Synthesis of *s*-Indacene Derivatives by Double Robinson-Type Cyclopentene Annulation

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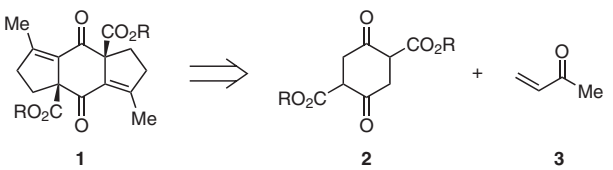
Abstract: Michael reactions of 2,5-dioxocyclohexane-1,4-dicarboxylates with methyl vinyl ketone yield bis-adducts that can be further cyclized in a Robinson-type annulation to give *s*-indacene derivatives as single diastereomers. The carboxylate functions of this scaffold can be deprotected and subsequently decarboxylated to yield tricyclic products with a central aromatic ring.

Key words: annulation, indacene, cyclopentene, conjugate addition, aldol reaction

The aldol reaction[1] and the Michael addition[2] are among the most important methods for C–C bond formation in carbonyl compounds. When performed as a sequence, they become a long established[3] and extraordinarily powerful tool for six-membered ring formation known as the Robinson annulation.[4] In close relation with our project on asymmetric metal-catalyzed Michael reactions,[5] we have applied the Robinson annulation to the preparation of bicyclic cyclohexenone derivatives.[6] In extending these studies to the reaction of bis-β-oxo esters **2** with methyl vinyl ketone (**3**) (MVK), we recently observed an unexpected and unusual dual cyclopentene annulation under conditions typical for Robinson annulation (Scheme 1).[7] A similar observation has already been reported using acrolein as the Michael acceptor but with low chemoselectivity and unpredictable yield.[8] The products of this process are *s*-indacene[9] derivatives **1**. This dicyclopenta[*a*,*d*]benzene skeleton is relatively rare in synthetic organic chemistry,[10] however, some natural products,[11] ligands,[12] and interesting materials[13] with this structural motif have been reported. We report herein full experimental details on the synthesis of the *s*-indacene derivatives **1** and further transformations of these materials.

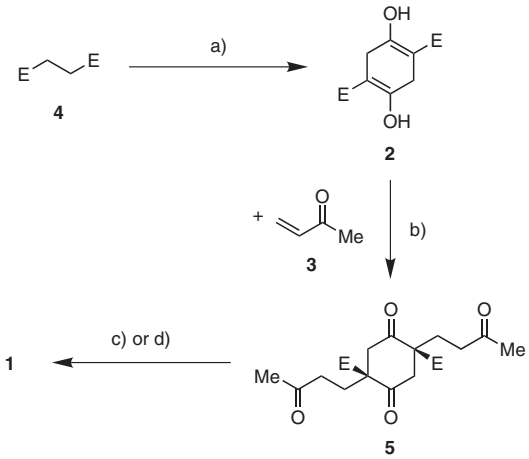


Scheme 1 Synthesis of *s*-indacene derivatives **1** from bis-β-oxo esters **2** and methyl vinyl ketone (**3**)

2,5-Dioxocyclohexane-1,4-dicarboxylates ('succinyl succinates') **2** are known compounds that exist almost completely as the double enol tautomers as shown in Scheme 2. They are conveniently prepared by twofold Claisen–Dieckmann condensation of succinates **4**. We prepared five products **2a–e** from succinates **4a–e** according to a standard protocol reported for methyl and ethyl esters **2a** and **2b**; compounds **2c–e** and **4c** are novel, the latter was prepared from succinic anhydride and octan-1-ol in 96% yield.

In extending our studies of iron-catalyzed Michael reactions[14] of β-oxo esters, we were interested in the reactions of bis(β-oxo esters) **2** with MVK (**3**). The donors **2** were converted, however, at ambient temperature only into monoadducts;[15] at 60 °C and using ten equivalents of MVK (**3**) and 10 mol% of catalyst, the bis-adducts **5** were obtained. In the case of **5a** and **5b**, the crude products are mixtures of *cis*- and *trans*-diastereomers, with the relative *cis*-configuration predominating. Stereochemically unique *cis*-configurated materials (one signal set in the NMR spectra) are obtained by recrystallization of these mixtures with yields in the range of 43–79% (Table 1).

The relative configuration of compounds **5** should be elucidable by GLC on a chiral phase, since *cis*-isomers should be racemates, whereas *trans*-isomers would be *meso* compounds. However, we were not able to achieve



Scheme 2 Three-step synthesis of *s*-indacene derivatives **1** from succinates **4**. For yields and ester substituents E, see Table 1. *Reaction conditions*: (a) NaH, DMSO, 50 °C, 1 h; (b) $FeCl_3 \cdot 6\,H_2O$ (0.1 equiv), MVK (**3**) (10 equiv), CH_2Cl_2, 60 °C, 2 d; (c) concd H_2SO_4, 0 °C, 1 h, then 23 °C, 16 h (**1a–c**); (d) pyrrolidine, AcOH, CH_2Cl_2, 0 °C, 1 h then 50 °C, 16 h (**1d,e**).

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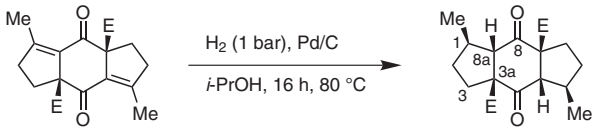
Table 1 Substituents and Yields of Products **1**, **2**, and **5**

Ester	E	Diester **2**	Yield (%)	Tetraketone **5**	Yield[a] (%)	Indacene **1**	Yield (%)
4a	CO_2Me	**2a**	76	**5a**	60	**1a**[b]	57
4b	CO_2Et	**2b**	84	**5b**	53	**1b**[b]	70
4c	$CO_2(CH_2)_7Me$	**2c**	70	**5c**	43	**1c**[b]	69
4d	CO_2Bn	**2d**	81	**5d**	79	**1d**[c]	46
4e	CO_2allyl	**2e**	76	**5e**	60	**1e**[c]	29

[a] Yield of pure *cis*-diastereomer (de >95%) after recrystallization.
[b] Cyclization with concd H_2SO_4.
[c] Cyclization with pyrrolidine–AcOH.

sufficient resolution with various chiral phases. Therefore, we envisioned reducing the conformational flexibility by subsequent Robinson annulation, which has, in the past, proved to be a useful strategy in our laboratory to overcome this problem.[16] Under standard conditions for this annulation (concd H_2SO_4 or pyrrolidine–AcOH) we did not observe the formation of six-membered annulation products with an anthracene skeleton, but surprisingly, *s*-indacene derivatives **1** were formed. GLC on a chiral phase now suggests the *cis* configuration of the two stereogenic centers since these materials turned out to be racemates, which clearly contradicts an earlier report with acrolein as the Michael acceptor.[8]

In order to access the fully saturated *s*-indacene skeleton we submitted compounds **1a–c** to catalytic hydrogenation of the C=C bonds yielding tricyclic products **6a–c** as single diastereomers (one set of signals in the NMR spectra). The relative configuration was established based on ^3J(H,H) and ^3J(H,^{13}C) coupling constants: The vicinal coupling constant ^3J(H8a,H1) = 9.1 Hz observed as a doublet for the bridgehead proton H8a (see Scheme 3 for atom numbering) is compatible only with a close to almost antiperiplanar, *trans* orientation of H8a to H1 in the five-membered ring. This configuration is in accord with a detailed analysis of the ^{13}C,^{1}H multiple bond coupling correlation (HMBC). The HMBC correlation plot displays prominent cross peaks between H1 and C2, C8a, and the methyl carbon; these ^2J correlations are independent of any torsional angle. For the three possible ^3J correlations, the 2D plot shows an equally pronounced cross peak of H1 only to the C8 carbonyl resonance while no cross peaks appear for the H1/C3 and the H1/C3a correlation. With an all-*cis* configuration of both Me and both CO_2Me groups, and a boat or tub conformation for the central six-membered ring, dihedral angles of ca. 90° between H1 and both C3 and C3a, and of ca. 30° between H1 and C8 can be taken from a molecular model, thus explaining the missing ^3J(H1,^{13}C3) and ^3J(H1,^{13}C3a) cross peaks in the HMBC spectra. Therefore, we conclude that all three cycles are *cis* annulated, with an all-*cis* configuration for the two methyl and the two ester groups.



1a (E = CO_2Me)
1b (E = CO_2Et)
1c (E = CO_2Oct)

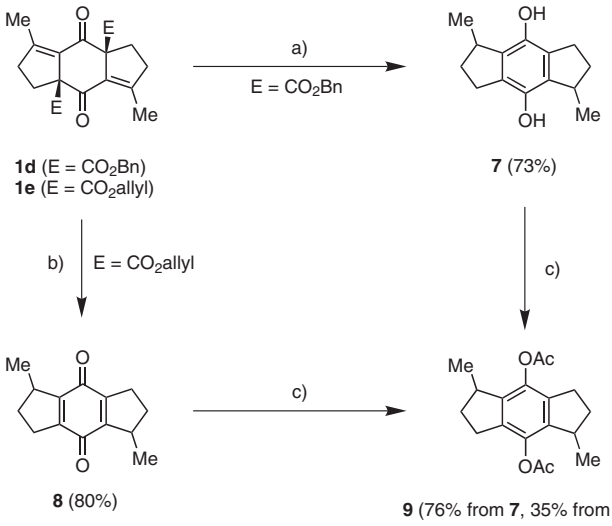
6a (70%, de >98%)
6b (86%, de >98%)
6c (60%, de >98%)

Scheme 3 Hydrogenation of alkyl esters **1a–c**

At first view, this finding implies a formal *trans*-dihydrogenation of substrates **1a–c**, which is clearly the result of a *cis*-dihydrogenation followed by an epimerization at C8a and C4a. Since the convex face of substrates **1a–c** is blocked by the two ester moieties, the catalytic *cis*-dihydrogenation has obviously occurred from the inner, concave side of the molecule. *cis*-Dihydrogenation enforces a double *trans* annulation of the six-membered and the two five-membered rings. This extremely strained configuration is readily released by spontaneous epimerization at the tertiary stereocenters α to the carbonyl groups via the enol tautomers, resulting in the *trans* configuration of H1, H8a and H4a, H5, respectively, and thus simulating formal *anti*-dihydrogenation.

We have undertaken several attempts to saponify esters **1a–c**, but presumably due to the strained neopentyl-type situation, no nucleophilic attack to the ester carbonyl groups was observed. Therefore, we prepared the benzyl (**1d–5d**) and allyl ester series (**1e–5e**), since these protective groups could be cleaved by hydrogenolysis or transition-metal-catalyzed allylic substitution.

Catalytic hydrogenolysis of the dibenzyl ester **1d** gave the decarboxylated derivative **7** (Scheme 4) as a mixture of two diastereomeric hydroquinones (*rac*/*meso* 2:1 by GLC on an achiral phase; GLC on a chiral phase gave a 1:1:1 ratio). The product is not stable under ambient conditions, presumably due to oxidation to the corresponding quinone derivative **8**. Acetylation of partially oxidized hydroquinone **7** under reductive conditions (Zn, AcCl, NaOAc)[17] yielded the diester **9**, once again in the form of two diastereomers, which are sufficiently stable under ambient conditions to allow detailed structural analysis.



Scheme 4 Deprotection of esters **1d** and **1e**. *Reaction conditions*: (a) H_2 (1 bar), Pd/C, *i*-PrOH, 80 °C, 16 h, 73% (*rac*/*meso* 2:1); (b) HCO_2H, Et_3N, cat. $Pd(OAc)_2$, cat. Ph_3P, THF, 23 °C, 4 h, 80%; (c) Zn, AcCl, NaOAc, 60 °C, 2 h then 23 °C, 24 h, 76% (from **7**), 35% (from **8**).

Compound **9** shows a doubled signal set in the NMR spectra (dr 2:1).

We also cleaved the allyl ester groups in compound **1e** by palladium-catalyzed allylic substitution[18] and obtained quinone derivative **8** as a mixture of tautomers that were difficult to purify. This mixture showed multiple signal sets in the NMR spectra, but only one signal in GLC, indicating rapid equilibrium of the tautomers. This mixture can be converted into diacetate **9** by applying the same conditions as for **7**, but the yield of **9** was low (35%). Again, compound **9** showed a doubled signal set in the NMR specta (dr 2:1), and the major diastereomer is the same as that obtained in the preparation of compound **9** from hydroquinone **7**.

In summary, 2,5-dioxocyclohexane-1,4-dicarboxylates **2** ('succinyl succinates') are conveniently prepared by condensation of two equivalents of succinates **4** under strongly basic reaction conditions. These can be converted with methyl vinyl ketone **3** in a double Michael reaction into bis-adducts **5** with high diastereoselectivity. Pure *cis*-diastereomers of these bis-adducts **5** are obtained by recrystallization. They can be cyclized in a Robinson-type annulation, a process that yields no six-membered rings, but *s*-indacene derivatives **1** as single diastereomers due to the rather unusual cyclopentene annulation. The C=C bonds of these tricyclic scaffolds can be hydrogenated to furnish, again, single diastereomers of diketones **6**. Derivatives with benzyl and allyl esters groups can be cleaved followed by twofold decarboxylation to yield *s*-indacene derivatives with a central aromatic ring.

Preparative column chromatography was carried out using Merck silica gel 60 with hexanes (PE, bp 40–60 °C) and EtOAc as eluents. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500, an Avance DPX 300, and an AC 250. Multiplicities were determined with DEPT experiments. EI-MS and HRMS spectra were obtained with a Finnigan MAT 95 spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer equipped with a 'GoldenGate' diamond-ATR unit. Elemental analyses were measured with an EA 1108 from Fisons Instruments. All starting materials were commercially available, except **2a**,[19] **2b**,[20] and **4d**,[21] which were prepared according to literature procedures. The preparation of and data for **1a**, **5a**, **5b**,[15] **6a**, **7**, and **9** have been previously reported.[7] Compounds **2c**,[22] **2d**,[23] **2e**,[22] and **4c**[24] have been previously reported, but without characterization.

Diethyl *cis*-1,5-Dimethyl-4,8-dioxo-2,3,3a,4,6,7,7a,8-octahydro-*s*-indacene-3a,7a-dicarboxylate (1b); Typical Procedure

Ice-cold, concd H_2SO_4 (1.5 mL) was added dropwise at 0 °C to **5b** (200 mg, 504 μmol). The mixture was stirred at 0 °C for 1 h, then at 23 °C for 16 h, and finally sat. $NaHCO_3$ soln (20 mL) was added dropwise. The aqueous layer was extracted with CH_2Cl_2 (5 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was removed and the residue purified by chromatography (silica gel, PE–EtOAc, 2:1, R_f = 0.45) to give **1b** (127 mg, 70%) as yellowish crystals; mp 89 °C.

IR (ATR): 2984 (m), 1724 (vs), 1694 (vs), 1613 (s), 1471 (m), 1447 (m), 1422 (s), 1388 (m), 1365 (s), 1332 (m), 1246 (s), 1219 (s), 1200 (s), 1168 (m), 1145 (m), 1125 (s), 1069 (s), 1022 (s), 961 (m), 814 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 6 H), 2.31 (s, 6 H), 2.28–2.33 (m, 2 H), 2.43–2.53 (m, 4 H), 2.72–2.76 (m, 2 H), 4.07–4.16 (m, 4 H).

$^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 13.9 (CH_3), 17.2 (CH_3), 31.7 (CH_2), 38.9 (CH_2), 62.0 (CH_2), 70.9 (C), 130.4 (C), 164.8 (C), 171.2 (C), 192.1 (C).

MS (EI, 70 eV): *m*/*z* (%) = 360 (50) [M^+], 332 (3), 315 (3), 287 (42), 240 (28), 213 (38), 180 (100), 152 (39).

Anal. Calcd for $C_{20}H_{24}O_6$ (360.41): C, 66.65; H, 6.71. Found: C, 66.54; H, 6.87.

Dioctyl *cis*-1,5-Dimethyl-4,8-dioxo-2,3,3a,4,6,7,7a,8-octahydro-*s*-indacene-3a,7a-dicarboxylate (1c)

Following the typical procedure for **1b** using concd H_2SO_4 (4 mL) and **5c** (1.00 g, 1.78 mmol) followed by sat. $NaHCO_3$ soln (140 mL) and extraction with CH_2Cl_2 (4 × 40 mL). Purification used chromatography (silica gel, PE–EtOAc, 5:1, R_f = 0.43) to give **1c** (648 mg, 69%) as a yellowish oil.

IR (ATR): 2956 (m), 2926 (s), 2856 (s), 1725 (vs), 1694 (vs), 1612 (s), 1458 (m), 1428 (m), 1373 (m), 1328 (m), 1252 (s), 1217 (s), 1164 (s), 1124 (s), 1073 (s), 948 (m), 809 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 6 H), 1.17–1.32 (m, 20 H), 1.57 (quint, *J* = 6.6 Hz, 4 H), 2.10–2.29 (m, 2 H), 2.27 (s, 6 H), 2.38–2.48 (m, 4 H), 2.68–2.73 (m, 2 H), 3.93–4.05 (m, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.1 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 28.2 (CH_2), 29.07 (CH_2), 29.10 (CH_2), 31.66 (CH_2), 31.69 (CH_2), 38.9 (CH_2), 66.0 (OCH_2), 70.9 (C), 130.5 (C), 164.5 (C), 171.2 (C), 192.0 (C).

MS (EI, 70 eV): *m*/*z* (%) = 528 (31) [M^+], 500 (4), 371 (42), 215 (100), 152 (54), 164 (21).

HRMS (EI, 70 eV): *m*/*z* [$M]^+$ calcd for $C_{32}H_{48}O_6$: 528.3451; found: 528.3450.

Dibenzyl *cis*-1,5-Dimethyl-4,8-dioxo-2,3,3a,4,6,7,7a,8-octahydro-*s*-indacene-3a,7a-dicarboxylate (1d); Typical Procedure

Pyrrolidine (110 mg, 1.5 mmol) and AcOH (93 mg, 1.5 mmol) were subsequently added at 0 °C to a soln of **5d** (400 mg, 768 μmol) in

CH_2Cl_2 (2 mL). The mixture was stirred at 0 °C for 1 h, then at 50 °C for 16 h. After removal of the solvent, the residue was chromatographed (silica gel, PE–EtOAc, 2:1, R_f = 0.43) to give **1d** (170 mg, 46%) as a brown oil.

IR (ATR): 2965 (m), 1721 (vs), 1690 (vs), 1608 (vs), 1498 (m), 1454 (m), 1426 (m), 1372 (s), 1328 (m), 1246 (m), 1211 (s), 1158 (s), 1122 (m), 1069 (s), 945 (m), 821 (s), 793 (m), 735 (vs), 696 (vs), 583 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.27–2.29 (m, 2 H), 2.31 (s, 6 H), 2.40–2.52 (m, 4 H), 2.68–2.74 (m, 2 H), 5.04 (A part of an AB system, *J* = 12.6 Hz, 2 H), 5.05 (B part of an AB system, *J* = 12.6 Hz, 2 H), 7.26–7.35 (m, 10 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 17.2 (CH_3), 31.5 (CH_2), 39.1 (CH_2), 67.4 (OCH_2), 70.9 (C), 127.8 (2 CH), 128.1 (CH), 128.5 (2 CH), 130.4 (C), 135.5 (C), 165.2 (C), 171.2 (C), 191.8 (C).

MS (EI, 70 eV): *m*/*z* (%) = 484 (19) [M^+], 456 (2), 349 (7), 91 (100).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{30}H_{28}O_6$: 484.1886; found: 484.1886.

Diallyl *cis*-1,5-Dimethyl-4,8-dioxo-2,3,3a,4,6,7,7a,8-octahydro-*s*-indacene-3a,7a-dicarboxylate (1e)

Following the typical procedure for **1d** using pyrrolidine (1.69 g, 23.8 mmol), AcOH (1.43 g, 23.8 mmol), and **5e** (5.00 g, 11.9 mmol) in CH_2Cl_2 (6 mL) gave, after chromatography (silica gel, PE–EtOAc, 3:1, R_f = 0.36), **1e** (1.31 mg, 29%) as a brown oil.

IR (ATR): 3085 (w), 2950 (m), 1725 (vs), 1692 (vs), 1608 (vs), 1426 (m), 1247 (s), 1211 (vs), 1162 (s), 1071 (m), 990 (m), 947 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 6 H), 2.30–2.37 (m, 2 H), 2.40–2.53 (m, 4 H), 2.70–2.79 (m, 2 H), 4.52 (ddt, *J* = 13.3, 5.7, 1.4 Hz, 2 H), 4.57 (ddt, *J* = 13.3, 5.7, 1.5 Hz, 2 H), 5.22 (dq, *J* = 10.5, 1.3 Hz, 2 H), 5.29 (dq, *J* = 17.2, 1.5 Hz, 2 H), 5.89 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 17.2 (CH_3), 31.8 (CH_2), 39.0 (CH_2), 66.4 (OCH_2), 70.8 (C), 118.5 (CH_2), 130.3 (C), 131.6 (CH), 165.1 (C), 171.0 (C), 191.9 (C).

MS (El, 70 eV): *m*/*z* (%) = 384 (70) [M^+], 327 (15), 299 (100), 214 (16), 192 (23).

Anal. Calcd for $C_{22}H_{24}O_6$ (384.43): C, 68.74; H, 6.29. Found: C, 68.85; H, 6.32.

Dioctyl 2,5-Dihydroxycyclohexa-1,4-diene-1,4-dicarboxylate (2c); Typical Procedure

Compound **4c** (20.0 g, 58.4 mmol) was added dropwise to a cooled (5 °C) suspension of NaH (4.68 g, 117 mmol, 60% dispersion in mineral oil) in abs DMSO (80 mL). After stirring at 0 °C for 30 min, additional abs DMSO (20 mL) was added, and the mixture was stirred at 23 °C for a further 1 h and then at 50 °C for 1 h. The mixture was cooled to 0 °C, then neutralized by dropwise addition of 6 M HCl (ca. 80 mL). The precipitate was filtered off, washed with H_2O (40 mL), dried under high vacuum, and recrystallized [PE (30 mL)–CH_2Cl_2 (33 mL)] to yield **2c** as colorless crystals (8.69 g, 70%); mp 89 °C.

IR (ATR): 2956 (s), 2922 (s), 2853 (s), 1737 (s), 1651 (m), 1614 (s), 1469 (m), 1404 (vs), 1329 (s), 1210 (br, vs), 1164 (m), 1066 (s), 944 (s), 816 (s), 779 (vs) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 6 H), 1.26–1.40 (m, 20 H), 1.67 (quint, *J* = 6.9 Hz, 4 H), 3.17 (s, 4 H), 4.17 (t, *J* = 6.6 Hz, 4 H), 12.20 (s, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 25.9 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 29.15 (CH_2), 29.18 (CH_2), 31.8 (CH_2), 64.9 (OCH_2), 93.3 (C), 168.4 (C), 171.4 (C).

MS (EI, 70 eV): *m*/*z* (%) = 424 (8) [M^+], 395 (8), 312 (20), 294 (96), 200 (35), 182 (100), 164 (21), 137 (15).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{24}H_{40}O_6$: 424.2825; found: 424.2824.

Dibenzyl 2,5-Dihydroxycyclohexa-1,4-diene-1,4-dicarboxylate (2d)

A soln of **4d** (5.00 g, 16.8 mmol) in abs DMSO (15 mL) was added dropwise to a cooled (5 °C) suspension of NaH (1.36 g, 34.0 mmol, 60% dispersion in mineral oil) in abs DMSO (20 mL). After stirring at 0 °C for 1 h, additional abs DMSO (10 mL) was added, and the mixture stirred at 23 °C for a further 30 min, and then at 50 °C for 1 h. The mixture was cooled to 0 °C, then neutralized by dropwise addition of 6 M HCl (ca. 30 mL). The precipitate was filtered off, washed with H_2O (4 × 10 mL), dried under high vacuum, and recrystallized [PE (50 mL)–CH_2Cl_2 (100 mL)–toluene (70 mL)] to yield **2d** as colorless crystals (2.60 g, 81%); mp 169 °C.

IR (ATR): 3300 (w, br), 2896 (m), 1651 (vs), 1620 (vs), 1497 (s), 1456 (s), 1423 (s), 1395 (s), 1336 (vs), 1212 (vs), 1067 (vs), 969 (m), 951 (m), 830 (m), 802 (m), 735 (vs) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.23 (s, 4 H), 5.23 (s, 4 H), 7.33–7.40 (m, 10 H), 12.12 (s, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 28.6 (CH_2), 66.3 (OCH_2), 93.1 (C), 128.0 (2 CH), 128.4 (CH), 128.6 (2 CH), 135.5 (C), 168.8 (C), 171.0 (C).

MS (EI, 70 eV): *m*/*z* (%) = 380 (8) [M^+], 289 (7), 91 (100).

Anal. Calcd for $C_{22}H_{20}O_6$ (380.40): C, 69.46; H, 5.30. Found: C, 69.56; H, 5.36.

Diallyl 2,5-Dihydroxycyclohexa-1,4-diene-1,4-dicarboxylate (2e)

Following the typical procedure for **2c** using **4e** (20.0 g, 101 mmol) with NaH (8.08 g, 202 mmol, 60% dispersion in mineral oil) in abs DMSO (50 mL) at 0 °C, and stirring at 0 °C for 1 h; additional abs DMSO (20 mL) and stirring at 23 °C for 1 h and 50 °C for 1 h. Workup used 6 M HCl (ca. 30 mL), the precipitate was washed with H_2O (100 mL), and recrystallization [PE (30 mL)–CH_2Cl_2 (50 mL)] to yield **2e** as colorless crystals (10.7 g, 76%); mp 109 °C.

IR (ATR): 3094 (w), 2950 (w), 2832 (m), 1664 (vs), 1646 (vs), 1616 (vs), 1451 (s), 1439 (s), 1424 (s), 1388 (vs), 1372 (s), 1326 (vs), 1201 (vs), 1131 (s), 1099 (s), 1060 (vs), 1002 (s), 960 (s), 928 (vs), 834 (vs) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.23 (s, 4 H), 4.70 (dt, *J* = 5.5, 1.4 Hz, 4 H), 5.27 (dq, *J* = 10.3, 1.1 Hz, 2 H), 5.35 (dq, *J* = 17.4, 1.5 Hz, 2 H), 5.95 (ddt, *J* = 17.2, 10.5, 5.4 Hz, 2 H), 12.12 (s, 2 H).

$^{13}C\{^1H\}$ NMR (125 Hz, $CDCl_3$): δ = 28.5 (CH_2), 65.2 (OCH_2), 93.1 (C), 118.4 (CH_2), 131.8 (CH), 168.8 (C), 170.9 (C).

MS (EI, 70 eV): *m*/*z* (%) = 280 (33) [M^+], 239 (10), 222 (16), 181 (22), 154 (12), 137 (12), 41 (100).

Anal. Calcd for $C_{14}H_{16}O_6$ (280.28): C, 59.99; H, 5.75. Found: C, 59.74; H, 5.83.

Dioctyl Succinate (4c)

A mixture of succinic anhydride (25.0 g, 250 mmol), octan-1-ol (97.7 g, 118 mL, 750 mmol), and concd H_2SO_4 (2.45 g, 25.0 mmol) in toluene (80 mL) was refluxed for 16 h using a Dean–Stark trap. Subsequently, the mixture was neutralized by dropwise addition of sat. aq $NaHCO_3$ (200 mL). Then the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and all volatile materials were removed in vacuo. The residue was submitted to fractional distillation using a 15-cm Vigreux column to yield **4c** (82.6 g, 96%) as colorless liquid; bp 210 °C/0.14 mbar.

IR (ATR): 2955 (m), 2925 (vs), 2856 (s), 1736 (vs), 1466 (m), 1352 (m), 1313 (m), 1157 (vs), 877 (m) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.5 Hz, 6 H), 1.12–1.33 (m, 20 H), 1.56 (quint, *J* = 6.8 Hz, 4 H), 2.56 (s, 4 H), 4.02 (t, *J* = 6.8 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.5 (CH_2), 25.8 (CH_2), 28.5 (CH_2), 29.1 (3 CH_2), 31.7 (CH_2), 64.7 (OCH_2), 172.2 (C).

MS (EI, 70 eV): *m*/*z* (%) = 343 (1) [M + H^+], 231 (21), 213 (6), 119 (26), 101 (100).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{20}H_{38}O_4$: 342.2770; found: 342.2769.

Diethyl *cis*-2,5-Dioxo-1,4-bis(3-oxobutyl)cyclohexane-1,4-dicarboxylate (5b)

A mixture of $FeCl_3 \cdot 6\ H_2O$ (158 mg, 0.585 mmol), **2b** (1.50 g, 5.85 mmol), and MVK (**3**) (4.10 g, 58.5 mmol) in CH_2Cl_2 (5 mL) was stirred at 60 °C for 2 d in a tightly closed reaction vial. The mixture was filtered through silica gel, the residue was washed with MTBE (50 mL), and the solvent was removed to give the crude product (2.16 g, 93%) as a reddish solid, as a mixture of two diastereomers (*cis*/*trans* 4:1). Recrystallization of the crude product (PE–EtOAc, 60 mL, 1:2) furnished the pure *cis*-diastereomer (single set of signals in the NMR spectra) of **5b** (1.22 g, 53%) as a colorless solid; mp 108 °C. Spectroscopic data are in accord with the literature.[15]

Anal. Calcd for $C_{20}H_{28}O_8$ (396.44): C, 60.59; H,7.12. Found: C, 60.23; H, 7.14.

Dioctyl *cis*-2,5-Dioxo-1,4-bis(3-oxobutyl)cyclohexane-1,4-dicarboxylate (5c); Typical Procedure

A mixture of $FeCl_3 \cdot 6\ H_2O$ (319 mg, 1.18 mmol), **2c** (5.00 g, 11.8 mmol), and MVK (**3**) (8.27 g, 9.82 mL, 118 mmol) in CH_2Cl_2 (15 mL) was stirred at 60 °C for 2 d in a tightly closed reaction vial. After removal of the solvent, the residue was chromatographed (silica gel, PE–EtOAc, 2:1, R_f = 0.20) to give the crude product (4.82 g, only one signal set in NMR spectra). Recrystallization (PE–EtOAc, 30 mL, 1:1) furnished a colorless solid (2.88 g, 43%) consisting exclusively of the *cis*-diastereomer of **5c** (single signal set in the NMR spectra); mp 77 °C.

IR (ATR): 2954 (m), 2924 (s), 2854 (s), 1706 (vs), 1464 (m), 1370 (s), 1263 (s), 1187 (vs), 1108 (s), 1017 (s), 954 (s), 724 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6 H), 1.11–1.18 (m, 20 H), 1.62 (quint, *J* = 6.5 Hz, 4 H), 2.00–2.07 (m, 2 H), 2.13 (s, 6 H), 2.20–2.27 (m, 2 H), 2.39–2.52 (m, 4 H), 2.63 (d, *J* = 15.8 Hz, 2 H), 3.23 (d, *J* = 15.7 Hz, 2 H), 4.10 (t, *J* = 6.6 Hz, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 25.7 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 29.1 (2 CH_2), 29.9 (CH_3), 31.8 (CH_2), 38.3 (CH_2), 45.1 (CH_2), 59.7 (C), 66.6 (OCH_2), 169.6 (C), 201.3 (C), 206.6 (C).

MS (EI, 70 eV): *m*/*z* (%) = 564 (4) $[M^+]$, 494 (8), 434 (8), 424 (10), 406 (100), 388 (6), 337 (23), 322 (23), 294 (50), 276 (77), 251 (15), 152 (13), 125 (18).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{32}H_{52}O_8$: 564.3662; found: 564.3662.

Anal. Calcd for $C_{32}H_{52}O_8$ (564.76): C, 68.06; H, 9.28. Found: C, 68.46; H, 9.15.

Dibenzyl *cis*-2,5-Dioxo-1,5-bis(3-oxobutyl)cyclohexane-1,4-dicarboxylate (5d)

Following the typical procedure for **5c** using $FeCl_3 \cdot 6\ H_2O$ (316 mg, 1.17 mmol), **2d** (3.00 g, 7.89 mmol), and MVK (**3**) (5.53 g, 78.9 mmol) in CH_2Cl_2 (10 mL), with purification by chromatography (silica gel, PE–EtOAc, 2:1, R_f = 0.30) gave the crude product (3.90 g, only one signal set in NMR spectra). Recrystallization (PE–EtOAc, 90 mL, 2:1) gave a colorless solid (3.24 g, 79%) consisting exclusively of the *cis*-diastereomer of **5d** (single set of signals in the NMR spectra); mp 113 °C.

IR (ATR): 2932 (m), 1755 (s), 1707 (vs), 1497 (m), 1454 (m), 1425 (m), 1370 (s), 1300 (m), 1260 (m), 1135 (m), 1097 (s), 1027 (m), 952 (m), 917 (m), 824 (m), 754 (s), 736 (s), 697 (vs) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.98–2.02 (m, 2 H), 2.03 (s, 6 H), 2.23–2.37 (m, 6 H), 2.65 (d, *J* = 15.8 Hz, 2 H), 3.20 (d, *J* = 15.8 Hz, 2 H), 5.04 (A part of an AB system, *J* = 12.3 Hz, 2 H), 5.05 (B part of an AB system, *J* = 12.3 Hz, 2 H), 7.27–7.36 (m, 10 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 28.6 (CH_2), 29.8 (CH_3), 38.0 (CH_2), 45.0 (CH_2), 59.5 (C), 67.9 (OCH_2), 128.3 (2 CH), 128.6 (CH), 128.6 (2 CH), 134.9 (C), 169.4 (C), 201.1 (C), 206.6 (C).

MS (EI, 70 eV): *m*/*z* (%) = 520 (1) $[M^+]$, 502 (3), 450 (3), 393 (2), 321 (4), 181 (3), 91 (100).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{30}H_{32}O_8$: 520.2097; found: 520.2098.

Diallyl *cis*-2,5-Dioxo-1,4-bis(3-oxobutyl)cyclohexane-1,4-dicarboxylate (5e)

Following the typical procedure for **5c** using $FeCl_3 \cdot 6\ H_2O$ (202 mg, 749 μmol), **2e** (2.10 g, 7.49 mmol), and MVK (**3**) (5.25 g, 74.9 mmol) in CH_2Cl_2 (8 mL), with purification by chromatography (silica gel, PE–EtOAc, 2:1, R_f = 0.20) gave a crude product (2.91 g, only one signal set in NMR spectra). Recrystallization (PE–EtOAc, 15 mL, 2:1) gave a colorless solid (1.90 g, 60%) consisting exclusively of the *cis*-diastereomer of **5e** (single signal set in the NMR spectra); mp 101–103 °C.

IR (ATR): 3083 (w), 2975 (m), 2938 (m), 1751 (s), 1708 (vs), 1446 (m), 1425 (s), 1413 (m), 1372 (s), 1356 (m), 1299 (s), 1265 (s), 1203 (vs), 1168 (vs), 1137 (s), 1102 (s), 1060 (m), 1014 (m), 982 (s), 945 (s), 922 (s), 878 (s), 813 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.06–2.10 (m, 2 H), 2.13 (s, 6 H), 2.20–2.29 (m, 2 H), 2.40–2.49 (m, 4 H), 2.68 (d, *J* = 15.9 Hz, 2 H), 3.23 (d, *J* = 15.8 Hz, 2 H), 4.60 (dt, *J* = 5.8, 1.4 Hz, 4 H), 5.27 (dq, *J* = 10.4, 1.2 Hz, 2 H), 5.33 (dq, *J* = 17.1, 1.4 Hz, 2 H), 5.87 (ddt, *J* = 17.1, 10.5, 5.8 Hz, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 28.6 (CH_2), 29.9 (CH_3), 38.2 (CH_2), 45.1 (CH_2), 59.6 (C), 66.8 (OCH_2), 119.4 (CH_2), 131.0 (CH), 169.2 (C), 201.2 (C), 206.7 (C).

MS (El, 70 eV): *m*/*z* (%) = 420 (4) $[M^+]$, 362 (16), 321 (19), 251 (22), 231 (25), 207 (17), 169 (9), 125 (20), 41 (100).

Anal. Calcd for $C_{22}H_{28}O_8$ (420.46): C, 62.85; H, 6.71. Found: C, 62.95; H, 6.76.

Diethyl 1,5-Dimethyl-4,8-dioxododecahydro-*s*-indacene-3a,7a-dicarboxylate (6b); Typical Procedure

A suspension of **1b** (140 mg, 388 μmol) and 5% Pd/C (50 mg) in *i*-PrOH (2 mL) was degassed and subsequently stirred at 80 °C for 16 h under 1 atm of H_2 (balloon). After filtration, the solvent was removed and the residue was purified by chromatography (silica gel, PE–EtOAc, 2:1, R_f = 0.39) yielding **6b** (121 mg, 86%) as a colorless solid; mp 40 °C.

IR (ATR): 2965 (s), 1708 (vs), 1447 (s), 1366 (s), 1303 (m), 1291 (m), 1258 (m), 1231 (s), 1206 (m), 1180 (m), 1100 (s), 937 (m), 892 (s), 838 (m), 721 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.6 Hz, 6 H), 1.23 (ddt, *J* = 12.2, 7.1, 11.7 Hz, 2 H, 2-CH_{ax}H), 1.30 (t, *J* = 7.1 Hz, 6 H, CH_3), 1.75 (ddt, *J* = 12.5, 2.8, 6.6 Hz, 2 H, 2-CHH_{eq}), 1.87 (ddd, *J* = 13.7, 6.9, 2.7 Hz, 2 H, 3-CHH_{eq}), 2.24 (ddquint, *J* = 10.5, 9.0, 6.5 Hz, 2 H, 1-CH_{eq}), 2.44 (ddd, *J* = 13.8, 11.6, 6.7 Hz, 2 H, 3-

CH_{ax}H), 3.59 (d, J = 8.9 Hz, 2 H, CH), 4.16–4.22 (m, 2 H, CH_2), 4.30–4.36 (m, 2 H, CH_2).

$^{13}C\{^1H\}$ NMR (62 MHz, $CDCl_3$): δ = 12.9 (CH_3), 18.5 (CH_3), 31.5 (CH_2), 31.8 (CH_2), 35.2 (CH), 60.4 (CH), 61.5 (CH_2), 67.3 (C), 171.0 (C), 201.3 (C).

MS (EI, 70 eV): *m*/*z* (%) = 364 (29) [M^+], 318 (100), 291 (25), 262 (12), 217 (39), 109 (44), 81 (53).

Anal. Calcd for $C_{20}H_{28}O_6$ (364.44): C, 65.92; H, 7.88. Found: C, 65.64; H, 7.74.

Dioctyl 1,5-Dimethyl-4,8-dioxododecahydro-*s*-indacene-3a,7a-dicarboxylate (6c)

Following the typical procedure for **6b** using **1c** (60 mg, 113 μmol) and 5% Pd/C (8 mg) in *i*-PrOH (2 mL) with purification by chromatography (silica gel, PE–EtOAc, 10:1, R_f = 0.41) gave **6c** (36 mg, 60%) as a colorless oil.

IR (ATR): 2955 (s), 2926 (s), 2857 (s), 1712 (vs), 1461 (s), 1376 (m), 1306 (m), 1230 (s), 1176 (m), 1135 (m), 946 (m), 896 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.7 Hz, 6 H), 1.11 (d, J = 6.5 Hz, 6 H), 1.12–1.39 (m, 22 H), 1.63 (quint, J = 6.8 Hz, 4 H), 1.74 (ddt, J = 12.4, 2.5, 6.3 Hz, 2 H), 1.87 (ddd, J = 13.7, 6.9, 2.5 Hz, 2 H), 2.24 (ddquint, J = 10.3, 8.8, 6.6 Hz, 2 H), 2.43 (ddd, J = 13.4, 11.8, 6.7 Hz, 2 H), 3.59 (d, J = 8.8 Hz, 2 H), 4.06–4.15 (m, 2 H), 4.18–4.27 (m, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.5 (CH_3), 22.6 (CH_2), 25.9 (CH_2), 28.4 (CH_2), 29.1 (2 CH_2), 31.7 (CH_2), 32.5 (CH_2), 32.8 (CH_2), 36.2 (CH), 61.4 (CH), 66.7 (OCH_2), 68.3 (C), 172.1 (C), 202.3 (C).

MS (EI, 70 eV): *m*/*z* (%) = 532 (12) [M^+], 421 (13), 402 (100), 374 (21), 374 (4), 217 (31).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{32}H_{52}O_6$: 532.3764; found: 532.3764.

1,5-Dimethyl-1,2,3,5,6,7-hexahydro-*s*-indacene-4,8-dione (8)

Under an inert atmosphere, a mixture of HCO_2H (72 mg, 1.6 mmol) and Et_3N (160 mg, 1.6 mmol) in abs THF (0.5 mL) was added at 23 °C to a stirred soln of $Pd(OAc)_2$ (2.9 mg, 13 μmol) and Ph_3P (5.1 mg, 20 μmol) in abs THF (0.5 mL). After vigorously stirring the mixture for 15 min, a soln of **1e** (100 mg, 260 μmol) in abs THF (1.0 mL) was added. The mixture was then stirred at 23 °C for 4 h, subsequently the solvent was removed in vacuo, and the residue chromatographed (silica gel, PE–EtOAc, 3:1, R_f = 0.49) to give the product **8** (45.0 mg, 80%) as a mixture of several tautomers and as a brown solid. NMR spectra show several signal sets.

IR (ATR): 3417 (s, br), 2952 (vs), 2863 (m), 1689 (vs), 1476 (vs), 1446 (vs), 1372 (m), 1326 (m), 1262 (vs), 1224 (s), 1144 (s), 1052 (s), 939 (s), 814 (s) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 216 (66) [M^+], 201 (100), 186 (5), 174 (12).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1150.

4,8-Diacetoxy-1,5-dimethyl-1,2,3,5,6,7-hexahydro-*s*-indacene (9)

A suspension of quinone **8** (40.0 mg, 185 μmol), abs NaOAc (61 mg, 0.74 mmol), and Zn dust (182 mg, 2.78 mmol) in AcCl (3 mL) was stirred at 60 °C for 2 h and then at 23 °C for 16 h. The mixture was poured into ice water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (5 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was chromatographed (silica gel, PE–EtOAc, 3:1, R_f = 0.53) to yield **9** as a mixture of two diastereomers (dr 2:1) and as a yellowish oil (20 mg, 35%). Spectroscopic data are in accord with the literature.[7]

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References

(1) *Modern Aldol Reactions*; Mahrwald, R., Ed.; Wiley-VCH: Weinheim, **2004**.
(2) Christoffers, J. In *Encyclopedia of Catalysis*, Vol. 5; Horvath, I., Ed.; Wiley: New York, **2003**, 99.
(3) (a) Rapson, W. S.; Robinson, R. *J. Chem. Soc.* **1935**, 1285. Reviews: (b) Gawley, R. E. *Synthesis* **1976**, 777. (c) Jung, M. E. *Tetrahedron* **1976**, *32*, 3.
(4) Recent examples: (a) Kraft, P.; Weymuth, C.; Nussbaumer, C. *Eur. J. Org. Chem.* **2006**, 1403. (b) Röttger, S.; Waldmann, H. *Eur. J. Org. Chem.* **2006**, 2093. (c) Payette, J. N.; Honda, T.; Yoshizawa, H.; Favaloro, F. G.; Gribble, G. W. *J. Org. Chem.* **2006**, *71*, 416. (d) Gan, Y.; Spencer, T. A. *J. Org. Chem.* **2006**, *71*, 5870.
(5) (a) Kreidler, B.; Baro, A.; Christoffers, J. *Eur. J. Org. Chem.* **2005**, 5339. (b) Kreidler, B.; Baro, A.; Frey, W.; Christoffers, J. *Chem. Eur. J.* **2005**, *11*, 2660. (c) Kreidler, B.; Baro, A.; Christoffers, J. *Synlett* **2005**, 465. Review: (d) Christoffers, J. *Chem. Eur. J.* **2003**, *9*, 4862.
(6) (a) Christoffers, J. *Synlett* **2006**, 318. (b) Christoffers, J.; Scharl, H.; Frey, W.; Baro, A. *Eur. J. Org. Chem.* **2004**, 2701. (c) Christoffers, J.; Scharl, H.; Frey, W.; Baro, A. *Org. Lett.* **2004**, *6*, 1171. (d) Christoffers, J.; Scharl, H. *Eur. J. Org. Chem.* **2002**, 1505.
(7) Christoffers, J.; Zhang, Y.; Frey, W.; Fischer, P. *Synlett* **2006**, 624.
(8) Buchanan, G. L.; Kennedy, W. B.; Lawson, A. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 32.
(9) (a) García Cuesta, I.; Coriani, S.; Lazzeretti, P.; Sánchez de Merás, A. M. J. *ChemPhysChem* **2006**, *7*, 240. (b) Güell, M.; Matito, E.; Luis, J. M.; Poater, J.; Sola, M. *J. Phys. Chem. A* **2006**, *110*, 11569.
(10) (a) Dahrouch, M.; Burgos, F.; Castel, A.; Chavez, I.; Gornitzka, H.; Manriquez, J. M.; Riviere, P.; Riviere-Baudet, M.; Alvarez, J.; Onyszchuk, M. *Appl. Organomet. Chem.* **2007**, *21*, 31. (b) Lian, J.-J.; Lin, C.-C.; Chang, H.-K.; Chen, P.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 9661. (c) Dahrouch, M. R.; Jara, P.; Mendez, L.; Portilla, Y.; Abril, D.; Alfonso, G.; Chavez, I.; Manriquez, J. M. *Organometallics* **2001**, *20*, 5591. (d) Hafner, K.; Stowasser, B.; Krimmer, H.-P.; Fischer, S.; Böhm, M. C.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 630; *Angew. Chem.* **1986**, *98*, 646. (e) Birladeanu, L.; Chamot, E.; Fristad, W. E.; Paquette, L. A.; Winstein, S. *J. Org. Chem.* **1977**, *42*, 3260. (f) LeGoff, E.; LaCount, R. B. *Tetrahedron Lett.* **1964**, *5*, 1161.
(11) (a) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691. (b) Woodward, R. B.; Hoye, T. R. *J. Am. Chem. Soc.* **1977**, *99*, 8007.
(12) (a) Esponda, E.; Adams, C.; Burgos, F.; Chavez, I.; Manriquez, J. M.; Delpech, F.; Castel, A.; Gornitzka, H.; Riviere-Baudet, M.; Riviere, P. *J. Organomet. Chem.* **2006**, *691*, 3011. (b) Roussel, P.; Cary, D. R.; Barlow, S.; Green, J. C.; Varret, F.; O'Hare, D. *Organometallics* **2000**, *19*, 1071. (c) Bell, W. L.; Curtis, C. J.; Eigenbrot, C. W.; Pierpont, C. P.; Robbins, J. L.; Smart, J. C. *Organometallics* **1987**, *6*, 266.

(13) (a) Chen, H. Z.; Jin, Y. D.; Xu, R. S.; Peng, B. X.; Desseyn, H.; Janssens, J.; Heremans, P.; Borghs, G.; Geise, H. J. *Synth. Met.* **2003**, *139*, 529. (b) Halterman, R. L.; Jan, S.-T.; Abdulwali, A. H.; Standlee, D. J. *Tetrahedron* **1997**, *53*, 11277.
(14) (a) Bauer, M.; Kauf, T.; Christoffers, J.; Bertagnolli, H. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2664. (b) Pelzer, S.; Kauf, T.; van Wüllen, C.; Christoffers, J. *J. Organomet. Chem.* **2003**, *684*, 308. Review: (c) Christoffers, J. *Synlett* **2001**, 723.
(15) Christoffers, J.; Oertling, H.; Önal, N. *J. Prakt. Chem.* **2000**, *342*, 546.
(16) Christoffers, J.; Schuster, K. *Chirality* **2003**, *15*, 777.
(17) Christoffers, J.; Mann, A. *Eur. J. Org. Chem.* **2000**, 1977.
(18) Tsuji, J.; Nisar, M.; Shimizu, I. *J. Org. Chem.* **1985**, *50*, 3416.
(19) Liebermann, H. *Justus Liebigs Ann. Chem.* **1914**, *404*, 272.
(20) Moore, J. A. *Org. Prep. Proced. Int.* **1972**, *4*, 31.
(21) (a) Kan, R. O. *J. Am. Chem. Soc.* **1964**, *86*, 5180. (b) Bischoff, C. A.; von Hedenström, A. *Chem. Ber.* **1902**, *35*, 4073.
(22) Sinnreich, J.; Batzer, H. *Helv. Chim. Acta* **1979**, *62*, 1682.
(23) Akutsu, M. JP 61011290, **1986**; *Chem. Abstr.* **1986**, *105*, 33055.
(24) Takahashi, K.; Shibagaki, M.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2353.