Stereoselective Syntheses of Spirane Bridged Semi-titanocenes

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Abstract: The synthesis of bidentate cyclopentadienyl-alkoxide ligands and their complexation to titanium are described. The focus has been on methodology for stereoselective synthesis of *ansa* half-sandwich titanocenes with rigid C_2- and C_3-bridges which are embedded in a spirane scaffold. Intermediate reactions involve tandem acylation-alkylation in the conversion of a carbonyl carbon into a quaternary carbon and rhodium(I)-effected spiroannulations. Titanocene formation involved reaction between the dilithiated ligand and titanium(III) chloride, and subsequent oxidation of the trivalent titanium with lead(II) chloride whereby the semi-metallocene was formed.

Key words: spirane scaffold, *ansa* semi-titanocenes, C_2- and C_3-spirane bridges, geminal acylation-allylation, rhodium(I)-catalyzed spiroannulation

A large number of ligands have been developed in the search for specific catalysts for asymmetric synthesis and alkene polymerization.[1,2] In this connection, the cyclopentadienyl group has assumed a dominant role as a six-electron ligand for metallocene formation. In metallocenes of group IV metals, the bent bis(cyclopentadienyl)ligand system causes substantial steric blocking of the metal-centered reaction site. Hence enhancement of reactivity is observed when the two ligand rings are tied back, and the ligand flexibility is restricted by a common backbone as in Brintzinger-type ansa-metallocene complexes. A common backbone will also reduce the tendency for irreversible dissociation of a ligand in a metal complex and thereby affect reactivity and stereoselectivity. Small-ring spiranes provide a potentially useful scaffold for attachment of configurationally highly oriented coordinating functions for metal complexations.[3] The two rings in spirane are interconnected through a common ring atom and have an orthogonal relationship. Functionalities in the same relative positions in the two rings will have a pseudo-orthogonal relationship. Replacement of one of the cyclopentadienyl moieties in a bridged bis(cyclopentadienyl) ligand with a two-electron ligand may deshield the reactive metal center and increase the catalyst activity. Ansa-amido-ligated half-sandwich metallocenes show high productivity and have the ability to produce unique architecture in polymers with desirable properties because of the more open nature at the active site on the metal.[4,5] Bridged alkoxy-half-sandwich complexes, however, have received little attention.[6] We wanted to establish a synthetic route for the preparation of rigidly bridged bidentate cyclopentadienyl-alkoxide complexes of titanium. The synthetic targets were half-sandwich metallocenes as shown in Figure 1. The bidentate ligands were to have an annulated η^5-indenyl moiety with a pendant oxido-κ*O*-alkyl unit. Metal complexation requires a *cis*-relationship between the pendant oxidoalkyl and the cyclopentadienyl functionalities. The latter is part of a tetrahydrofluorene system where the C1 carbon will also become the spiro carbon in the final ligand scaffold.

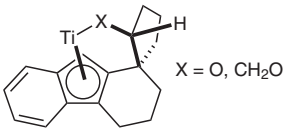

Figure 1

The starting material for spiroannulation was tetrahydrofluoren-1-one **3**.[7] We have modified the literature procedure so that the fluorene **3** has become readily available. The starting material was indene which, under basic conditions, was alkylated in the 3-position with 1-iodobutanenitrile to furnish 4-(1*H*-inden-3-yl)butanenitrile (**2**). Subsequent cyclization was effected by polyphosphoric acid treatment, which yielded the cyclic ketone **3** in 74% overall yield (Scheme 1). The procedure is well suited for large-scale synthesis, and has repeatedly performed well with 100–200 g preparations.

For the spiroannulation, the initial operation was to convert the fluorene C1 ketone into a spiro-carbon by way of Martin's efficient tandem acylation-alkylation,[8] and subsequent rhodium(I)-catalyzed hydroacylation.[9,10] The Martin methodology seemed very attractive, but appears to have enjoyed limited applications.[11] The co-solvent originally used in the tandem acylation-alkylation was the carcinogenic hexamethyphosphoramide. We recommend the use of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one as an equally useful co-solvent for this reaction. The target molecule was the 1-allyl-1-formyl derivative **7** (Scheme 1). The initial reaction of ketone **3** with lithiated diethyl (benzylideneamino)methylphosphonate furnished an 2-azadiene **4**. The diethyl (benzylideneamino)methylphosphonate reagent was prepared as described.[12] Treatment with one molar equivalent of butyllithium furnished a lithiated enamine adduct **5** that subsequently was C-alkylated with allyl bromide. Hydrolysis showed that the 9-allyl-1-formyl derivative **6** had been formed in preference to the *gem*-disubstituted target

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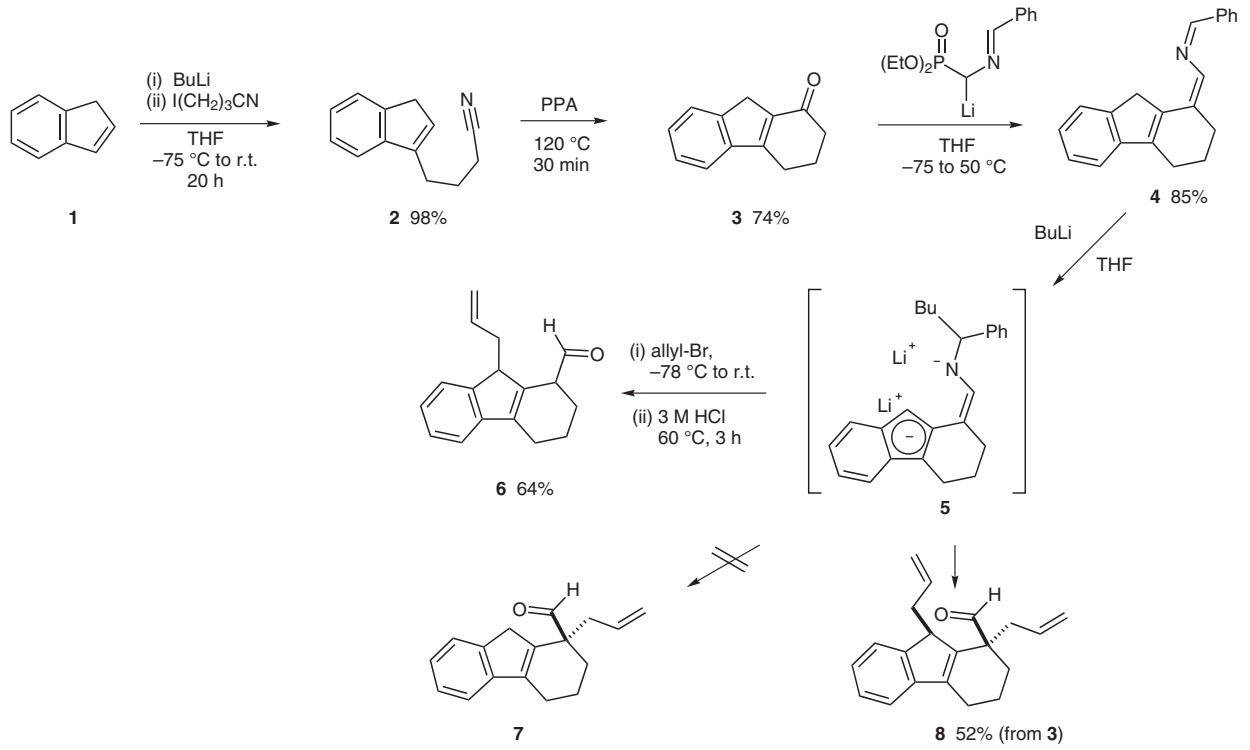
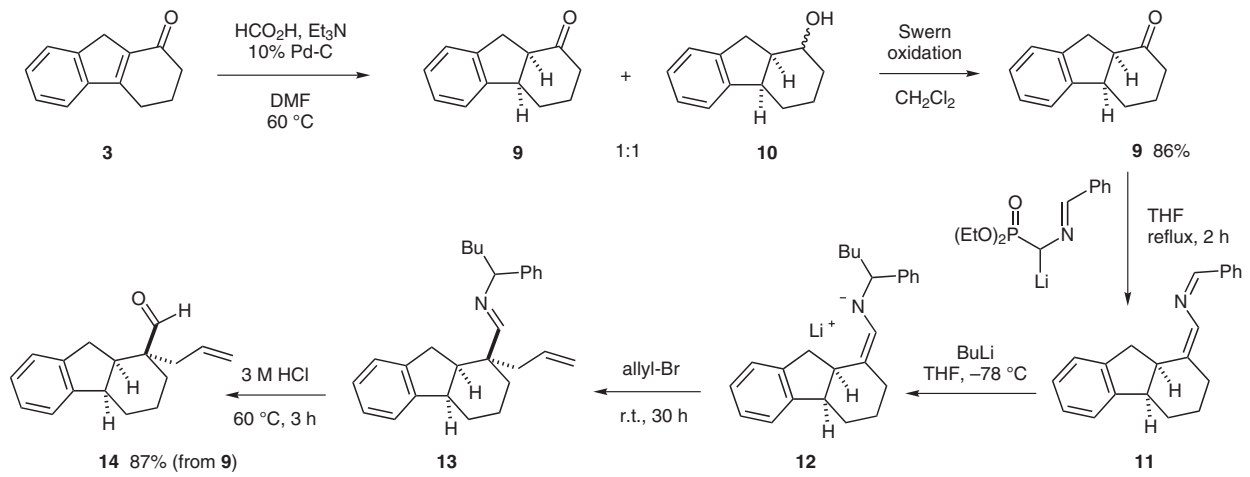


Scheme 1

7. With excess butyllithium, the final product was the diallylated derivative **8**. Presumably the initial metalation in substrate **4** is at the indenyl carbon with subsequent C1 alkylation. With excess butyllithium, an adduct-like structure **5** is an intermediate in the reaction towards diallylation and structure **8**. In further work, the acidity of the indenyl proton was to be reduced, which was effected by saturation of the 4a,9a-double bond. Once the desired constructions had been completed, the double bond was to be reintroduced later in the reaction sequence.

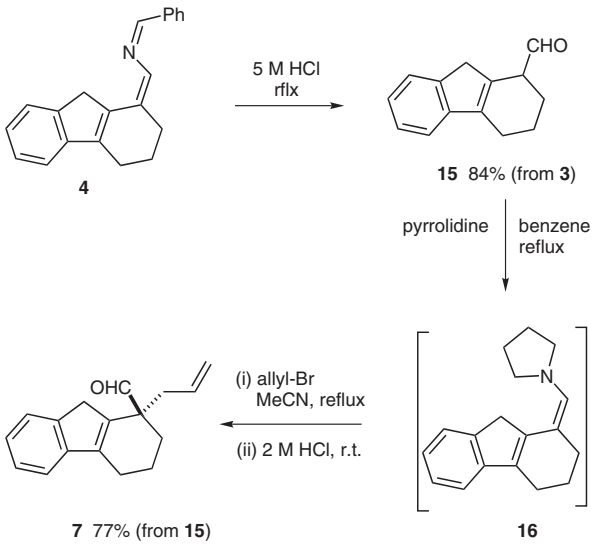
Diastereoselective saturation of the 4a,9a-double bond with ammonium formate over 10% palladium on charcoal provided compound **9** with a *cis*-ring junction (Scheme 2). The actual product in the reaction was a mixture of the desired ketone **9** and its reduction product, the alcohol **10**. Oxidation of the crude product mixture under Swern conditions provided the ketone **9** in an overall yield of 86%. One-pot acylation-alkylation of the ketone **9** furnished the enal **14**, after hydrolysis of the imine **13**, in high overall yield (87%) under excellent stereocontrol (de >95%) (Scheme 2). The stereochemistry of the product **14** indicates that the *cis*-fused ring system is an effective shield for the intermediate lithiated enamine **12** towards the incoming electrophile.

As an alternative to the reduction-reoxidation route hitherto described, we subsequently constructed a less elaborate synthetic pathway (Scheme 3). The carbaldehyde **15** became available in 84% overall yield from fluorenone **3**



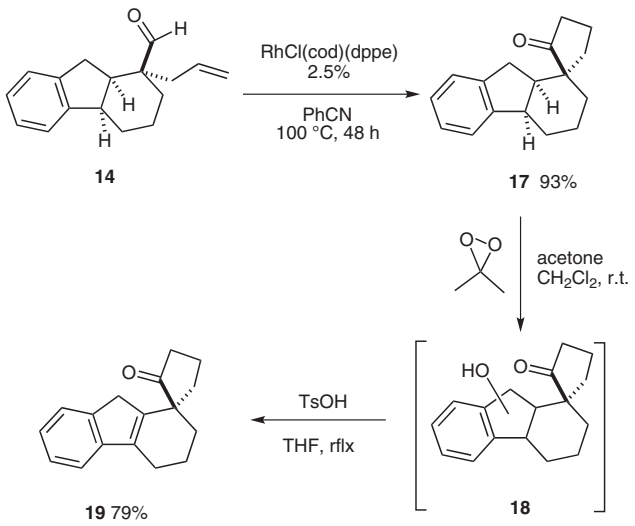
Scheme 2

using the Martin conditions and acid cleavage of the intermediate azadiene **4**. As the enamine **16** of pyrrolidine, the fluorene was regioselectively allylated in the 1-position and the alkylated product subsequently hydrolyzed to the enal **7** in good yield.



Scheme 3

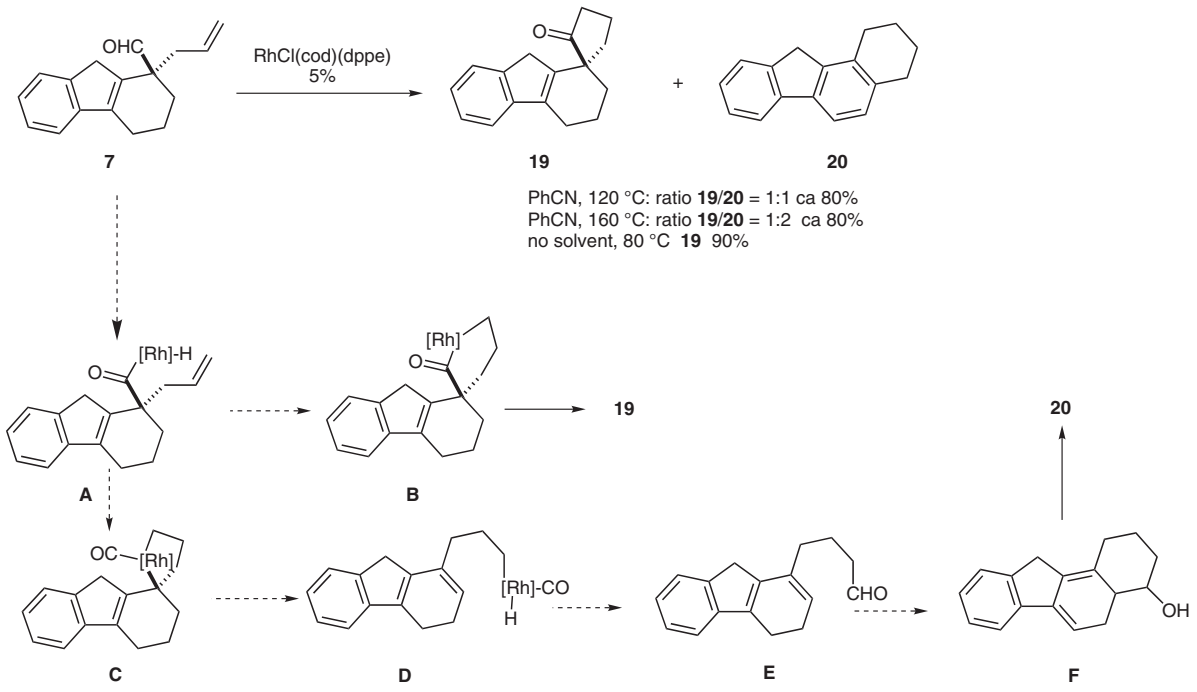
Cyclopentanones can be prepared from pent-4-enals by intramolecular hydroacylation catalyzed by rhodium(I)–diphosphine complexes. Chloro(η^4-cycloocta-1,5-diene)[1,2-bis(diphenylphosphino)ethane]rhodium(I) was an excellent catalyst system,[9] which we previously have applied to spirane annulations,[10] and this catalyst provided the spiroketone **17** in 93% yield (Scheme 4).



Scheme 4

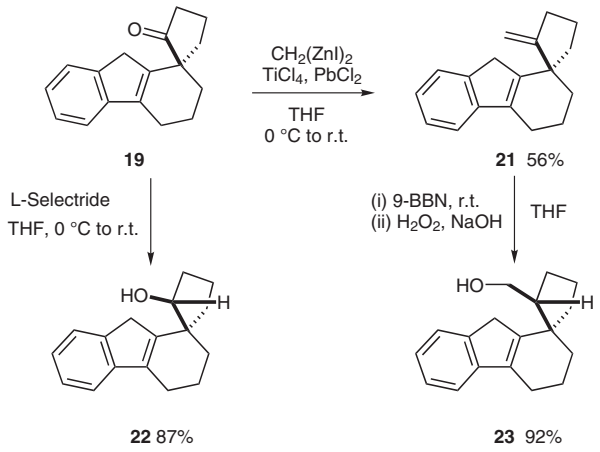
For the 4a,9a-dehydrogenation in the spiroketone **17**, a series of oxidation conditions were investigated and dimethyldioxirane,[13] although not a very effective reagent, was by far the best reagent (Scheme 4). The reaction was run in a mixture of acetone and dichloromethane. The product was a stereochemical mixture of alcohols **18**, which was dehydrated by 4-toluenesulfonic acid catalysis and heating in tetrahydrofuran and in this process was isomerized to the indene **19** in 79% yield.

The rhodium(I)-catalyzed hydroformylation reaction of substrate **7** resulted in formation of an anomalous product **20** in competition with the desired spiroketone **19** (Scheme 5); reactions were run in benzonitrile. The relative formation of the anomalous product **20** was favored



Scheme 5

by an increase in temperature. In the absence of a solvent, however, only the spiroketone **19** was obtained in high yield (90%). It was clear that the anomalous product **20** did not originate from ketone **19** since the latter was stable when subjected to the conditions of the reaction. The reaction is initiated by rhodium insertion into the formyl group with formation of a common intermediate (**A**) and the reaction presumably proceeds through a species **B** to the ketone **19**. An alternatively pathway may involve formation of the rhodium(III) species **C** followed by rapid β-hydride migration to give **D** and reductive elimination to the carbaldehyde **E**, which serves as a substrate for cyclization. Water elimination from the alcohol **F** and a cationic rearrangement lead to the aromatic structure **20**.



Scheme 6

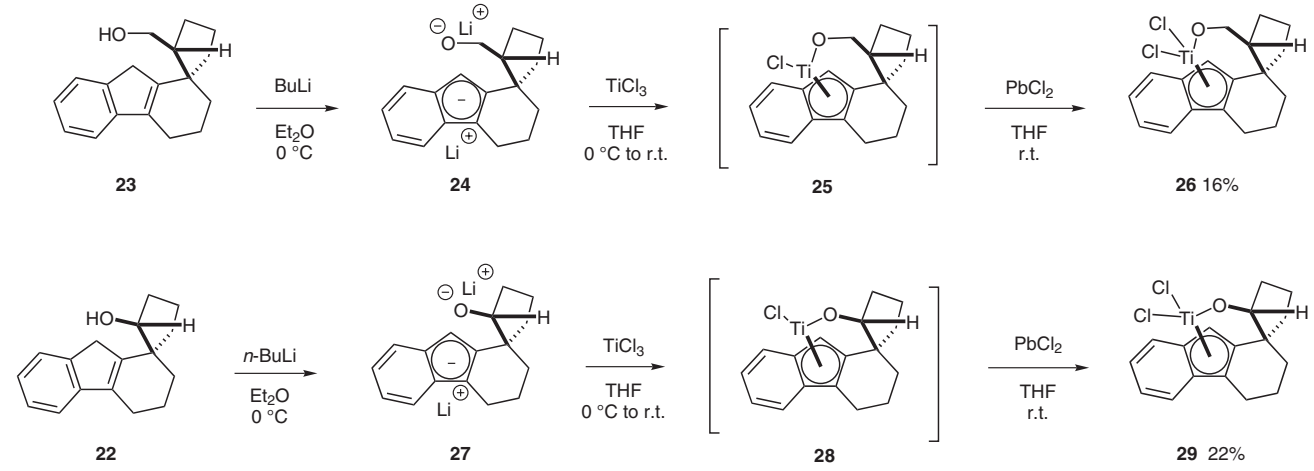
Attempts to methylenate the ketone **19** under Wittig conditions were thwarted because of the acidic indene proton. As an alternative, we turned to titanium(IV)-promoted methylenation with bis(iodozincio)methane.[14,15] The procedure successfully furnished the methylenated product **21** in 56% yield (Scheme 6). With 9-borabicyclo[3.3.1]nonane, selective addition occurred at the less sterically shielded face of the spirane, reaction of the adduct with hydrogen peroxide under alkaline conditions yielded 92% of the proligand **23**.

The second proligand **22** would provide a C_2-bridged semi-sandwich metallocene **29** in Scheme 7. Lithium aluminum hydride reduction of the ketone **19** in Scheme 6 provided the desired alcohol **22** as well as its epimeric alcohol in almost equimolar amounts. A modest selectivity was observed with 9-borabicyclo[3.3.1]nonane (de 34%) and Superhydride (de 54%) in tetrahydrofuran at reduced temperature. On the other hand, excellent stereocontrol (de >95%) was achieved with L-Selectride, and the proligand **22** was isolated in 87%.

For the metallocene formation, the proligands **22** and **23** were dilithiated by treatment with two equivalents of butyllithium in diethyl ether at 0 °C (Scheme 7). The respective dilithiated species **24** and **27** were precipitated from the diethyl ether solution. Attempts to produce the semi-metallocenes **26** and **29** by reaction between titanium(IV) chloride and the lithium salts **24** and **27** following standard literature procedures failed. However, the corresponding titanium(III) complexes **25** and **28** could be generated from the dianionic salts in reactions with titanium(III) chloride. No attempts were made to isolate the highly reactive titanium(III) complexes. Instead, the titanium(III) complexes were converted in situ into the more stabile titanium(IV) complexes **26** and **29**. Lead(II) chloride was a good oxidation agent for this purpose.[16] The yields of pure semi-metallocenes were low, however, due to the imposed limitations presented by the necessity of inert conditions during workup.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, respectively at 200 or 300 MHz and 50 or 75 MHz with a Bruker DPX 200 or 300 instrument; residual $CHCl_3$ (δ =7.24) and $CDCl_3$ (δ = 77) were used as internal reference. MS spectra were recorded at 70 eV ionizing potential. IR spectra were measured on a Nicolet Magma 550 spectrophotometer using ATR.

THF was dried by distillation from Na/benzophenone under N_2. CH_2Cl_2 was dried by distillation from CaH_2. Anhyd $ZnCl_2$ was heated at 200 °C under 0.013 mbar for 20 h shortly before use. Reactions



Scheme 7

requiring dry and/or O_2-free conditions were run under a slight positive pressure of argon gas.

4-(1*H*-Inden-3-yl)butanenitrile (2) and 2,3,4,9-Tetrahydro-1*H*-fluoren-1-one (3)

A 1.6 M soln of BuLi in hexane (219 mL, 0.35 mol) was added over 10 min to a soln of freshly distilled indene (40.7 g, 0.35 mol) in anhyd THF (500 mL) at –75 °C under a slight positive pressure of argon gas. The cooling bath was removed, the mixture left to reach r.t. overnight, cooled to –75 °C and 4-iodobutanenitrile (68.5 g, 0.35 mol) in THF (100 mL) added dropwise. When the addition was complete, the mixture was stirred at this temperature for 1 h, the cooling bath was removed, and the mixture was stirred at r.t. for 20 h. It was then added to a mixture of sat. brine (300 mL) and sat. NH_4Cl (150 mL) and the two phases were separated, the aqueous phase was extracted with Et_2O (3 × 100 mL). The combined Et_2O extracts were dried ($MgSO_4$) and the solvents distilled off. The residual tanned colored oily material was 4-(1*H*-inden-3-yl)butanenitrile (**2**); yield: 63 g (98%). ^1H and ^{13}C NMR spectra of the crude product were in accordance with the literature.[17]

The product **2** (63 g, 0.34 mol) and PPA (1 kg) were heated together at 120 °C for 30 min with manual stirring. The viscous mixture was added with stirring to H_2O (4 L) and the mixture heated under reflux for 30 min. The mixture was cooled to r.t. and the solid material was extracted into CH_2Cl_2 (400 mL), The extracts were shaken with sat. $NaHCO_3$ (100 mL), dried ($MgSO_4$), and evaporated to dryness. The residual material was recrystallized (hexane) to give a pale yellow powder; yield: 47.7 g (74%). ^1H and ^{13}C NMR spectra were in accordance with the literature.[7]

N-Benzylidene[1,2,3,4-tetrahydro-9*H*-fluoren-1-ylidene)methyl]amine (4)

Diethyl (benzylideneamino)methylphosphonate (3.06 g, 12 mmol) was added over 10 min to a soln of 1.6 M BuLi in hexane (7.5 mL, 12 mmol) in anhyd THF (40 mL) under argon at –75 °C. The mixture was stirred at this temperature for 1 h before **3** (1.84 g, 10 mmol) was added in one portion. The mixture was kept at 50 °C overnight, hexane (50 mL) was added, and the soln was washed with sat. NH_4Cl (30 mL), dried ($MgSO_4$), and the filtrate evaporated to dryness. Flash chromatography (silica gel 60, EtOAc–hexane, 1:6) furnished **4** as a yellow oil; yield: 2.44 g (85%).

^1H NMR (200 MHz, $CDCl_3$): δ = 2.03 (t, *J* = 5.7 Hz, 2 H, H4), 2.6–2.8 (m, 2 H, H3), 3.07 (t, *J* = 5.3 Hz, 2 H, H2), 3.60 (s, 2 H, H9), 7.12 (s, 1 H, =CHN), 7.2–7.4 (m, 7 H, H-Ar), 7.5–7.6 (m, 2 H, H-Ar), 8.24 (s, 1 H, CH=N).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.8 (C3), 23.1 (C4), 25.6 (C2), 36.1 (C9), 119.4 (=CHN), 123.8 (CH-Ar), 125.7 (CH-Ar), 126.2 (CH-Ar), 128.5 (CH-Ar), 129.0 (CH-Ar), 130.6 (CH-Ar), 135.0 (CH-Ar), 135.3 (C-Ar), 137.2 (C9a), 139.2 (C-Ar), 142.8 (C-Ar), 143.0 (C4a), 157.4 (CH=N).

MS (EI, 70 eV): *m*/*z* (%) = 285 (13) $[M]^+$, 258 (19), 229 (100), 181 (78), 167 (43).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{21}H_{19}N$: 285.1517: found: 285.1528.

9-Allyl-2,3,4,9-tetrahydro-1*H*-fluorene-1-carbaldehyde (6)

A 1.6 M soln of BuLi in hexanes (1.9 mL, 3.0 mmol) was added over 10 min to a soln of **4** (0.856 g, 3.00 mmol) in anhyd THF (10 mL) under argon at –75 °C and the mixture stirred at this temperature for 1 h. Allyl bromide (0.36 g, 3.0 mmol) in THF (2 mL) was added over 15 min to the cold mixture, which was allowed to reach r.t. and stirred for 28 h. 3 M HCl (15 mL) was added and the mixture was stirred vigorously under argon at 60 °C for 3 h. Sat. brine (10 mL) was added to the ice-cold mixture and the two phases separated. The aqueous soln was extracted with Et_2O (3 × 10 mL), the combined organic phases were washed with sat. $NaHCO_3$ (10 mL), dried ($MgSO_4$), and the soln concentrated at reduced pressure. The residual oil was subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:5) to give a mixture of diastereomers; yield: 0.46 g (64%).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.6–1.9 (m, 4 H, H2, H3), 2.2–2.8 (m, 5 H, H1, H4, C*H*$_2$CH=CH$_2$), 3.3–3.5 (m, 1 H, H9), 4.8–5.0 (m, 2 H, CH=C*H*$_2$), 5.1–5.3 (m, 1 H, C*H*=CH$_2$), 7.0–7.4 (m, 4 H, H5–H8), 9.66 (d, *J* = 1.7 Hz, 0.4 H, C*H*O, minor isomer), 9.70 (d, *J* = 1.8 Hz, 0.6 H, CHO major isomer).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9, 20.5, 22.0, 22.2, 24.1 (2 ×), 33.7, 34.8, 39.2, 41.1, 50.1, 51.3, 117.7, 118.0, 118.5, 119.6, 122.9 (2 ×), 125.2, 125.4, 126.6 (2 ×), 131.9, 132.8, 139.5, 139.7, 140.6

MS (EI, 70 eV): *m*/*z* (%) = 238 (41) $[M]^+$, 209 (79), 197 (100), 181 (18), 168 (39).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1353.

1-Allyl-2,3,4,9-tetrahydro-1*H*-fluorene-1-carbaldehyde (7)

A soln of **15** (23.0 g, 116 mmol) and pyrrolidine (12 g, 169 mmol) in benzene (100 mL) was refluxed with constant removal of H_2O with a Dean–Stark trap for 6 h under a slight positive pressure of argon gas. The soln was evaporated and the residual pyrrolidine enamine dissolved in MeCN (80 mL). Allyl bromide (28.0 g, 231 mmol) was added to the enamine soln and the mixture heated at gentle reflux under argon for 40 h. 2 M HCl (100 mL) was added to the cold mixture, which was stirred under argon at r.t. overnight. The mixture was extracted with hexane (3 × 100 mL) and the combined extracts were washed with H_2O (100 mL) and $NaHCO_3$ (100 mL), dried ($MgSO_4$), the filtrate evaporated, and the residual material subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:20) giving a yellow oil; yield: 21.1 g (77%).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.7–1.9 (m, 3 H, H2α, H3), 2.0–2.1 (m, 1 H, H2β), 2.4–2.6 (m, 4 H, H4, C*H*$_2$CH=CH$_2$), 3.0–3.4 (m, 2 H, H9), 5.0–5.1 (m, 2 H, CH=C*H*$_2$), 5.6–5.7 (m, 1 H, C*H*=CH$_2$), 7.2–7.4 (m, 4 H, H5–H8), 9.61 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (CH_2), 22.1 (CH_2), 28.4 (CH_2), 37.1 (*C*H$_2$CH=CH$_2$), 39.3 (C9), 52.1 (C1), 118.5 (CH=*C*H$_2$), 118.6 (CH-Ar), 123.6 (CH-Ar), 124.9 (CH-Ar), 126.3 (CH-Ar), 133.3 (*C*H=CH$_2$), 137.2, 141.7, 143.2, 144.8, 201.9 (CHO).

MS (EI, 70 eV): *m*/*z* (%) = 238 (11) $[M]^+$, 223 (50), 209 (100), 197 (39), 167 (40).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1368.

(1*R**,9*S**)-1,9-Diallyl-2,3,4,9-tetrahydro-1*H*-fluorene-1-carbaldehyde (8)

Diethyl (benzylideneamino)methylphosphonate (0.61 g, 2.4 mmol) was added over 5 min to a soln of 1.6 M BuLi in hexane (1.5 mL, 2.4 mmol) in anhyd THF (10 mL) under argon at –78 °C. The mixture was stirred at this temperature for 1 h before **3** (0.37 g, 2.0 mmol) was added in one portion. The mixture was heated under reflux for 2 h, cooled to –78 °C and 1.6 M BuLi in hexane (2.5 mL, 4.0 mmol) added over 10 min. The mixture was stirred at –78 °C for 2 h and then allyl bromide (1.2 g, 10 mmol) was added over 10 min and the mixture stirred at r.t. for 10 h. 3 M HCl (10 mL) was added and the mixture stirred vigorously under argon at r.t. for 10 h. Sat. aq brine (5 mL) was added and the two phases of the cold mixture were separated, the aqueous phase was extracted with Et_2O (3 × 10 mL); the combined organic solns were washed with aq sat. $NaHCO_3$ (10 mL), dried ($MgSO_4$), and concentrated under vacuum. The residual oil was subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:4) to give a yellow oil; yield: 0.29 g (52%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.5–1.9 (m, 4 H, H3, H4), 2.1–2.8 (m, 6 H, H2, C*H*$_2$CH=CH$_2$), 3.4–3.5 (m, 1 H, H9) 4.8–5.1 (m, 4 H, CH=C*H*$_2$), 5.2–5.4 (m, 1 H, 9-allyl-C*H*=CH$_2$), 5.5–5.7 (m, 1 H, 1-allyl-C*H*=CH$_2$), 7.1–7.4 (m, 4 H, H5–H8), 9.64 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7 (C3), 22.2 (C2), 30.1 (C4), 34.0 (9-allyl-CH_2), 38.9 (1-allyl-CH_2), 48.2 (C9), 51.4 (C1), 117.3 (CH=*C*H$_2$), 118.4 (CH=*C*H$_2$), 118.4 (CH-Ar), 123.1 (CH-Ar), 125.0 (CH-Ar), 126.5 (CH-Ar), 133.7 (9-allyl-*C*H=CH$_2$), 139.4, 142.3, 143.5, 146.6, 202.7 (CHO).

MS (EI, 70 eV): *m*/*z* (%) = 278 (38) [M]$^+$, 249 (50), 237 (91), 208 (52), 179 (48), 165 (100).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{20}H_{22}O$: 278.1671; found: 278.1666.

(4a*R,9a*R**)-2,3,4,4a,9,9a-Hexahydro-1*H*-fluoren-1-one (9)**

Et_3N (21.0 g, 0.21 mol), HCO_2H (8.28 g, 0.18 mol), and 10% Pd/C (2.65 g, 2.5 mmol Pd) were added to a soln of **3** (18.4 g, 0.1 mol) in DMF (60 mL). The mixture was stirred at 60 °C for 1 h, filtered through a bed of Celite, and the filtrate poured into H_2O (500 mL). The cold mixture was extracted with Et_2O (4 × 150 mL) and the combined extracts were washed with H_2O (2 × 150 ml), dried ($MgSO_4$), and evaporated to dryness. The residual material was further dried under vacuum overnight to give 17.5 g of a 1:1 mixture **9/10**. The mixture was subjected to Swern oxidation using oxalyl chloride (6.35 g, 50 mmol) in anhyd CH_2Cl_2 (120 mL) at –60 °C under N_2 with addition of DMSO (7.81 g, 0.1 mol) in CH_2Cl_2 (30 mL) over 5 min. Stirring was continued for 10 min, the crude intermediate (~45 mmol alcohol) was transferred by a syringe into CH_2Cl_2 (40 mL). The cooling bath was removed after 15 min, the mixture left to stand for 5 min, cooled to –60 °C and Et_3N (25 g, 0.25 mol) added over 5 min, the cooling bath removed, and H_2O (150 mL) added. The mixture was stirred for 10 min and the two layers separated and the aqueous layer extracted with Et_2O (3 × 50 mL). The combined ether extracts were dried ($MgSO_4$), evaporated to dryness, and the residual material crystallized (MeOH, 2.5 mL/g) to give a solid product; yield: 12.8 g (69%). The mother liquor from the crystallization was evaporated to dryness and the residual material subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:10); yellow solid; combined yield: 16.0 g (86%); mp 82–83 °C.

IR (film): 3041 (m), 3032 (m), 2989 (w), 2905 (s), 2832 (m), 1733 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.6–1.9 (m, 4 H, H3, H4a, H4α), 2.0–2.1 (m, 1 H, H4β), 2.29 (t, *J* = 7.6 Hz, 2 H, H2), 2.85 (dd, *J* = 15.5, 8.1 Hz, 1 H, H9α), 3.0–3.1 (m, 1 H, H9a), 3.35 (dd, *J* = 15.5, 10.7 Hz, 1 H, H9β), 7.1–7.3 (m, 4 H, H5–H8).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (C3), 27.7 (C4), 33.6 (C9), 40.7 (C2), 47.2 (C4a), 52.89 (C9a), 123.2 (CH-Ar), 125.2 (CH-Ar), 127.0 (CH-Ar), 127.2 (CH-Ar), 142.9 (C-Ar), 145.1 (C-Ar), 213.1 (C1).

MS (EI, 70 eV): *m*/*z* (%) = 186 (100) [M]$^+$, 158 (49), 142 (23), 130 (78), 115 (51).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{13}H_{14}O$: 182.1045; found: 186.1036.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.52; H, 7.44.

(1*S*/*R*,4a*R,9a*R**)-2,3,4,4a,9,9a-Hexahydro-1*H*-fluoren-1-ol (10)**

The mixture of the ketone **9** from above and its alcohol epimers **10** (129 mg) was subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:10) for analytical purposes. Separation yielded 2,3,4,9-tetrahydro-1*H*-fluoren-1-one (61 mg) and an inseparable mixture of the alcohol epimers 2,3,4,4a,9,9a-hexahydro-1*H*-fluoren-1-ol (**10**) (51 mg).

IR (film): 3333 (s), 3040 (w), 2995 (w), 2904 (s), 2830 (s), 1420 (m) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.2–1.5 (m, 4 H), 1.6–1.9 (m, 7 H), 2.0–2.2 (m, 2 H), 2.33 (s, 2 H, OH), 2.7–3.1 (m, 6 H), 3.2–3.3 (m, 1 H, H9), 3.3–3.4 (m, 0.5 H, C*H*OH), 4.0–4.1 (m, 0.5 H, C*H*OH), 7.1–7.4 (m, 8 H, H-Ar).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.1, 23.2, 25.4, 29.6, 29.9, 29.9, 33.8, 35.2, 44.0, 44.9, 46.1, 48.8, 70.4 (C-OH), 70.8 (C-OH), 122.1 (CH-Ar), 122.9 (CH-Ar), 125.1 (CH-Ar), 125.9 (CH-Ar), 126.2 (CH-Ar), 141.7 (C-Ar), 143.2 (C-Ar), 145.5 (C-Ar), 148.6 (C-Ar);

MS (EI, 70 eV): *m*/*z* (%) = 188 (76) [M]$^+$, 170 (100), 155 (9), 145 (18), 142 (65), 129 (49), 116 (70).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{13}H_{16}O$: 188.1201; found: 188.1210.

(1*R,4a*R**,9a*R**)-1-Allyl-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene-1-carbaldehyde (14)**

Diethyl (benzylideneamino)methylphosphonate (9.79 g, 38.4 mmol) was added over 10 min to a soln of 1.6 M BuLi in hexane (24 mL, 38.4 mmol) in anhyd THF (160 mL) under argon at –78 °C. The mixture was stirred at this temperature for 1 h before **9** (6.49 g, 34.9 mmol) was added in one portion. The mixture was heated under reflux for 2 h, cooled to –78 °C and 1.6 M BuLi in hexane (43.7 mL, 70 mmol) was added over 10 min. The mixture was stirred at –78 °C for 1 h before allyl bromide (16.9 g, 140 mmol) was added over 15 min and the mixture stirred at r.t. for 30 h. 3 M HCl was added and the mixture stirred vigorously under argon at 60 °C for 3 h. The two phases of the cold mixture were separated and the aqueous phase was extracted with Et_2O (3 × 75 mL). The combined organic phases washed with aq sat. $NaHCO_3$, dried ($MgSO_4$), and concentrated under vacuum. The residual brown oil was subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:5) to give a yellow oil; yield: 7.30 g (87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.0–1.2 (m, 1 H, H4α), 1.5–2.0 (m, 5 H, H2, H3, H4β), 2.3–2.9 (m, 5 H, H9, H9a, C*H*$_2$CH=CH$_2$), 3.16 (dt, *J* = 6.0, 12.1 Hz, 1 H, H4a), 5.1–5.2 (m, 2 H, CH=C*H*$_2$), 5.6–5.8 (m, 1 H, C*H*=CH$_2$), 7.2–7.3 (m, 4 H, H5–H8), 9.63 (s, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (CH_2), 23.1 (CH_2), 29.5 (C4), 31.5 (C9), 37.8 ($CH_2CH=CH_2$), 41.8 (C4a), 44.7 (C9a), 50.5 (C1), 118.2 (CH=CH_2), 122.9 (CH-Ar), 124.9 (CH-Ar), 126.3 (CH-Ar), 126.35 (CH-Ar), 132.9 (*C*H=CH$_2$), 141.2 (C-Ar), 147.9 (C-Ar), 205.7 (CHO).

MS (EI, 70 eV): *m*/*z* (%) = 240 (40) [M]$^+$, 222 (42), 211 (17), 199 (22), 169 (56), 143 (95), 130 (100).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1525.

2,3,4,9-Tetrahydro-1*H*-fluorene-1-carbaldehyde (15)

Diethyl (benzylideneamino)methylphosphonate (30.6 g, 120 mmol) was added over 10 min to a soln of 1.6 M BuLi in hexane (75 mL, 120 mmol) in anhyd THF (400 mL) under argon at –78 °C. The mixture was stirred at this temperature for 1 h before **3** (18.4 g, 100 mmol) was added in one portion and the mixture was kept at 50 °C overnight. 5 M HCl (400 mL) was added and the mixture stirred vigorously under reflux for 3 h. The two phases of the ice-cold mixture were separated and the aqueous phase extracted with Et_2O (3 × 200 mL). To reduce oxidative reactions, the empty space over the soln in the separatory funnel was flushed and kept under argon gas. The combined organic phases were washed with aq sat. $NaHCO_3$ (200 mL), dried ($MgSO_4$), and the filtrate evaporated. The residual material was dried at 50 °C under vacuum overnight for removal of benzaldehyde and 1-chlorobutan-4-ol (generated from THF). Flash

chromatography (silica gel 60, EtOAc–hexane, 1:4) furnished a yellow oil; yield: 16.6 g (84%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.8–2.2 (m, 4 H, H2, H3), 2.3–2.6 (m, 3 H, H1, H4), 3.3–3.4 (m, 2 H, H9), 7.2–7.4 (m, 4 H, H5–H8), 9.71 (d, *J* = 1.9 Hz, 1 H, CHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CH_2), 22.0 (CH_2), 23.3 (CH_2), 39.2 (C9), 50.1 (C1), 118.5 (CH-Ar), 123.5 (CH-Ar), 125.0 (CH-Ar), 127.4 (CH-Ar), 134.7, 140.9, 143.4, 145.6, 202.1 (CHO).

MS (EI, 79 eV): *m*/*z* (%) = 198 (48) $[M]^+$, 180 (13), 169 (100), 155 (16), 143 (84).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1056.

(1*R**,4a′*R**,9a′*R**)-2′,3′,4′,4a′,9′,9a′-Hexahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-one (17)

$[Rh_2Cl_2(cod)_2]$ (0.408 g, 0.828 mmol) and dppe (0.659 g, 1.66 mmol) were added to a soln of **14** (7.95 g, 33.1 mmol) in PhCN (30 mL) and the mixture heated at 100 °C under argon for 48 h. The cold mixture was poured slowly into vigorously stirred hexane (200 mL) and filtered through a bed of Celite. The hexane was removed on a rotary evaporator, and the remaining PhCN distilled off at reduced pressure at 80 °C to give a yellow oil; yield: 7.39 g (93%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (qd, *J* = 13.1, 3.7 Hz, 1 H, H4′α), 1.08 (d, *J* = 13.5 Hz, 1 H, H5α), 1.23 (qt, *J* = 13.4, 3.1 Hz, 1 H, H3′α), 1.4–1.5 (m, 1 H, H3′β), 1.6–1.8 (m, 5 H, H2′, H4′β, H4α, H5β), 2.0–2.2 (m, 4 H, H9a′, H3, H4β), 2.29 (dd, *J* = 15.7, 7.5 Hz, 1 H, H9′α), 2.8–3.0 (m, 2 H, H4a′, H9′β), 6.9–7.1 (m, 4 H, H5′–H8′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3 (C2′), 20.8 (C3′), 28.4 (C5), 29.4 (C4′), 31.9 (C9′), 35.9 (C4), 37.2 (C3), 42.1 (C4a′), 43.4 (C9a′), 50.2 (C1), 122.6 (CH-Ar), 124.7 (CH-Ar), 125.8 (CH-Ar), 126.0 (CH-Ar), 141.7 (C-Ar), 148.2 (C-Ar), 221.5 (C=O).

MS (EI): *m*/*z* (%) = 240 (27) $[M]^+$, 222 (5), 212 (12), 156 (68), 141 (69), 128 (76), 115 (100).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1514.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.35; H, 8.27.

2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-one (19)

A 0.1 M soln of dimethyldioxirane in acetone (150 mL, 0.15 mmol) was added to a soln of **17** (5.50 g, 23 mmol) in CH_2Cl_2 (500 mL). The soln was stirred at r.t. in a light-protected round-bottom flask equipped with an air lock for 2 d. The solvents were removed at reduced pressure, the residual material dissolved in THF (100 mL), TsOH (0.8 g) was added and the mixture was heated under reflux for 6 h. THF was distilled off and Et_2O (100 mL) added and the ethereal soln was washed with aq sat. $NaHCO_3$ (3 × 30 mL), dried ($MgSO_4$), the solvent evaporated, and the residual material subjected to flash chromatography (silica gel 60, acetone–hexane, 1:5) to give a colorless oil; yield: 4.32 g (79%).

IR (film): 3035 (m), 3016 (m), 2992 (m), 2907 (s), 2863 (s), 1720 (s) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.6–1.7 (m, 3 H, CH_2), 1.8–1.9 (m, 4 H, CH_2), 2.0–2.1 (m, 1 H, CH_2), 2.2–2.3 (m, 1 H, CH_2), 2.3–2.4 (m, 3 H, CH_2), 3.01 (dt, *J* = 21.9, 2.8 Hz, 1 H, H9′α), 3.08 (dt, *J* = 21.8, 2.7 Hz, 1 H, H9′β), 7.0–7.3 (m, 4 H, H5′–H8′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (CH_2), 19.1 (CH_2), 22.0 (CH_2), 31.5 (CH_2), 36.5 (C9′), 36.9 (CH_2), 37.9 (C3), 51.8 (C1), 118.0 (CH-Ar), 123.3 (CH-Ar), 124.3 (CH-Ar), 126.0 (CH-Ar), 139.4 (C9a′), 140.3 (C4a′), 142.5 (C-Ar), 144.9 (C-Ar), 221.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 238 (35) $[M]^+$, 210 (21), 182 (100), 167 (38), 152 (24).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O$: 238.1358; found: 238.1367.

Rhodium(I)-Catalyzed Cyclizations; Coformation of 2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-one (19) and 2,3,4,11-Tetrahydro-1*H*-benzo[*a*]fluorene (20)

$[Rh_2Cl_2(cod)_2]$ (0.259 g, 0.525 mmol) and dppe (0.418 g, 1.05 mmol) were added to a soln of **7** (5.00 g, 21.0 mmol) in PhCN (5 mL) and the mixture heated at 120 °C under argon for 40 h. The cold mixture was poured into hexane (150 mL) and the mixture filtered through a plug of Celite. The filtrate was evaporated in vacuo and the residual oil subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:4).

2,3,4,11-Tetrahydro-1*H*-benzo[*a*]fluorene (20)

This was identified as the faster moving product and isolated as a yellow solid; yield: 1.65 g (36%); mp 127–129 °C.

H^1 NMR (200 MHz, $CDCl_3$): δ = 1.9–2.1 (m, 4 H, H2 H3), 2.8–3.0 (m, 4 H, H1 H4), (s, 2 H, H11), 7.2–7.5 (m, 4 H, H7–H10), 7.62 (d, *J* = 6.1 Hz, 1 H, H5), 7.83 (d, *J* = 6.1 Hz, 1 H, H6).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.8 (CH_2), 24.0 (CH_2), 27.4 (CH_2), 30.7 (CH_2), 35.8 (C11), 117.6 (CH-Ar), 120.0 (CH-Ar), 125.2 (CH-Ar), 126.9 (CH-Ar), 127.1 (C6), 128.5 (C5), 133.8 (C-Ar), 136.0 (C-Ar), 139.3 (C-Ar), 142.5 (C-Ar), 142.7 (C-Ar), 143.1 (C-Ar).

MS (EI, 70 eV): *m*/*z* (%) = 220 (100) $[M]^+$, 208 (11), 192 (39), 178 (25), 165 (30).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{16}$: 220.1252; found: 220.1253.

2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-one (19)

This was the slower moving product and was isolated as a yellow oil; yield: 1.95 g (39%). Spectroscopic data were in agreement with those for compound **19** as described above.

2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-one (19) by Chemoselective Formation

A soln of **7** (4.76 g, 20.0 mmol), $[Rh_2Cl_2(cod)_2]$ (0.246 g, 0.500 mmol), and dppe (0.398 g, 1.00 mmol) under argon was heated at 80 °C for 50 h. The cold mixture was added to cyclohexane (100 mL) with stirring, the mixture was filtered through a small bed of Celite, and the filtrate was evaporated. The residual oily material was subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:4); yield: 4.27 g (90%). ^{1}H NMR and ^{13}C NMR data of the compound were identical with the previously recorded data for **19**.

2-Methylene-2′,3′,4′,9′-tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluorene] (21)

Li wire (0.156 g, 22.4 mmol) was cut in a glove box under an argon atmosphere and placed together with naphthalene (0.287 g, 2.24 mmol) in a 50-mL round-bottom flask. The flask was then sealed with a rubber septum, THF (25 mL) added and the mixture stirred at r.t. under argon for 15 min. Dry $ZnCl_2$ (1.60 g, 11.7 mmol) in THF (25 mL) was introduced via a syringe over 3 h with vigorous stirring; when the addition was complete stirring was continued for 30 min. The precipitated Rieke zinc was washed with THF to a total volume of 25 mL. The stirred suspension was cooled to –20 °C before CH_2I_2 (1.43 g, 5.33 mmol) was added over 20 min and the mixture was stirred for 30 min. Neat $PbCl_2$ (52 mg, 0.11 mmol) was added and the mixture was stirred for 1 h, then the cooling bath was removed and it was stirred at r.t. for 30 min. The mixture cooled to –20 °C and $TiCl_4$ (0.677 g, 3.56 mmol) in CH_2Cl_2 (2 mL) was added

dropwise. The mixture was allowed to reach r.t. over 45 min then **19** (0.762 g, 3.20 mmol) in THF (3 mL) was added over 5 min. The mixture was stirred for 1 h, hexane (25 mL) was added, and the soln was washed with sat. brine–sat. $NaHCO_3$ (1:1, 20 mL) and subsequently with sat. brine (20 mL). The brine washings were extracted with hexane (2 × 10 mL) and the combined extracts were dried ($MgSO_4$), evaporated, and the residual material subjected to flash chromatography (silica gel 60, hexane). The product was a pale yellow oil; yield: 0.420 g (56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.7–2.0 (m, 6 H, 3 × CH_2), 2.5–2.7 (m, 4 H, CH_2), 3.30 (d, *J* = 19.0 Hz, 1 H, H9′α), 3.08 (dt, *J* = 18.9 Hz, 1 H, H9′β), 5.72 (s, 2 H, =CH_2), 7.3–7.6 (m, 4 H, H5′–H8′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH_2), 20.6 (CH_2), 22.3 (CH_2), 29.9 (CH_2), 33.4 (CH_2), 37.0 (C9′), 38.6 (C3), 52.3 (C1), 117.8 (=CH_2), 123.3 (CH-Ar), 123.8 (CH-Ar), 125.5 (CH-Ar), 126.0 (CH-Ar), 136.6, 142.8, 145.5, 145.9, 146.5.

MS (EI, 70 eV): *m*/*z* (%) = 236 (100) [M]$^+$, 221 (12), 193 (12), 165 (57), 141 (49).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{18}H_{20}$: 236.1565; found: 236.1571.

(1*R**,2*R**)-2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-ol (22)

A 1 M soln of L-Selectride in THF (8.0 mL, 8 mmol) was added to a soln of **19** (1.60 g, 6.7 mmol) in anhyd THF (5 mL) in an ice bath and the mixture stirred at this temperature overnight. NaOH (1.3 g, 33 mmol) in H_2O (10 mL) was added followed by 30% H_2O_2 (3.7 g, 33 mmol). The mixture was stirred vigorously at r.t. for 2 h, hexane (10 mL) was added, the two phases were separated and the aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic solns were washed with sat. brine (10 mL), dried ($MgSO_4$), and concentrated at reduced pressure. Butan-2-ol was azeotropically removed from the crude product with hexane (2 × 50 mL), and pure **22** was isolated by flash chromatography (silica gel 60, hexane–EtOAc, 4:1) as a solid; yield: 1.40 g (87%); mp 67–68 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.5–1.6 (m, 2 H, CH_2), 1.7–1.8 (m, 4 H, CH_2), 1.9–2.0 (m, 3 H, CH_2), 2.2–2.3 (m, 2 H, CH_2), 2.2–2.4 (m, 2 H, H4′), 3.49 (dt, *J* = 22.5, 2.6 Hz, 1 H, H9′α), 3.65 (dt, *J* = 21.5, 2.8 Hz, 1 H, H9′β), 3.97 (t, *J* = 4.8 Hz, 1 H, H2) 7.2–7.5 (m, 4 H, H5′–H8′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (C3′), 21.5 (CH_2), 22.4 (C4′), 34.4 (CH_2), 35.8 (CH_2), 37.9 (C3), 39.6 (C9′), 58.4 (C1), 81.5 (C2), 117.8 (CH-Ar), 123.1 (CH-Ar), 124.1 (CH-Ar), 125.9 (CH-Ar), 138.4 (C9a′), 143.3 (C-Ar), 143.6 (C-Ar), 145.2 (C4a′).

MS (EI, 70 eV): *m*/*z* (%) = 240 (83) [M]$^+$, 222 (5.5), 195 (38), 182 (27), 169 (100), 152 (12), 141 (19).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1530.

Since the starting material and the product had very similar retention time in this chromatographic system as well as on GLC (semipolar column), IR spectroscopy was used to monitor the course of the reaction.

2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-ol (22) as an Alcohol Epimeric Mixture by Lithium Aluminum Hydride Reduction of Ketone 19

$LiAlH_4$ (0.042 g, 1.1 mmol) was dispersed in anhyd THF (5 mL), cooled to 0 °C and a soln of **19** (0.238 g, 1.00 mmol) in anhyd THF (1 mL) under argon was added slowly. The mixture was stirred at r.t. for 3 h and poured into aq sat. NH_4Cl (50 mL). The mixture was extracted with Et_2O (3 × 15 mL), the combined extracts were washed with sat. brine (15 mL), dried ($MgSO_4$), and the filtrate evaporated. The residual white oil was a 1:1 mixture of the alcohol diastereomers. The diastereomers were separated by flash chromatography (silica gel 60, EtOAc–hexane, 1:4).

(1*R**,2*R**)-2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-ol (22)

The faster-moving diastereomer; yield: 0.109 g (45%). ^{1}H NMR and ^{13}C NMR data of the compound was identical with the previously collected spectral data for the title compound.

(1*R**,2*S**)-2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluoren]-2-ol (22)

The slower-moving diastereomer; yield: 0.098 g (41%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.4–1.8 (m, 4 H, CH_2), 1.9–2.3 (m, 4 H, CH_2), 2.4–2.7 (m, 4 H, CH_2), 3.3–3.4 (m, 2 H, H9′), 3.7–3.8 (m, 1 H, OH), 4.17 (t, *J* = 4.6 Hz, 1 H, H2), 7.2–7.5 (m, 4 H, H5′–H8′).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.5 (CH_2), 25.9 (CH_2), 27.4 (CH_2), 33.0 (CH_2), 34.1 (CH_2), 39.4 (CH_2), 44.6 (C9′), 53.6 (C1), 78.9 (C2), 117.4 (CH-Ar), 123.1 (CH-Ar), 123.3 (CH-Ar), 125.8 (CH-Ar), 138.5, 142.1, 145.4, 146.7.

MS (EI, 70 eV): *m*/*z* (%) = 240 (100) [M]$^+$, 222 (23), 194 (28), 169 (46), 153 (17).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{17}H_{20}O$: 240.151; found: 240.1516.

(1*R**,2*R**)-2′,3′,4′,9′-Tetrahydrospiro[cyclopentane-1,1′-[1*H*]-fluorene]-2-methanol (23)

A 0.5 M soln of 9-BBN in THF (4.4 mL, 2.2 mmol) and **21** (0.42 g, 1.8 mmol) under argon was stirred at r.t. for 20 h. A mixture of EtOH (1 mL), H_2O (2 mL), NaOH (0.40 g, 10 mmol), and 30% H_2O_2 (1.2 g, 10 mmol) was added and the mixture stirred vigorously at 50 °C for 3 h. H_2O (20 mL) was added and the mixture extracted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), the solvent distilled off, and the residual material subjected to flash chromatography (silica gel 60, EtOAc–hexane, 1:2) which yielded a white solid; yield: 92%; mp 76–78 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.6–2.0 (m, 10 H, CH_2), 2.1–2.3 (m, 2 H, H2, OH), 2.4–2.5 (m, 2 H, H6′), 3.2–3.3 (m, 2 H, H9′), 4.0–4.2 (m, 2 H, C*H*$_2$OH), 7.1–7.4 (m, 4 H, H5′–H8′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_2), 20.1 (CH_2), 22.5 (CH_2), 33.0 (CH_2), 36.8 (C4′), 39.5 (C9′), 39.6 (CH_2), 45.8 (C2), 53.8 (C1), 79.9 (CH_2OH), 117.8 (CH-Ar), 123.1 (CH-Ar), 123.9 (CH-Ar), 126.1 (CH-Ar), 137.2, 142.5, 145.3, 145.6**.**

MS (EI, 70 eV): *m*/*z* (%) = 254 (39) [M]$^+$, 236 (100), 223 (27), 193 (14), 167 (65).

HRMS (EI, 70 eV): *m*/*z* [M]$^+$ calcd for $C_{18}H_{22}O$: 254.1671; found: 254.1693.

Semi-titanocene Formation; General Procedure

Compound **23** or **22** (2.00 mmol) was dissolved in anhyd Et_2O (10 mL), the soln cooled in an ice-water bath and 1.6 M BuLi (2.8 mL, 4.5 mmol) in hexane added dropwise under argon. The mixture was stirred overnight at r.t. and anhyd pentane (20 mL) added to precipitate the salt. Most of the supernatant was removed from the precipitated dilithium salt which was dissolved in anhyd THF (15 mL). A syringe was used to transfer the soln into a stirred suspension of $TiCl_3$ (0.308 g, 2.00 mmol) in anhyd THF (75 mL) at 0 °C. The mixture was left to reach r.t. overnight. Dried $PbCl_2$ (0.278 g, 1.00 mmol) was added and the mixture stirred at r.t. for 7 h. Most of the solvents were removed at reduced pressure and the precipitate triturated with anhyd CH_2Cl_2 (30 mL). Filtration under argon and precipitation from CH_2Cl_2 yielded a dark colored solid which was ground to a powder with a spatula under argon, triturated with anhyd pentane (20 mL) with stirring and the solvent decanted off. Re-

moval of the remaining volatiles under high vacuum furnished the crude semi-titanocenes.

Dichloro{(1*R,2*R**)-2-(oxido-κ*O*-methyl)-1′,2′,3′,4′-tetrahydrospiro[cyclopentane-1,1′-(4a,4b,8a,9,9a-η)-fluorenyl]}titanium (26)**

The crude product, obtained as above, was subjected to sublimation at 140 °C at 0.067 mbar to give a red amorphous solid; yield: 0.120 g (16%); mp 210 °C (dec).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.8–2.3 (m, 9 H, CH_2), 2.6–2.8 (m, 2 H, CH_2), 3.2–3.3 (m, 1 H, CH_2), 5.3–5.5 (m, 2 H, CH_2OTi), 7.00 (s, 1 H, H9′), 7.4–7.5 (m, 2 H, H6′, H7′), 7.6–7.8 (m, 2 H, H7′, H9′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (C3′), 24.1 (CH_2), 24.9 (CH_2), 34.2 (CH_2), 38.6 (CH_2), 41.5 (CH_2), 41.7 (CH_2), 55.8 (CH_2OTi), 75.9 (C2), 110.1 (C9′), 119.7, 123.3, 124.8, 126.3, 128.1, 129.0, 131.1, 144.0.

MS (EI, 70 eV): *m*/*z* (%) = 370 (40%) $[M]^+$, 335 (19), 330 (13) 318 (100), 305 (16).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{18}H_{20}Cl_2OTi$: 370.0371; found: 370.0360.

Dichloro{(1*R,2*R**)-2-(oxido-κ*O*)-1′,2′,3′,4′-tetrahydrospiro[cyclopentane-1,1′-(4a,4b,8a,9,9a-η)-fluorenyl]}titanium (29)**

The crude product, obtained as above, was subjected to sublimation at 120 °C at 0.067 mbar to give a red amorphous solid; yield: 0.155 g (22%); mp 240 °C (dec).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.7–2.0 (m, 4 H, CH_2), 2.2–2.4 (m, 5 H, CH_2), 2.5–2.6 (m, 1 H, CH_2), 2.7–2.9 (m, 1 H, H4′α), 3.38 (dd, *J* = 24.7, 7.2 Hz, 1 H, H4′β), 5.75 (t, *J* = 10.0 Hz, 1 H, H2), 6.91 (s, 1 H, H9′), 7.4–7.5 (m, 2 H, H6′, H7′), 7.7–7.8 (m, 2 H, H7′, H9′).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 (C3′), 24.8 (CH_2), 24.9 (CH_2), 35.8 (CH_2), 37.8 (CH_2), 40.0 (CH_2), 53.0 (C1), 77.2 (C2), 110.0 (CH-Ar), 120.0 (CH-Ar), 123.5 (CH-Ar), 124.8 (CH-Ar), 126.6 (C9a′), 128.0 (CH-Ar), 128.1 (C-Ar), 130.2 (C-Ar), 146.5 (C-Ar).

MS (EI, 70 eV): *m*/*z* (%) = 356 (78) $[M]^+$, 321 (25), 302 (100), 222 (54), 169 (13).

HRMS (EI, 70 eV): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}Cl_2OTi$: 356.0214, found: 356.0208.

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