Austauschdienst for a DAAD award and T. Bell thanks the European Community for an ERASMUS/SOKRATES fellowship.

[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. Wrobleski, K. Sahasrabudhe, 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. Verdaguer, 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. Serratosa, Tetrahedron Lett. **26**, 2475 (1985); e) C. Exon, P. Magnus, J. Am. Chem. Soc. **105**, 2477 (1983).

[7] X. Verdaguer, 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. Verdaguer, 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).