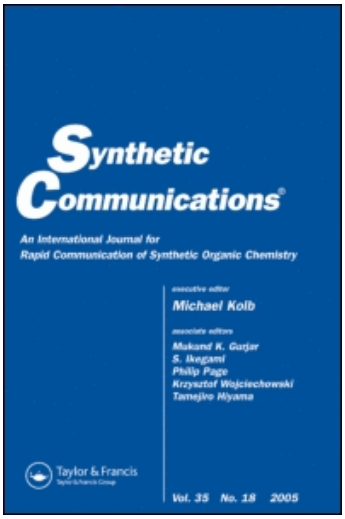

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AN EFFICIENT PALLADIUM CATALYZED STEREOCONTROLLED SYNTHESIS OF 4a-ANGULAR METHYL SUBSTITUTED HYDROFLUORENES

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Abstract : A high yield stereoselective synthesis of 4a-angularly methyl substituted cis-hexahydrofluorenes **5a-h** and tetrahydrofluorenes **7a,b** has been developed by palladium-catalyzed intramolecular Heck-type cyclization of the respective exo-olefins **4a-h** and **4a,b** through exclusive 5-exo-trig mode.

There are relatively scarce references[1-6] on the synthesis of 4a-methyl hexahydrofluorenes. The acid catalyzed intramolecular cyclization[2,3,5] of substituted benzylcyclohexanols or the related substrates used for the synthesis of hydrofluorenes **5a** and **5b** in only moderate yields, did not lead to a general solution to the problem. The cyclialkylation approach often given complicated results[1,3,4] because of the formation of isomeric bridged bicyclo[3.3.1]nonene systems. There is an isolated recent report[6] on the synthesis of a 4a-methylhexahydrofluorene having aromatic methoxy substituents, by intermolecular Friedel-Crafts type cyclization of a benzylic cation with methylcyclohexene.

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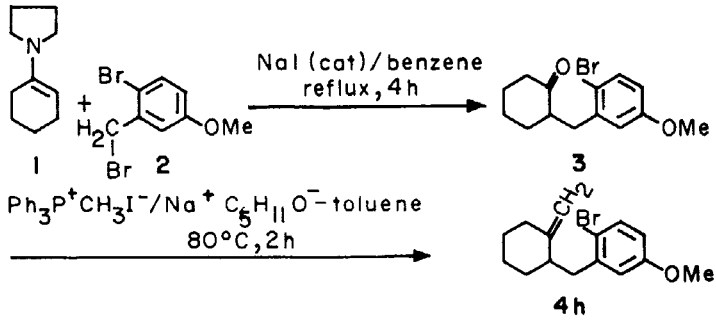
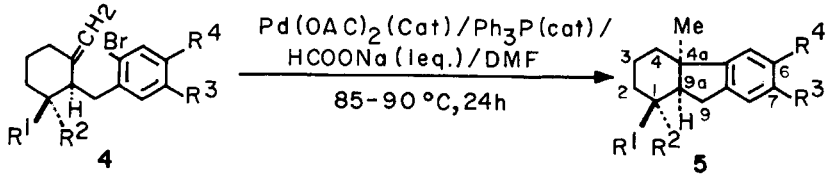
In continuation of our recent work[7] on the stereocontrolled synthesis of trans-octahydroanthracene derivatives through an efficient and highly regioselective 6-endo-trig-aryl radical cyclization of the respective exo-olefins **4a-g**, we have carried out intramolecular Heck-type reactions[8-11] on those and a new substrate **4h**. In this paper we present our results of a highly efficient general stereocontrolled route to 4a-angular methyl substituted hydrofluorene derivatives **5a-h** and **7a,b** by exclusive 5-exo-cyclizations of the exo-olefins **4a-h** and **4a,b** under palladium-catalyzed cyclizations with and without hydride transfer reagent, respectively.

While the preparation of the exo-olefins **4a-g** have been described earlier,[7] the new olefin **4h** was obtained by Wittig alkenation[12,13] of the ketone **3**, which in turn was prepared by alkylation of enamine **1** with the bromide **2**. The cyclization of the olefins **4a-h**



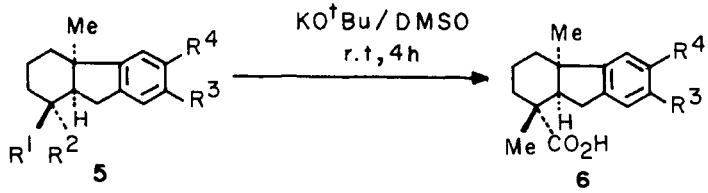
in dimethylformamide with 5 mole% of palladium acetate and 20 mole% of triphenylphosphine in the presence of

molar equivalent of sodium-formate[8] at 85-90°C for 24h furnished the respective cis-hydrofluorene derivatives **5a-h**, in excellent yields. The structures of the esters **5a**[2,5] adn **5b**[5] were assigned by comparison with the spectral (^{1}H NMR and IR) data.



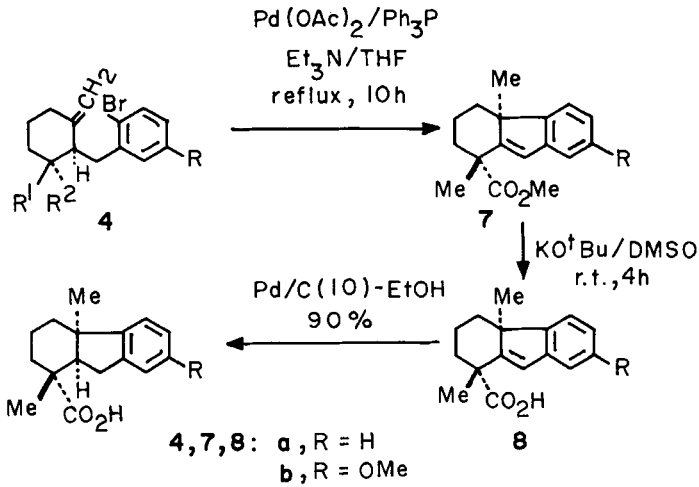
4,5
a, R^1=Me, R^2=CO_2Me, R^3,R^4=H
b, R^1=Me, R^2=CO_2Me, R^3=OMe, R^4=H
c, R^1=Me, R^2=CO_2Me, R^3=H, R^4=OMe
d, R^1=R^2=Me, R^3=R^4=H
e, R^1=R^2=Me, R^3=OMe, R^4=H
f, R^1=R^2=Me, R^3=H, R^4=OMe
g, R^1=R^2=R^3=R^4=H
h, R^1=R^2=H, R^3=OMe, R^4=H

The ester **5a-c** were further characterized through their transformation to the respective acids **6a**, **6b** and **6c** in over 90% yield by treatment with potassium-tert-butoxide in dimethylsulfoxide[14] for 4h at room temperature. The identity of each of the known acids **6a**[2] and **6b**[5] was confirmed by direct mixture m.p. determination with the authentic sample. The stereostructures of the previously unreported ester **5c** and the acid **6c** were assigned by analogy. Similarly, the cis-ring junction stereochemistry to **5d-h** has been assigned from the afore-mentioned analogy.

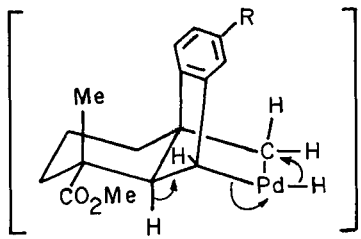


5,6
a, $R^3=R^4=H$
b, $R^3=OMe$, $R^4=H$
c, $R^3=H$, $R^4=OMe$

The attempted cyclization of **4a** and **4b** with 5-20 mol% of palladium acetate and 20-30 mole% of triphenylphosphine in dimethylformamide in the presence of various amines[8-11] mostly led to the recovery of the olefins. However, on refluxing in tetrahydrofuran for 10 h with 1.2 equivalent of palladium acetate and 1.5 equivalent of triphenylphosphine in the presence of a large excess of triethylamine, the olefins **4a** and **4b** gave the respective tetrahydrofluorene esters **7a** and **7b** in 74% and 67% yields. The ^{1}H NMR spectral data of **7a** (Table 2) are identical to that reported[15] for the optically active compound. The assigned stereostructures for **7a** and **7b** have been established through their transformations to the respective acids **8a** and **8b** by treatment with potassium-tert-butoxide in dimethylsulfoxide, followed by catalytic hydrogenation over 10% palladium-charcoal in ethanol leading to the known acids **6a** and **6b**, in excellent yields. The formation of the tetrahydrofluorene esters **7a** and **7b** in



the cyclization of **4a** and **4b** most probably proceeds through an intramolecular oxidative addition[16] of a benzylic C-H bond to Pd(II) followed by base catalyzed elimination of Pd(II) as shown below :



9 (R = H or OMe)

In conclusion, unlike the exclusive 6-endo-aryl radical cyclization[7] of the exo-olefins **4a-g** resulting in the respective trans-octahydroanthracenes, the present results show that palladium-catalyzed intramolecular Heck-type reaction proceeds through regiospecific 5-exo-mode leading to an efficient

synthetic route to 4a-angular methyl substituted hydrofluorene derivatives, which is complementary to the recent applications[17-19] of similar metal-catalyzed reactions for synthesis of some C-9a-angularly functionalized hexahydrofluorene derivatives.

EXPERIMENTAL

The compounds described are all racemates. all reagents were of commercial qualities, all solvents were dried by standard method before use. Petroleum ether used here b.p. 60-80°C. Melting points were determined in open capillary tubes and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer 298 instrument. Elemental analyses were performed by S. Sarkar of this laboratory ^{1}H NMR spectra were obtained at 100 MHz on an FX-100 spectrometer, unless otherwise mentioned.

2-(5-Methoxy-2-bromobenzyl)-cyclohexanone (3)

A solution of the crude enamine **1** [prepared from cyclohexanone (5g, 51 mmol) and pyrrolidine (12.3 mL, 137 mmol)] and the bromide **2** (16 g, 57.2 mmol) in anhydrous benzene (100 mL) was refluxed for 4h in the presence of a catalytic amount of anhydrous NaI (200 mg, 1.3 mmol). The mixture was diluted with H_2O (100 mL) and the benzene layer was separated. The aqueous layer was extracted with benzene (2x40 mL). The

combined organic layer was washed with 3N HCl (2x25 mL) and brine, and dried (Na_2SO_4). The solvent was removed and the residue on evaporative distillation at 160-165 °C (bath temp.) 0.1 mm Hg, gave **3** as a colourless oil; yield : 10.9g(72%); IR (film) : 1705 cm^{-1}; ^1H NMR (200MHz) δ 1.32-2.80 (m, 10H), 3.18-3.42 (m, 1H), 3.79 (s, 3H, OCH_3), 6.68 (dd, 1H, J = 8,2), 6.85 (d, 1H, J = 2), 7.45 (d, 1H, J = 8); Anal Calcd for $C_{14}H_{17}O_2Br$: C, 56.58, H, 5.77. Found : C, 56.41, H, 5.62.

2-(5-Methoxy-2-bromobenzyl)-1-methylenecyclohexane (4h)

To a stirred suspension of methyltriphenylphosphonium-iodide (4.1 g, 10.2 mmol) and freshly prepared sodium-tert-pentoxide (5.1 mL, 2.0 M) in toluene at r.t., a solution of **3** (1.0 g, 3.4 mmol) in anhydrous toluene (7 mL) was added dropwise and the mixture was heated at 80°C for 2h. After being quenched with sat. aq. NH_4Cl (5 mL), the product was extracted with Et_2O (3x25 mL). The organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. The residue was dissolved in petroleum ether (100 mL) and immediately filtered through a short column of silica gel (20g); the filtrate was concentrated in vacuo to give the alkene, which was finally purified by silica gel (20g) chromatography with petroleum ether as the eluent to give **4h**, as a colourless oil; yield : 875 mg (88%); IR

(film) : 1640, 1605 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.18-2.50 (m, 9H), 2.60-2.76 (m, 1H), 2.96-3.10 (m, 1H), 3.77 (s, 3H, OCH_3), 4.61 (br s, 1H), 4.71 (br s, 1H), 6.63 (dd, 1H, J = 8,2), 6.73 (d, 1H, J = 2), 7.43 (d, 1H, J = 8); Anal. Calcd for $C_{15}H_{19}OBr$: C, 61.03, H, 6.49. Found : C, 60.86, H, 6.31.

(1RS, 4aRS, 9aRS)-Methyl 1,2,3,4,4a,9a-Hexahydro-1,4a-dimethylfluorene-1-carboxylate (5a)

A stirred solution of the exo-olefin **4a** (250 mg, 0.74 mmol) in DMF (8 mL), $Pd(OAc)_2$ (9 mg, 0.04 mmol), Pn_3P (39 mg, 0.15 mmol) and HCOONa (51 mg, 0.74 mmol) was heated at 85-90°C for 24h under dry N_2. The cooled reaction mixture was diluted with H_2O (20 mL) and extracted with Et_2O (3x20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated. The residue was chromatographed over silica gel (10g) using petroleum ether : Et_2O (19:1) as eluent, to afford pure known ester[2] **5a** as a thick colourless oil; yield : 140 mg (73%), this on seeding with an authentic sample[2] of **5a** slowly solidified which on recrystallization once from petroleum ether in the cold, afforded thick shining plates mp 48°C (lit[2] mp 48°C) alone or mixed with an authentic sample. IR (KBr): 1730 cm^{-1}; ^1H NMR δ 1.24 (s, 6H, $2CH_3$), 1.26-1.84 (m, 6H), 2.04-2.28 (bd, 1H), 2.84 (br s, 2H), 3.72 (s, 3H, CO_2Me), 7.08-7.44 (m, 4H).

(1RS, 4aRS, 9aRS)-Methyl 1,2,3,4,4a,9a-Hexahydro-1,4a-dimethyl-7-methoxy-fluorene-1-carboxylate (5b)

The exo-olefin **4b** (280 mg, 0.76 mmol) on cyclization as above gave the known[5] ester **5b**, as a colourless oil; yield : 170 mg (77%); IR (film) : 1730, 1610 cm^{-1}; ^1H NMR δ 1.16 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.24-1.96 (m, 6H), 2.00-2.20 (bd, 1H), 2.80 (br s, 2H), 3.71(s, 3H, CO_2Me), 3.77 (s, 3H, OCH_3), 6.73 (dd, 1H, J =8,1), 6.80 (br s, 1H), 7.00 (d, 1H, J = 8)

(1RS, 4aRS, 9aRS)-Methyl 1,2,3,4,4a,9a-Hexahydro-1,4a-dimethyl-6-methoxy-fluorene-1-carboxylate (5c)

Compound **4c** (280 mg, 0.76 mmol) on cyclization as above gave the pure ester **5c** as a colourless oil; yield : 160 mg (73%); IR (film) : 1730, 1610 cm^{-1}; ^1H NMR(400MHz) δ 1.19 (s,3H, CH_3), 1.20 (s, 3H, CH_3), 1.22-1.67 (m, 6H), 2.10 (bd, 1H), 2.73-2.86 (m, 2H), 3.69 (s, 3H, OCH_3), 3.78 (s, 3H, CO_2Me), 6.66-6.69 (m, 2H), 7.12 (d, 1H, J=8). Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97, H, 8.39; Found : C, 74.83, H, 8.76.

(4aRS, 9aSR)-1,2,3,4,4a,9a-Hexahydro-1,1,4a-trimethyl-fluorene (5d)

Compound **4d** (250 mg, 0.85 mmol) on cyclization as described for **5a** gave an inseprable mixture (172 mg) containing ca 13:1 ratio of **5d** and the uncyclized debrominated olefin (^1H NMR). This mixture was

dissolved in THF (5 mL) and treated with borane-THF complex (1 mL, 0.8 M) at 0°C for 2h under N_2. The reaction mixture was quenched with H_2O and treated with 3N aq. NaOH (2 mL) and H_2O_2 (1 mL, 30% v/v) during 10 min at 0-5°C. After 30 min another lot of H_2O_2 (0.5 mL, 30% v/v) was added, and left overnight at r.t. The reaction mixture was diluted with H_2O (20 mL) and extracted with Et_2O (3x20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated to give the crude hydrocarbon which on chromatography over silica gel (10g) using petroleum ether as the eluent, gave **5d** as a colourless oil; yield : 150 (82%); IR (film) : 1605, 1590 cm^{-1}; ^1H NMR δ 0.96 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.20-1.96 (m, 7H), 2.80 (d, 2H, J = 8), 7.04-7.52 (m, 4H). Anal. Calcd. for $C_{16}H_{22}$: C, 89.65, H, 10.35. Found C, 89.62, H, 10.47.

(4aRS, 9aSR)-1,2,3,4,4a,9a-Hexahydro-1,1,4a-trimethyl-7-methoxyfluorene (5e)

Compound **4e** (250 mg, 0.77 mmol) on cyclization as described for **5a** and purification of the product as for **5d** gave pure **5e** as a colourless oil; yield : 170mg (90%); IR (film) : 1605, 1585 cm^{-1}; ^1H NMR δ 0.94 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.00-1.64 (m, 6H), 1.88 (t, 1H, J = 10), 2.76 (d, 2H, J= 10), 3.80 (s, 3H, OCH_3), 6.72 (dd, 1H, J = 8.1), 6.76

(bd, 1H), 7.00 (d, 1H, J = 8). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55, H, 9.90. Found : C, 83.73, H, 10.30.

(4aRS, 9aSR)-1,2,3,4,4a,9a-Hexahydro-1,1,4a-trimethyl-6-methoxyfluorene (5f)

Compound **4f** (310 mg, 0.96 mmol) on cyclization as described for **5a** and purification of the product as for **5d** gave pure **5f** as a colourless oil. yield : 210 mg (89%); IR (film) : 1610, 1590 cm^{-1}. ^1H NMR(400 MHz) δ0.92(s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 0.98-1.68 (m, 6H), 1.88 (t, 1H, J = 8), 2.68-2.75 (m, 2H), 3.68 (s, 3H, OCH_3), 6.63-6.88 (m, 2H), 7.08 (d, 1H, J = 8). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55, H, 9.90. Found : C, 83.42, H, 9.73.

(4aRS, 9aRS)-1,2,3,4,4a,9a-Hexahydro-4a-methylfluorene (5g)

Compound **4g** (260 mg, 0.98 mmol) on cyclization as described for **5a** and purification of the product as for **5d** gave pure **5g** as a colourless oil; yield : 140 mg (77%). IR (film) : 1610, 1585 cm^{-1}. ^1H NMR δ1.24 (s, 3H, CH_3), 1.26-1.96 (m, 8H), 1.98-2.14 (m, 1H), 2.56-3.06 (m, 2H), 7.04-7.46 (m, 4H). Anal. Calcd for $C_{14}H_{18}$: C, 90.26, H, 9.74. Found : C, 89.94, H , 9.60.

(4aRS, 9aRS)-1,2,3,4,4a,9a-Hexahydro-4a-methyl-7-methoxyfluorene (5h)

Compound **4h** (200 mg, 0.68 mmol) on cyclization as

described for **5a** and purification of the product as for **5d** gave pure **5h** as a colourless oil; yield : 120 mg (82%). IR (film) : 1610, 1585 cm^{-1}. ^1H NMR δ 1.20 (s, 3H, CH_3), 1.32-2.12 (m, 9H), 2.60-3.00 (m, 2H), 3.80 (s, 3H, OCH_3), 6.64-6.88 (m, 2H), 7.00 (d, 1H, J = 8). Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28, H 9.32. Found : C, 82.94, H, 9.03.

(1RS, 4aRS, 9aRS)-1,2,3,4a,9a-Hexahydro-1,4a-dimethyl-fluorene-1-carboxylic acid (6a)

The ester **5a** (100 mg, 0.38 mmol) was stirred with KO^tBu (425 mg, 3.8 mmol) in anhydrous DMSO (5 mL) at room temperature for 4h. The reaction mixture was poured into water and acidified with 6N HCl. The liberated acid was extracted with Et_2O (3x20 mL) and the crude solid acid, thus obtained, was recrystallizaed from EtOAc-petroleum ether to afford the acid **6a** (90 mg, 95%); mp 170-171°C (lit[2] 170-171°C) alone or mixed with an authentic sample.[2]

(1RS, 4aRS, 9aRS)-1,2,3,4,4a,9a-Hexahydro-1,4a-dimethyl-7-methoxyfluorene-1-carboxylic acid (6b)

Yield 96% as a colourless solid, mp 190-191°C (EtOAc-petroleum ether) (lit[5] 190-191°C) alone or mixed with an authentic sample.[5]

(1RS, 4aRS, 9aRS)-1,2,3,4,4a,9a-Hexahydro-1,4a-dimethyl-6-methoxyfluorene-1-carboxylic acid (6c)

Yield 96% as a colourless soild, mp 146-147°C (EtOAc-petroleum ether). Anal. Calcd. for $C_{17}H_{22}O_3$: C,74.42, H, 8.08. Found : C, 74.29, H, 8.03.

(1RS, 4aRS)-Methyl 2,3,4,4a-tetrahydro-1,4a-dimethyl-1H-fluorene-1-carboxylate (7a)

A stirred solution of the exo-olefin **4a** (350 mg, 1.04 mmol) in anhydrous-THF (15 mL), $Pd(OAc)_2$ (280 mg, 1.25 mmol), Ph_3P (400 mg, 1.56 mmol) and NEt_3 (5 mL, 36 mmol) was refluxed for 10h under N_2. The mixture was diluted with H_2O (40 mL) and extracted with Et_2O (3x30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated. The residue on chromatography over silica gel (10g) using Et_2O-petroleum ether (1:19) as eluent gave the pure ester **7a** as a colourless solid yield 200 mg (75%), m.p 84°C (petroleum ether) IR (KBr): 1730, 1610 cm^{-1}. ^1H NMR δ 1.12 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 0.80-2.64 (m, 6H), 3.64 (s, 3H, CO_2Me), 6.58 (s, 1H), 7.12-7.52 (m, 4H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65, H, 7.86. Found C, 79.48, H, 7.62.

(1RS, 4aRS)-Methyl 2,3,4,4a-tetrahydro-1,4a-dimethyl-7-methoxy-1H-fluorene-1-carboxylate (7b)

The compound **4b** (290 mg, 0.79 mmol) on cyclization as described for **7a** gave pure **7b** as a colourless oil; yield : 150 mg (66%). IR (film) : 1730, 1615 cm^{-1}. ^1H NMR δ 1.16 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.00-2.76

(m, 6H), 3.58 (s, 3H, CO_2Me), 3.84 (s, 3H, OCH_3), 6.51 (s, 1H), 6.66 (dd, 1H, J = 8,1), 6.89 (d, 1H, J = 1), 7.16 (d, 1H, J = 8). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49, H, 7.74. Found : C, 75.61, H, 7.89.

(1RS, 4aRS)-2,3,4,4a-tetrahydro-1,4a-dimethyl-1H-fluorene-1-carboxylic acid (8a)

Compound **7a** (100 mg, 0.39 mmol) was subjected to cleavage as described for **6a**, gave **8a** as a colourless solid; yield : 90 mg (95%), mp. 220-221°C (EtOAc-petroleum ether). Anal. Calcd. For $C_{16}H_{18}O_2$: C, 79.31, H, 7.49. Found : C, 79.52, H, 7.55.

(1RS, 4aRS)-2,3,4,4a-tetrahydro-1,4a-dimethyl-7-methoxy-1H-fluorene-1-carboxylic acid (8b)

Compound **7b** (100 mg, 0.35 mmol) was subjected to cleavage reaction as described for **6a**, gave **8b** as a colourless solid; yield : 89.5 mg (95%), mp. 195°C (EtOAc-petroleum ether). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97, H, 7.40. Found : C, 74.83, H, 7.32.

Reduction of 7a to 6a

The unsaturated acid **8a** (100 mg, 0.41 mmol) in EtOH (15 mL) was hydrogenated in presence of 10% Pd-C (50 mg) under 1 atom. Evaporation of the solvent left a crystalline solid which on recrystallization from EtOAc-petroleum ether gave pure **6a**; yield : 90 mg

(90%), mp 170-171°c alone or mixed with the sample described earlier.

Reduction of 7b to 6b

Compound **8b** (100 mg, 0.37 mmol) on catalytic hydrogenation gave pure **6b**; yield : 90 mg (90%), mp 190-191°C (EtOAc-petroleum ether) alone or mixed with the sample described earlier.

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