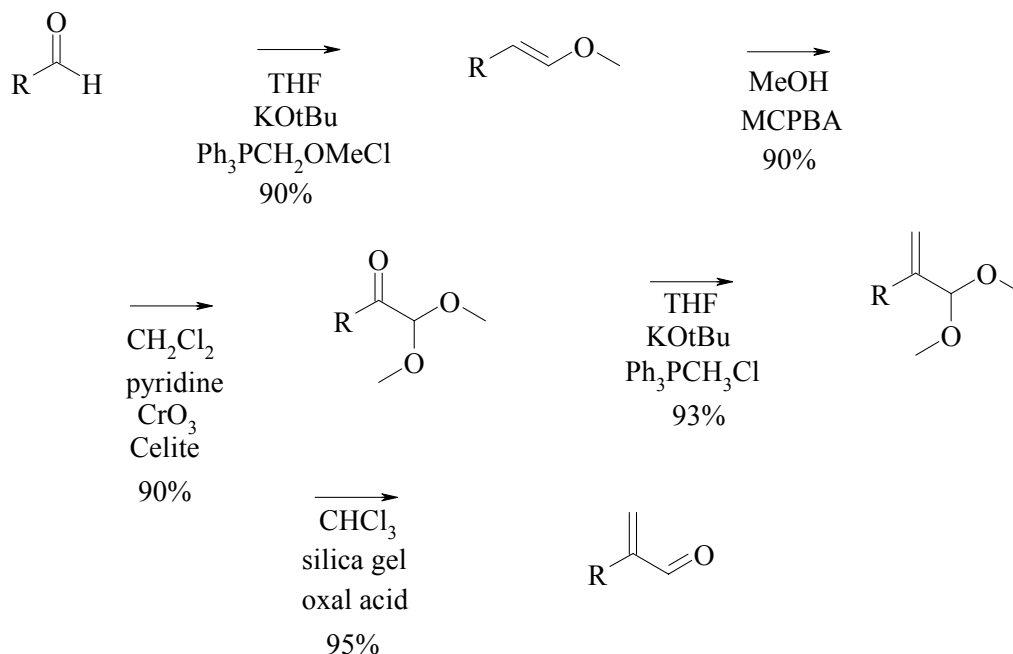
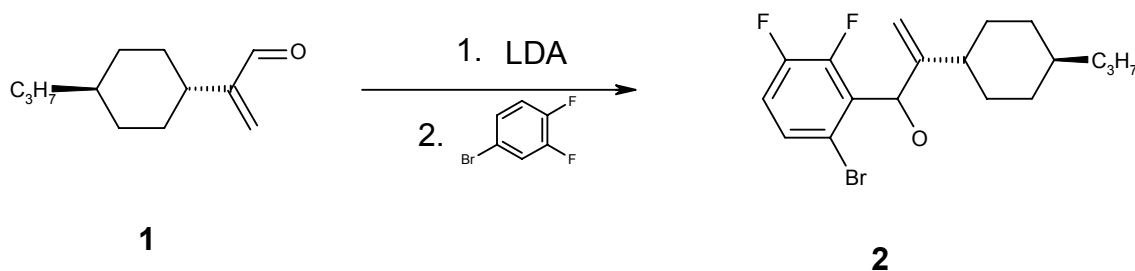


Synthesis of the α,β -unsaturated Aldehyde



The synthesis of the α,β -unsaturated aldehyde shown in the scheme above is described in F. Huet, M. Pellet, A. Lechevalier, J.-M. Conia, *J. Chem. Res. Miniprint*, **1982**, 9, 2528 - 2551.

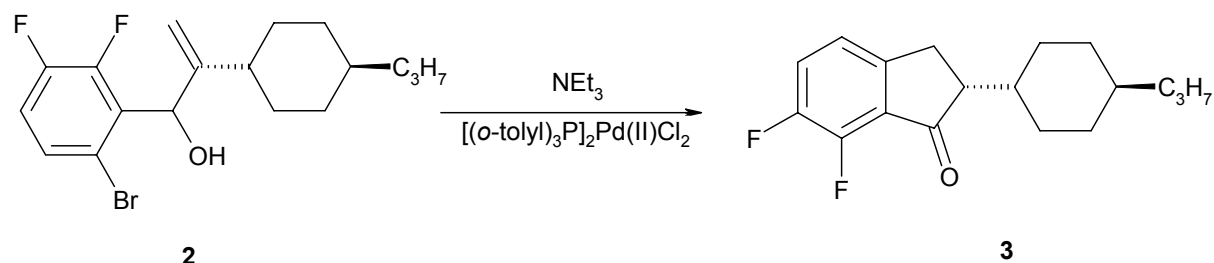
Synthesis of 1,1,6,7-Tetrafluoroindanes



Under nitrogen 60.4 g (313 mmol) 1-bromo-3,4-difluorobenzene dissolved in 60 ml THF was slowly added to a solution of 167 ml (324 mmol) 2M LDA in cyclohexane/ethylbenzene/THF diluted with 580 ml THF at -70°C . After 1h 49.9 g (277 mmol) of the α,β -unsaturated aldehyde **1** dissolved in 60 ml THF were added. After additional 2h the reaction mixture was allowed to warm to room temperature and was stirred over night. After acidification with 1N HCl the aqueous layer was extracted three times with mtb-ether. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by column

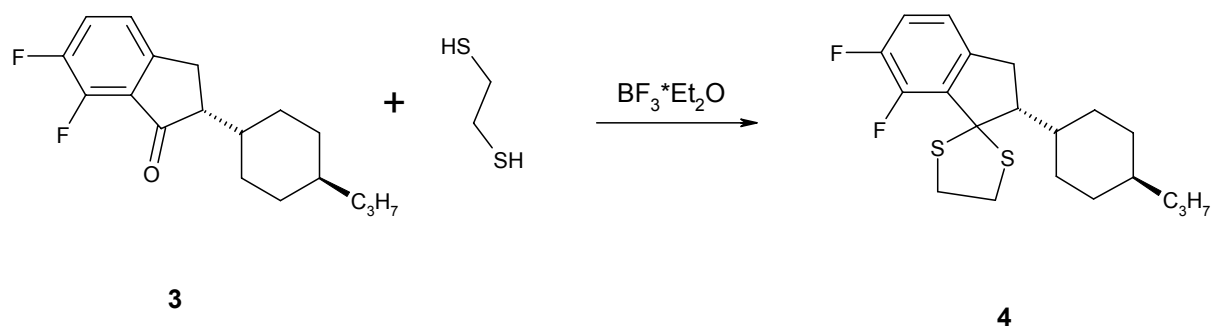
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chromatography (mtb-ether/*n*-heptane 1:10, *r_f* = 0.3) to obtain 85.7g of the allylic alcohol **2** as a yellow oil (92% GC, 84%). The substance was identified via GC-MS (*M* = 373.28).

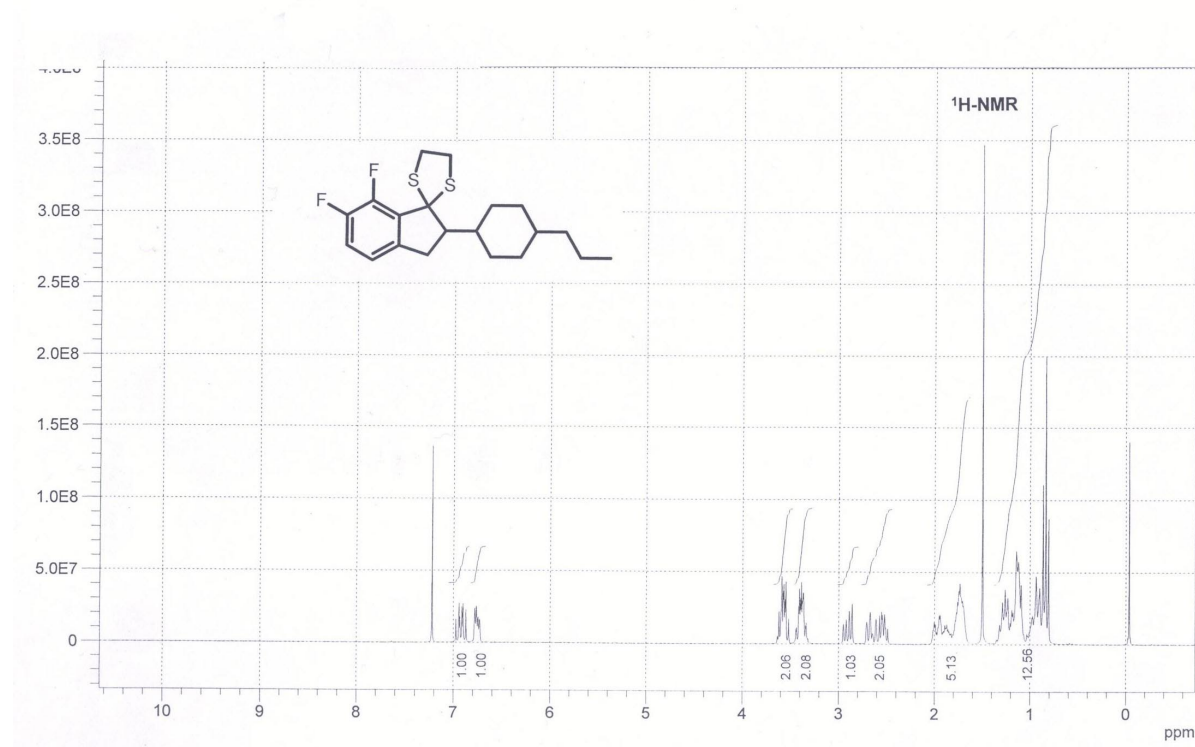


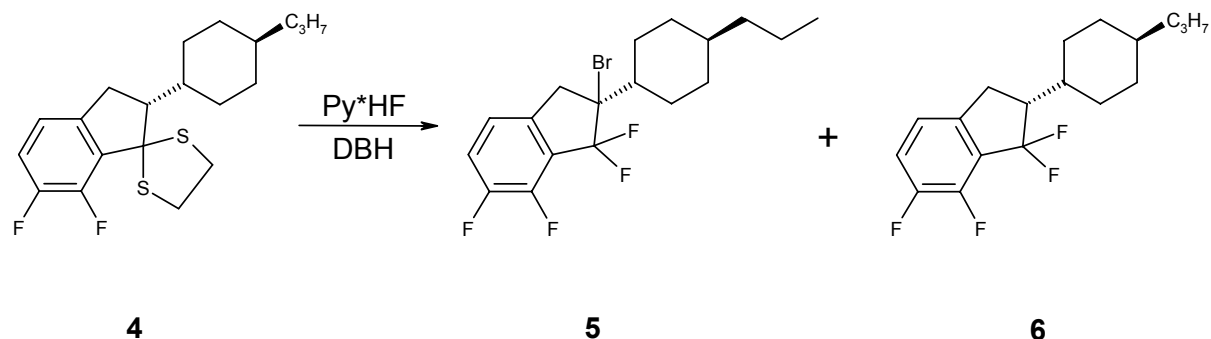
Under nitrogen 85.7g (92%) (211 mmol) of the allylic alcohol **2** was dissolved in 800 ml acetonitrile. 122 ml triethylamine and 12.25g Pd-catalyst were added, and the mixture was warmed to 87°C until the starting material was no longer detectable (2 nights, additional 10.0g catalyst was added after 24 h), (HPLC, RP-18 Superspher 250-4, UV (210 nm)). The solution was diluted with 300 ml mtb-ether and poured into brine. The aqueous layer was extracted with mtb-ether three times, the organic layer was dried (Na_2SO_4) and evaporated. After column chromatography (mtb-ether/*n*-heptane 1:10, *r_f* = 0.3) 40.1g (87% GC, (57%)) indanone **3** was obtained as yellow oil. The substance was identified via GC-MS (*M* = 292.37).

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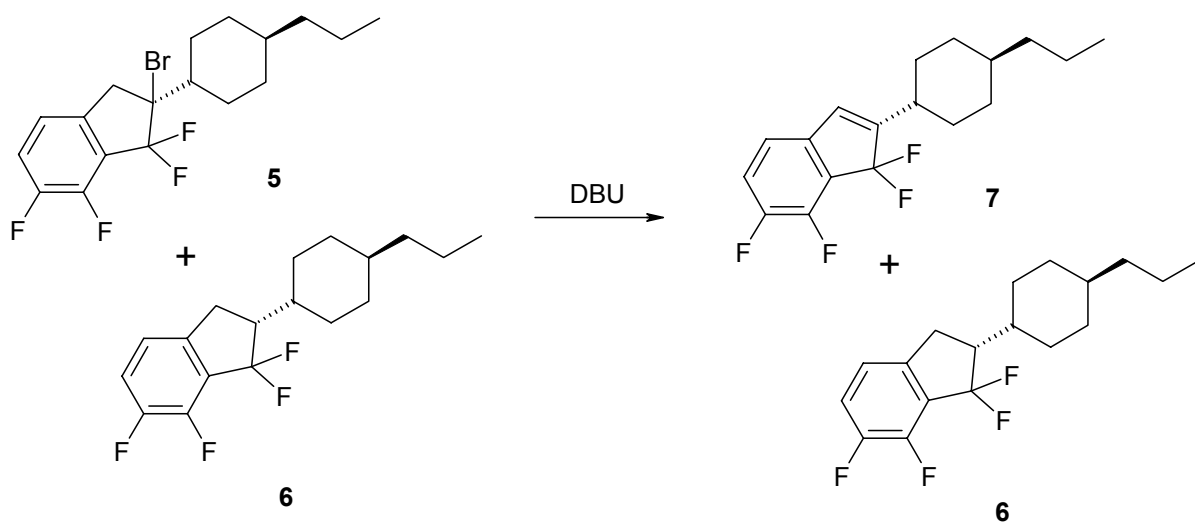


Under nitrogen 40.0g (87%) (119 mmol) indanone **3** and 24.0 ml (285 mmol) 1,2-ethanedithiol were dissolved in 260 ml dichloromethane and cooled to -15°C . 82.6 ml boron trifluoride-diethyl ether complex was added at this temperature. The mixture was stirred for an additional 3h at -15°C - -10°C and at room temperature over night. The solution was poured carefully into saturated NaHCO_3 -solution. Stirring was continued until CO_2 evolution subsided. Ph 8 was adjusted using 2N NaOH. The aqueous layer was extracted three times with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (mtb-ether/*n*-hexane 1:30, rf = 0.6) and recrystallization from boiling methanol (36.6g colourless crystals (83%)).





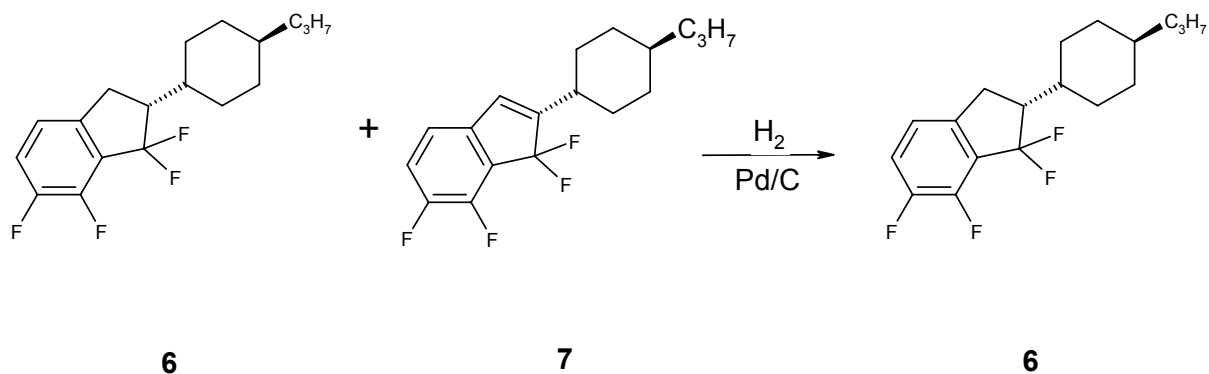
Under nitrogen 118.2 ml (4.38 mmol) of a 65% solution of HF in pyridin was added to a suspension of 115.9 g (405 mmol) 1,3-dibromo-dimethylhydantoin and 330 ml dichloromethane. The mixture was cooled to -74°C and a solution of 36.5g (99.0 mmol) thioketal **4** in 100 ml CH_2Cl_2 was added at a temperature below -65°C . After 4h the cooling bath was removed. The reaction mixture was stirred over night and was poured into 2.5 l 2N NaOH containing 140 ml 39% NaHSO_3 solution. pH 8 was adjusted. The aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with 1n HCl and brine, dried (Na_2SO_4) and evaporated. The residue was filtered through silica gel (*n*-hexane). After removal of the solvent the solid was recrystallized from boiling methanol to obtain 28.2g (88%) of a 1:3-mixture of the indanes (identified via GC-MS) **5** ($M = 393.27$) and **6** ($M = 314.37$).



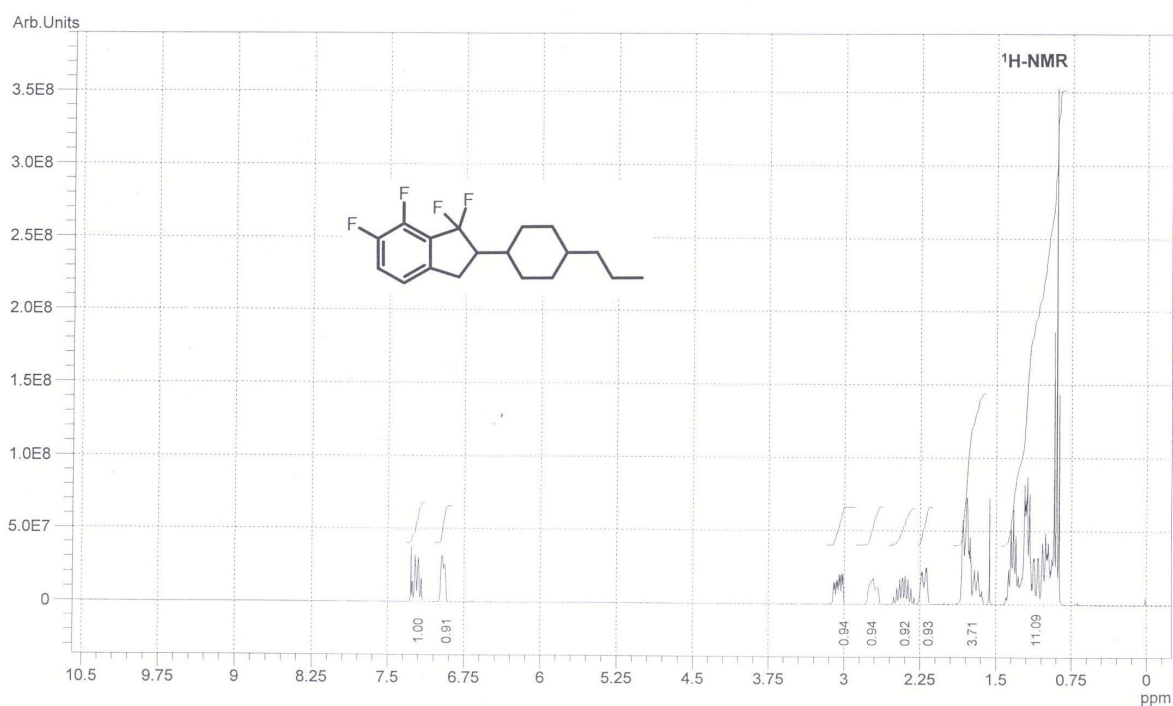
Under nitrogen 28.2g of the mixture of indanes **5** and **6** was dissolved in 90 ml dichloromethane. 22 ml DBU diluted with 20 ml CH_2Cl_2 was added to the solution. After stirring over night the reaction mixture was acidified with 150 ml 1N HCl. The aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with

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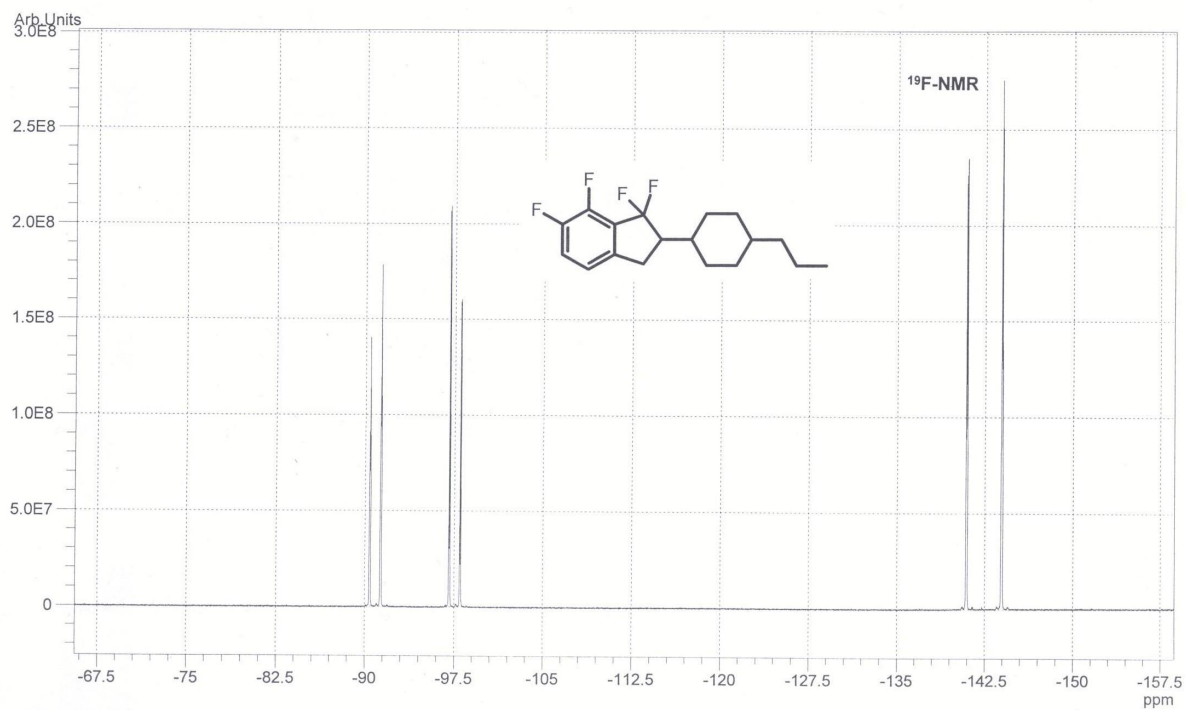
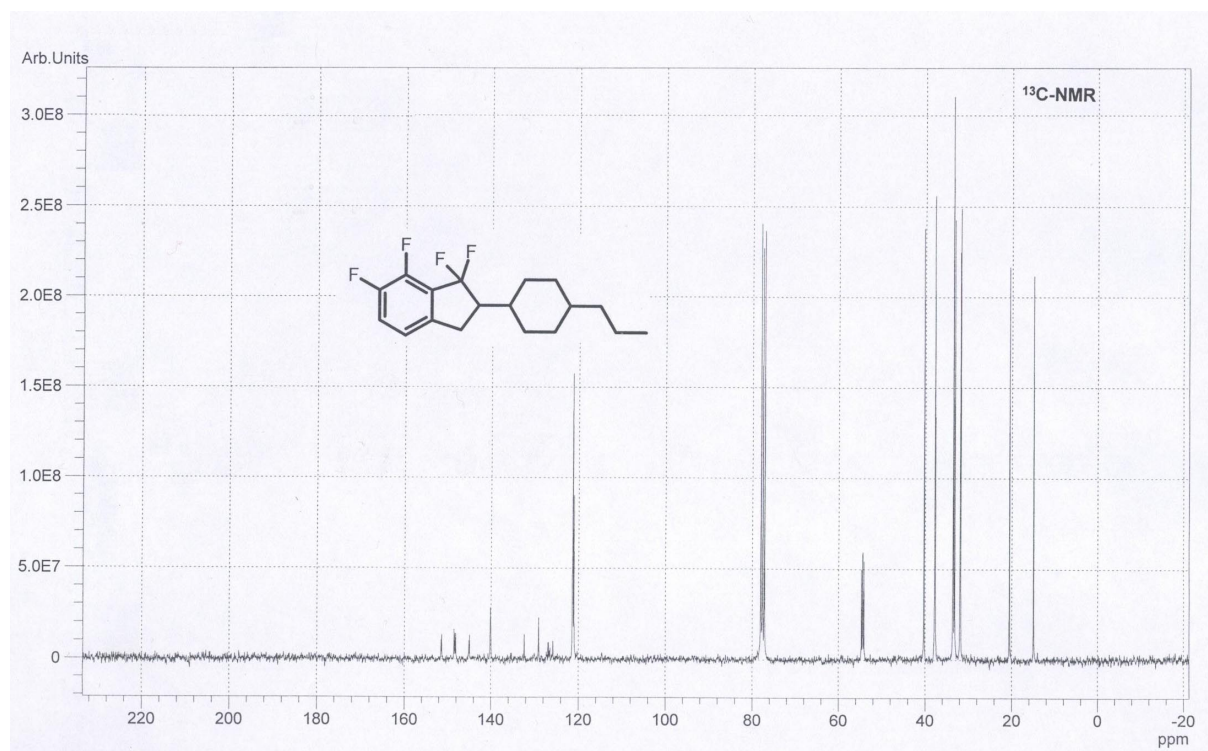
brine, dried (Na_2SO_4) and evaporated. The residue was filtered through silica gel (*n*-hexane). After removal of the solvent 23.2g of a mixture of the indanes (identified via GC-MS) **7** ($M = 312.25$) and **6** ($M = 314.37$) was obtained.



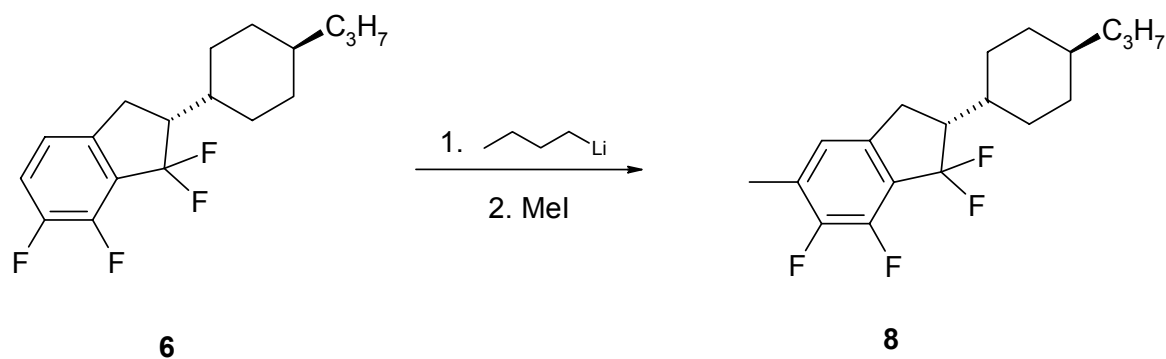
25.0g of the indane/indene mixture was dissolved in THF and was hydrogenated till the end of hydrogen uptake at ambient pressure. The solution was evaporated. The residue was filtered through silica gel (*n*-hexane). After removal of the solvent the solid was recrystallized from boiling methanol to obtain 19.3g of the indane **6** as colourless crystals.



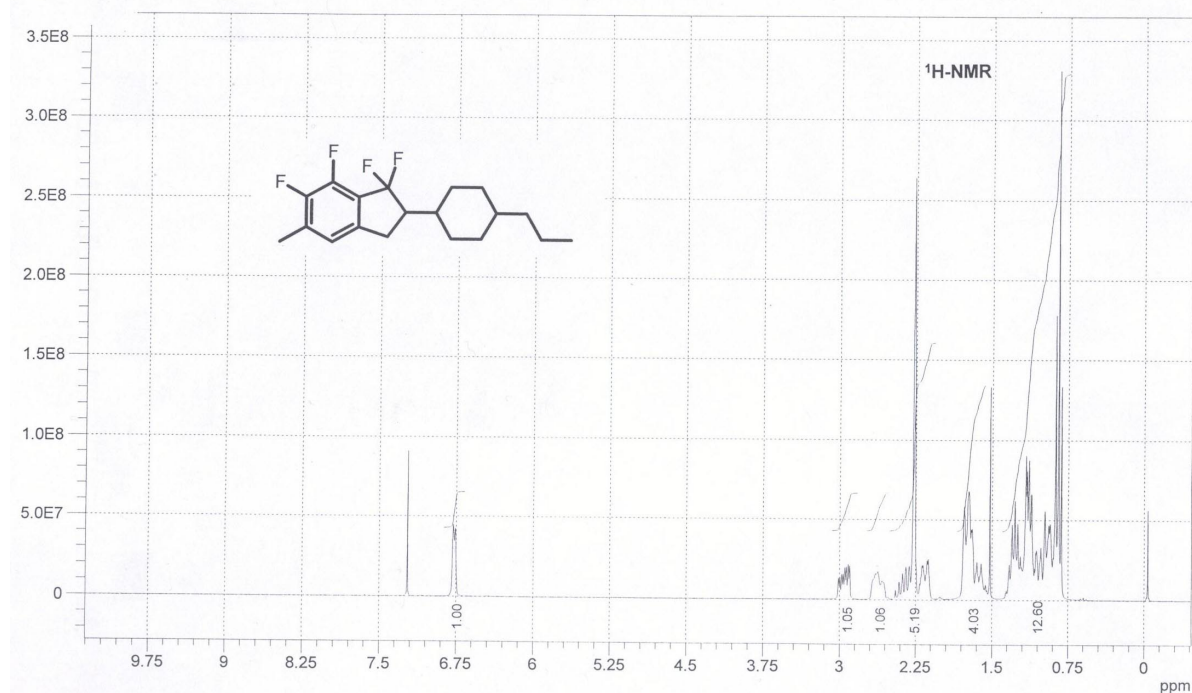
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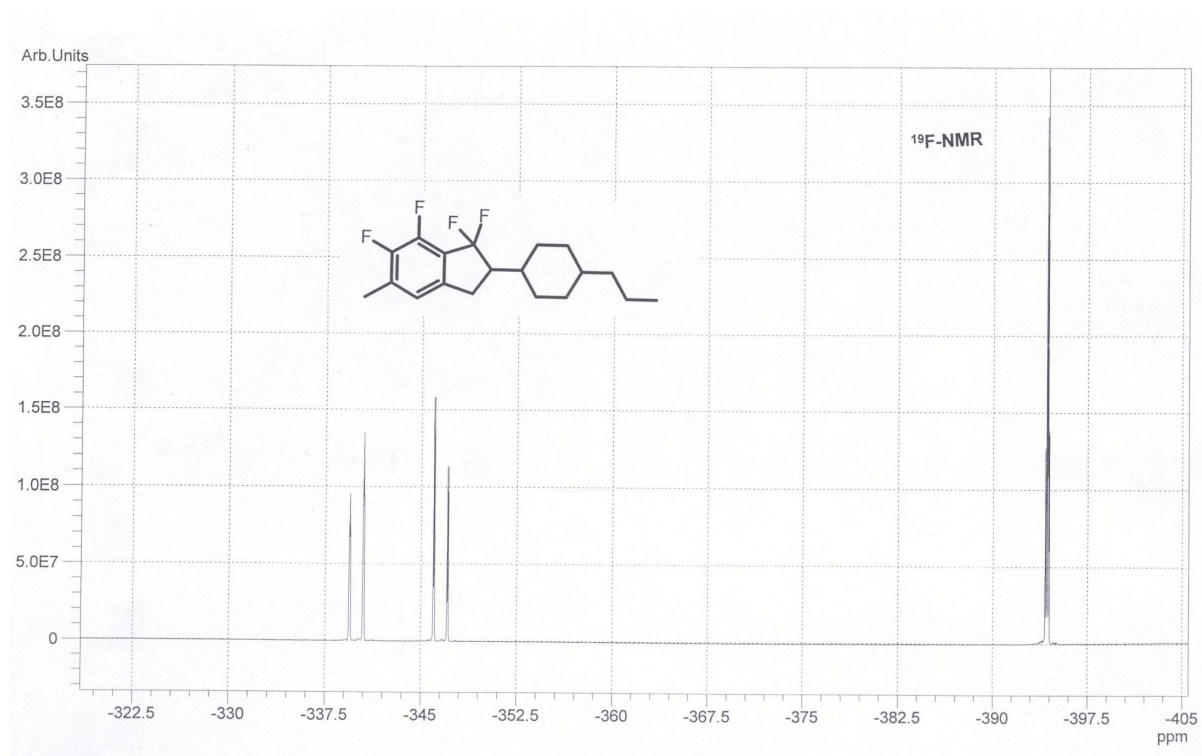
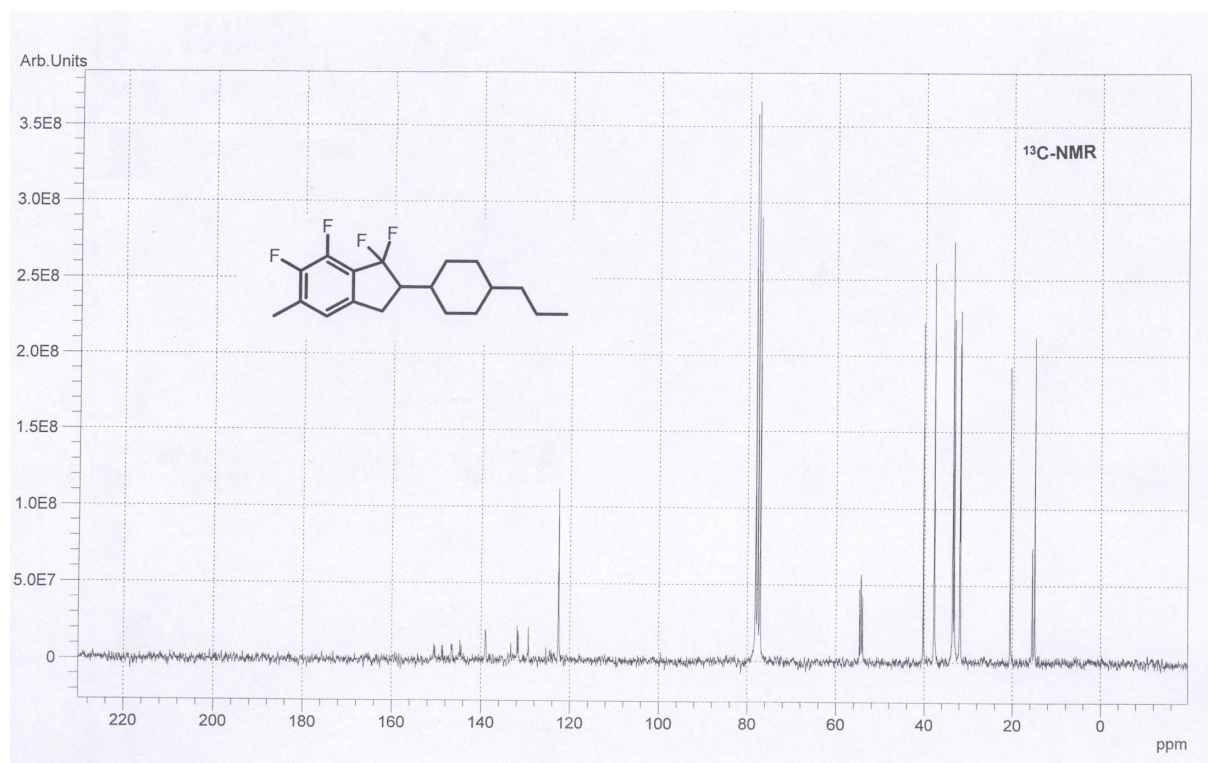
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Under nitrogen 11.3 ml (18.0 mmol) 15% $n\text{BuLi}$ in hexane was slowly added to a solution of 4.8g (15.3 mmol) indane **6** in 150 ml THF. After 1h 5.0 ml (80 mmol) methyl iodide were injected into the reaction mixture. The reaction was quenched with 2.3 ml trimethyl borate for additional 4h. The mixture was allowed to warm to 5°C and was acidified with 2N HCl. The aqueous layer was extracted three times with mtb-ether. The combined organic layers were washed with brine, dried (Na_2SO_4) and evaporated. The residue was filtered through silica gel (n -hexane). After removal of the solvent the solid was recrystallized from boiling methanol to obtain 3.0g (60%) indane **8** as colourless crystals.



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