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Total Synthesis of (±)-*cis*-Trikentrin A

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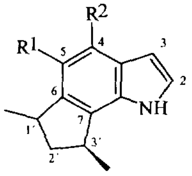
Abstract: Two pathways towards the construction of the trikentrin skeleton are presented, one leading to the total synthesis of (±)-*cis*-Trikentrin A (**1**). The key step is the intramolecular Heck coupling of the triflate **21** to form the five-membered ring of the indenes **22** and **23**.

INTRODUCTION

In the course of our investigations on the synthesis of indole alkaloids, we became interested in the trikentrins. Trikentrins[1](**1-5**) as well as the structurally related herbindoles[2] have been isolated from marine sponges *Trikentrion flabelliforme* and *Axinella* respectively and show cytotoxic activity. Both constitute a cyclopentane ring annulated to the benzene portion of the indole and the unusual nonsubstituted 2- and 3-positions of the indole (scheme 1).



R^1 = H	R^2 = Et	1′ Me: β	*cis*-trikentrin A (**1**)
	"	1′ Me: α	*trans*-trikentrin A (**2**)
R^1 = Buten-1-yl	R^2 = H	1′ Me: β	*cis*-trikentrin B (**3**)
	"	1′ Me: α	*trans*-trikentrin B (**4**)
R^1 = H	R^2 = Buten-1-yl	1′ Me: α	*iso*-trans-trikentrin B (**5**)

Scheme 1

The major challenge of their synthesis[3] represents the regioselective introduction of the functionalities to obtain the highly alkyl-substituted aromatic system present in the trikentrins and herbindoles. We envisaged to use the Heck reaction[4] to annulate the cyclopentane ring to the aromatic nucleus.

Two pathways were explored:

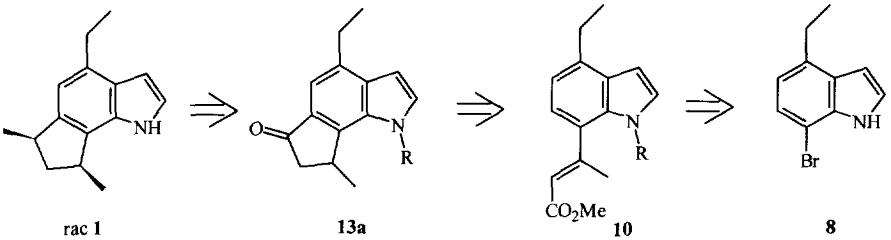
a. using the Heck reaction to attach a suitable side chain to the 7-position of the indole **9**, which was subsequently cyclized to form the five-membered-ring of **13a** (scheme 2) and

b. using an intramolecular Heck reaction to form the five-membered-ring of the nitroindane **22**, which was subsequently transformed into an indole (scheme 5).

RESULTS AND DISCUSSION

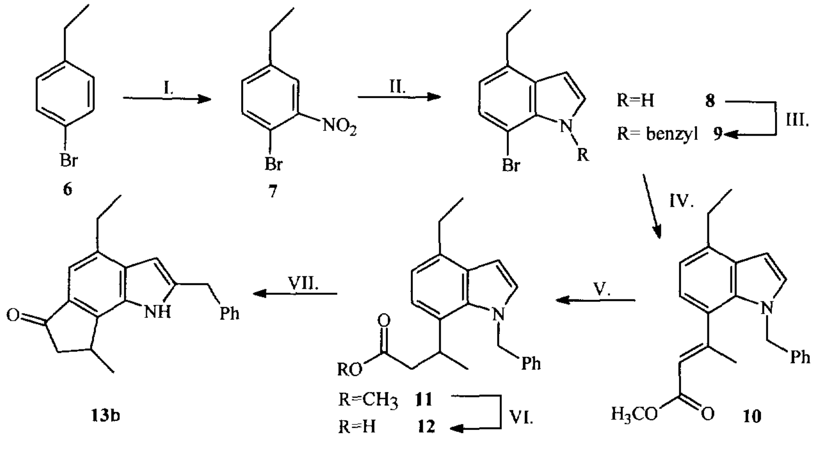
Pathway a.

Our initial strategy[5a,b] consisted of preparing the indole derivative **8**, employing a Heck reaction to attach a side chain and cyclizing it in a Friedel-Crafts manner to yield the ketone **13a**. Methylenation of the carbonyl group and catalytic hydrogenation would then afford (±)-*cis*-trikentrin A (**1**) (scheme 2).



Scheme 2

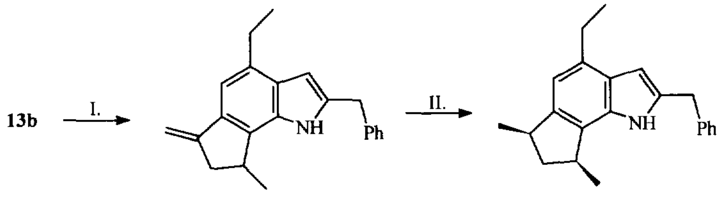
The bromoindole **8** was prepared starting from 4-ethyl-bromobenzene (**6**), which was nitrated and subsequently treated with 3 equivalents of vinylmagnesium bromide according to Bartoli's protocol[6]. After protecting the indole-nitrogen of **8** with benzyl bromide,[7] the bromoindole **9** was coupled with the methyl crotonate under Heck conditions. With tri(*o*-tolyl)phosphine as the ligand for palladium and an excess of the alkene satisfactory yields were obtained. Reduction of the conjugated double bond in **10** with magnesium in methanol[8] and saponification of the methyl ester **11** with potassium hydroxide in a *tert*-butanol/water mixture provided the acid **12** in good yield (scheme 3).



I. 100% HNO_3, 0°C, 3h, 37%; II. 3 eq. vinylmagnesium bromide, THF, -40°C, 25 min, 47%; III. KOH, DMSO, rt., 1h, then BnBr, 0°C, 1h, 89%; IV. methyl crotonate, 4 mol% $Pd(OAc)_2$, 9 mol% $P(o\text{-tolyl})_3$, NEt_3, CH_3CN, 115°C, 14h, 61%; V. 10 eq. Mg, dry MeOH, 1.5h, 86%; VI. KOH, t-BuOH/H_2O (20:1), 90°C, 3.5h, 85%; VII. polyphosphoric acid, 85°C, 3.5h, 58%.

Scheme 3

Upon treatment with polyphosphoric acid (PPA), the Friedel-Crafts cyclization of **12** was unexpectedly accompanied with rearrangement of the benzyl group into the 2-position. To explore the feasibility of introducing a methyl group at C-6, the rearranged ketone **13b** was methylenated employing dimethyltitanocene.[9] This was followed by hydrogenation with H_2 and Pd-C to give the racemic 2-benzyl derivative of *cis*-Trikentrin A (**15**) (scheme 4).



14 rac **15**

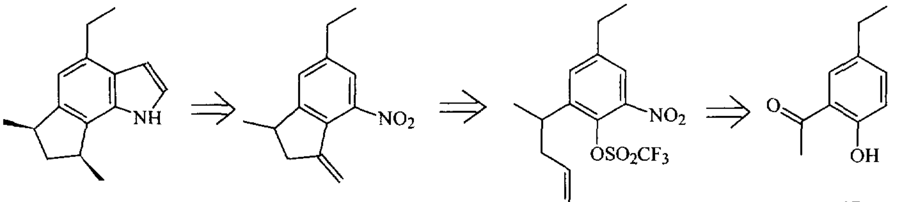
I. 3 eq.Cp_2TiMe_2, THF, 65°C, 17h; II. Pd-C (5%), 1 atm H_2, MeOH, rt., 4h, 40% (overall yield I. and II.)

Scheme 4

To avoid the benzyl rearrangement, a modified method of cyclization as well as an exchange of the protective group were examined,[5c] but only unsatisfactory results were obtained.

Pathway b.

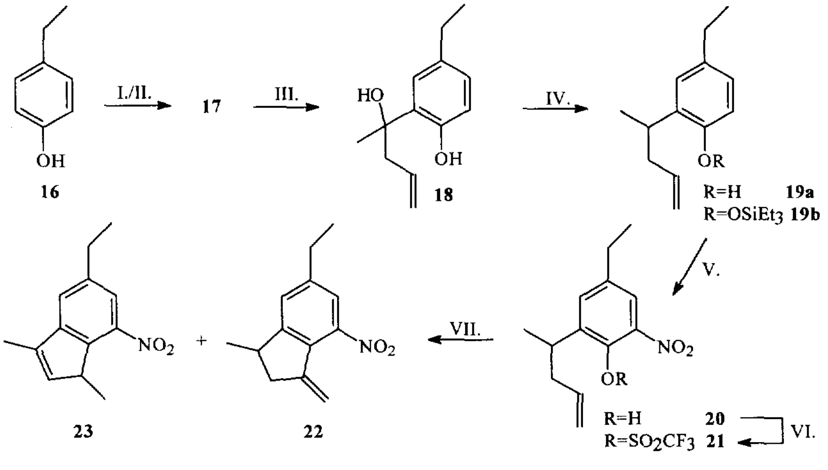
In our alternative approach, the intramolecular Heck reaction of an aryltriflate[10] was utilized to effect ring closure to the 5-membered ring of the indane **22**. The corresponding retrosynthetic analysis is shown in scheme 5.



rac **1** **22** **21** **17**

Scheme 5

The triflate **21** was efficiently prepared starting from 4-ethyl-phenol (**16**) (scheme 6). **16** was acylated according to Effenberger's protocol[11] and, without purification, subjected to Fries rearrangement[12] to yield the ketone **17** in 76 % overall yield. Allylmagnesium chloride added smoothly to the carbonyl group of **17** to give the tertiary alcohol **18** nearly quantitatively. The deoxygenation[13] of **18** with triethylsilane and trifluoroacetic acid provided a mixture of the phenol **19a** and the silylether **19b** in a combined yield of 80 %. The products could easily be separated by chromatography and were nitrated with concentrated nitric acid in different solvents (**19a**: hexane; **19b**: acetic acid). In both cases, the nitrophenol **20** was obtained in 70 % yield. The trifluoromethanesulphonyl group was next introduced by treating **20** with trifluoromethanesulphonic anhydride and 2,4,6-collidine (88 % yield of **21**).[14]



I. CH_3COCl, CF_3SO_3H (cat.), CH_2Cl_2, rt., 30 min; II. $AlCl_3$, 140°C, 15 min, 76% (overall yield I. and II.); III. allylmagnesium chloride, THF, 0° to 65°C, 25 min, 96%; IV. Et_3SiH, CF_3CO_2H, CH_2Cl_2, rt., 30 min, 47% **19a** , 35% **19b**; V. 65% HNO_3, hexane (for **19a**) or CH_3CO_2H (for **19b**), rt., 2h, 69%; VI. $(CF_3SO_2)_2O$, 2,4,6-collidine, CH_2Cl_2, -20°C, 2h, 88%; VII. $Pd(OAc)_2$ (5.5 mol%), PPh_3(11 mol%), Et_4NCl, Et_3N, CH_3CN/H_2O (25:1), rt. to 50°C, 1h, 42% **22**, 32% **23**.

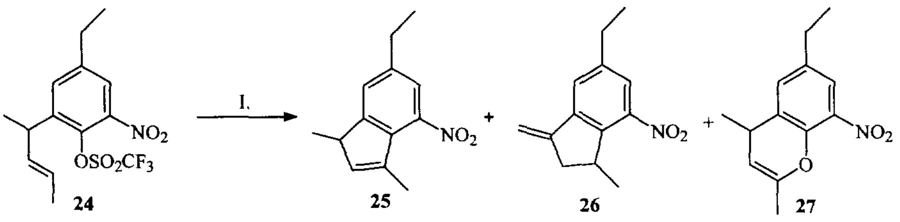
Scheme 6

Interestingly, the triflate **21** did not undergo the intramolecular Heck reaction until small amounts of water, typically about 5 % of the solvent volume, were added to the reaction mixture. Two isomeric products **22** and **23**, the structures of which were assigned on the basis of NOE-experiments, were formed in good yield. Either 5 mol% $Cl_2Pd(PPh_3)_2$ or 5 mol% $Pd(OAc)_2$ and 10 mol% PPh_3 could be used as catalysts. Both, acetonitrile and N,N-dimethylformamide turned out to be suitable organic solvents.

Very recently, Jeffery[15] reported that water can considerably accelerate the rate and thereby improve the yield of Heck couplings carried out in the presence of tetrabutylammonium salts. However, we observed constant yields around 80 % for **22** and **23** in the presence and in the absence of tetraethylammonium chloride or/and LiCl as additives when employing a water containing solvent system. Nevertheless the additives affected the product ratio. With LiCl (3 eq.) only the isomer **23** was formed; with Et_4NCl (1 eq.) isomer **22** was favoured over **23** with a 4:3 ratio.

The isomerization of the double bond, examplified by **23**, results from repeated Pd-H-elimination and -addition and is not an unusual phenomenon following a Heck type reaction.[4]

Apart from water as a necessary additive, the mode of ring closure appeared to be crucial. The isomeric triflate[5c] **24** containing an internal double bond required more drastic conditions for conversion and gave, in addition to decomposition, only low yields of the desired cyclization products **25** and **26** (scheme 7).



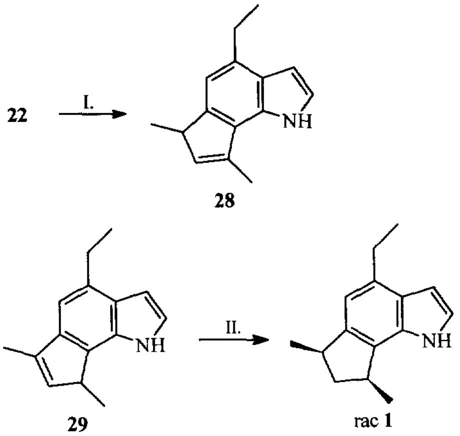
I. Pd(OAc)$_2$ (12 mol%), PPh$_3$ (24 mol%), Et$_4$NCl, K$_2$CO$_3$, LiCl, DMF, 100°C, 5h, 25% (combined yield of **25**, **26** and **27**)

Scheme 7

These experiments confirm results[16] recently reported, that cyclizations catalyzed by transition metals obey the Baldwin rules. The ring closure of triflate **21** represents the favoured 5-*exo*-trig mode, whereas that of triflate **24** represents the 5-*endo*-trig mode.

Both isomers **22** and **23** were transformed into the indoles **28** and **29** respectively by Bartoli's method[6](scheme 8). The indole syntheses proceeded with unsatisfactory yield and with another double-bond isomerization when converting **22** into **28**.

Simple hydrogenation of **29** with 1 atm H$_2$ and Pd-C diastereoselectively provided the racemic *cis*-Trikentrin A (**1**) in 80 % yield. The NMR and mass spectra of the synthetic material correspond to those reported[1] for the natural material (scheme 8).



I. vinylmagnesium bromide (3eq.), THF, -50°C, 25 min, 10% **28**, 14% **29**; II. 1 atm H$_2$, Pd-C (10%), MeOH, rt., 22h, 80%.

Scheme 8

EXPERIMENTAL

Melting points (mp) were determined on a Büchi SMP 20 apparatus and are not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WH 90, AC 200 and AM 400 spectrometers. The chemical shifts δ are reported in parts per million (ppm) relative to CHCl$_3$ as internal standard. The ^{1}H NMR signal multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, br = broadened) and the coupling constants J in Hz are given in brackets. The number of protons bound to each carbon atom was determined by DEPT-experiments and is reported with the corresponding ^{13}C NMR signals. Infrared-spectra (IR) were recorded on Perkin-Elmer 157 G and 881 and on a Nicolet Magna FTIR spectrometer with the sample as a $CHCl_3$- or CCl_4-solution and the intensities of the bands as indicated (s = strong, m = medium, w = weak). Mass spectra as well as high-resolution mass spectra were recorded with A.E.I. MS 30 and MS 50 and a Varian MAT 711 with an EI-potential of 70 eV (relative peak intensities given in brackets). Microanalyses were obtained from a Perkin-Elmer CHNO/S-Analysator 2400. Flash chromatography was performed on Baker or Merck silica gel (0.04-0.06 mm), preparative thin-layer chromatography was performed on ICN Silica-Rapid-plates F 254 (0.25 mm thick) and analytical thin-layer chromatography was carried out with Merck Kieselgel 60 F 254 aluminium sheets. Solvents were distilled prior to use and dried when anhydrous conditions were applied (tetrahydrofuran from potassium, diethyl ether from sodium benzophenone ketyl, benzene and dichloromethane from calcium hydride and methanol from magnesium). Various Heck couplings were performed in thick-walled Wheaton Reacti-Vials (volume 5 mL) or Schott glass bottles (volume 50 mL).

7-Bromo-4-ethyl-indole (8). A solution of 1-bromo-4-ethyl-2-nitro-benzene (**7**, 5.20 g) in dry tetrahydrofuran (50 mL) was cooled to -50°C under an atmosphere of argon. Under vigorous stirring, a solution of vinylmagnesium bromide (68 mmol, 3 eq.), prepared from 1.66 g (68 mmol) magnesium and 5.9 mL (82 mmol) vinyl bromide, in dry tetrahydrofuran (50 mL) was added within 3 min. The dark reaction mixture was stirred at -40°C for 25 min, quenched with sat. ammonium chloride solution (100 mL) and extracted with tert-butyl methyl ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (petroleum ether/tert-butyl methyl ether 10:1) afforded 2.40 g (47 %) of **7** as a brown oil. *^1H NMR* (90 MHz, $CDCl_3$): δ 8.3 (s, br, 1 H, NH); 7.29 (d, 3.4 Hz, 1 H); 7.24 (d, 4 Hz, 1 H); 6.84 (d, 7.5 Hz, 1 H); 6.67 (dd, 4/2 Hz, 1 H); 2.89 (q, 8 Hz, 2 H); 1.30 (t, 8 Hz, 3 H); *IR* ($CHCl_3$): 3490 (s), 3020 (m), 2980 (m), 2950 (m), 1490 (m), 1460 (m), 1420 (m), 1350 (s), 1135 (m), 820 (m), 730 (m) cm^{-1}; *MS*: m/z 225 (M^++2, 44), 223 (M^+, 47), 210 (95), 208 (100), 144 (24), 129 (22), 115 (22); *exact mass* calcd. for $C_{10}H_{10}NBr$: 222.9997, found: 222.9961.

1-Benzyl-7-bromo-4-ethyl-indol (9). Powdered potassium hydroxide (2.80 g, 50 mmol) was suspended in dimethylsulphoxide, before a solution of **8** (2.70g, 12 mmol) in dimethylsulphoxide (10 mL) was added. The mixture was stirred for 1 h at room temperature, then cooled to 0°C, treated with benzyl bromide (1.7 ml, 14 mmol) and stirred for 1 h at room temperature. The mixture was poured into water and extracted with diethyl ether (5x). After washing the combined organic layers with water, drying ($MgSO_4$) and removal of the solvents, the residue was purified by flash chromatography (petroleum ether/ethyl acetate 40:1) to give **9** (3.37 g, 89 %) as a yellow oil. *^1H NMR* (200 MHz, $CDCl_3$): δ 7.4-7.2 (m, 6 H); 7.09 (d, 3.3 Hz, 1 H); 7.0 (m, 2 H); 6.79 (d, 7.5 Hz, 1 H); 6.60 (d, 3.3 Hz, 1 H); 5.82 (s, 2 H); 2.90 (q, 7.5 Hz, 2 H); 1.34 (t, 7.5 Hz, 3 H); *IR* ($CHCl_3$): 3000 (w), 2960 (w), 1480 (m), 1440 (m), 1350 (m) cm^{-1}; *MS*: m/z 315 (M^++2, 17), 313 (M^+, 18), 300 (4), 298 (4), 91 (100); *exact mass* calcd. for $C_{17}H_{16}NBr$: 313.0466, found: 313.0466.

3-(7-(1-Benzyl-4-ethyl)-indolyl)-but-2-enoic acid methylester (10). A mixture of **9** (2.75 g, 8.76 mmol), methyl crotonate (15 mL, 141 mmol), $Pd(OAc)_2$ (89 mg, 4.3 mol%), tri(*o*-tolyl)phosphine (282 mg, 10 mol%), triethylamine (1.5 mL, 10 mmol) and acetonitrile (5 mL) were heated in a thick-walled glass bottle for 14 h at 115°C. After cooling, the precipitated ammonium salt was filtered off and thoroughly washed with tert-butyl methyl ether. The filtrate was concentrated under reduced pressure and purified by flash chromatography (petroleum ether/tert-butyl methyl ether 10:1) to afford **10** (1.80 g, 61 %) as a yellow crystalline solid (mp. 61°C). *^1H NMR* (200 MHz, $CDCl_3$): δ 7.3-7.2 (m, 3 H); 7.10 (d, 3.3 Hz, 1 H); 6.93 (dt, 7/1 Hz, 1 H); 6.82 (d, 7 Hz, 1 H); 6.8 (m, 2 H); 6.65 (d, 3.3 Hz, 1 H); 5.72 (q, 1.5 Hz, 1 H); 5.35 (m, 2 H); 3.70 (s, 3 H); 2.97 (q, 7.7 Hz, 2 H); 2.27 (d, 1.5 Hz, 3 H); 1.38 (t, 7.7 Hz, 3 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 166.8 (Cq), 156.4 (Cq), 138.2 (Cq), 136.5 (Cq), 133.2 (Cq), 131.7 (Cq), 130.2 (CH), 129.5 (Cq), 128.6 (CH), 127.3 (CH), 126.2 (CH, 2 C), 121.8 (CH), 119.7 (CH), 117.7 (CH), 100.6 (CH), 52.1 (CH_3), 51.0 (CH_2), 26.0 (CH_2), 21.9 (CH_3), 14.6 (CH_3); *IR* ($CHCl_3$): 3000 (m), 2980 (m), 1710 (s), 1630 (m), 1500 (m), 1460 (m), 1440 (m), 1340 (m), 1165 (m), 720 (m), 695 (m) cm^{-1}; *MS*: m/z 333 (M^+, 75), 304 (9), 274 (15), 260 (54), 244 (16), 196 (14), 168 (12), 91 (100); *Anal.* calcd. for $C_{22}H_{23}NO_2$: C 79.25, H 6.95, N 4.20, found: C 79.13, H 6.94, N 4.18.

3-(7-(1-Benzyl-4-ethyl)-indolyl)-butanoic acid methylester (11). Dry methanol (15 mL) was added to a mixture of **10** (1.02 g, 3.06 mmol) and magnesium turnings (730 mg, 30 mmol). The reaction vessel was cooled as a considerable evolution of heat and hydrogen started. After stirring for 1.5 h at room temperature, the magnesium was completely dissolved and the reaction mixture was poured into ice (200 mL) and dilute hydrochloric acid (15 mL). Extraction with tert-butyl methyl ether, washing of the combined organic layers with brine and removal of the solvents under reduced pressure was followed by flash chromatography (petroleum ether/tert-butyl methyl ether 10:1) to give **11** (877 mg, 85 %) as a colourless syrup. *^1H NMR* (200 MHz, $CDCl_3$): δ 7.3-7.2 (m, 3 H); 7.12 (d, 3 Hz, 1 H); 7.05-6.9 (m, 4 H); 6.62 (d, 3 Hz, 1 H); 5.77 (d, 17.3 Hz, 1H); 5.52 (d, 17.3 Hz, 1 H); 3.82 (m, 1 H); 3.58 (s, 3 H); 2.98 (q, 7.7 Hz, 2 H); 2.61 (dd, 15.2/5.5 Hz, 1 H); 2.45 (dd, 15.2/9.2 Hz, 1 H); 1.35 (t, 7.7 Hz, 3 H); 1.04 (d, 6.7 Hz, 3 H); *^{13}C NMR* (50.32 MHz,

$CDCl_3$): δ 173.0 (Cq), 139.1 (Cq), 134.5 (Cq); 132.8 (Cq), 131.0 (CH), 129.8 (Cq), 128.7 (CH, 2 C), 127.7 (Cq), 127.2 (CH), 125.7 (CH, 2 C), 119.6 (CH), 118.3 (CH), 100.0 (CH), 53.2 (CH_2), 51.3 (CH_3), 43.1 (CH_2), 29.7 (CH), 25.9 (CH_2), 21.7 (CH_3), 14.5 (CH_3); *IR* ($CHCl_3$): 3000 (w), 2960 (m), 1730 (s), 1500 (m), 1450 (m), 1290 (m) cm^{-1}; *MS*: m/z 335 (M^+, 100), 304 (5), 276 (5), 262 (97), 246 (12), 234 (20), 212 (9), 170 (6), 91 (50); *exact mass* calcd. for $C_{22}H_{25}NO_2$: 335.1895, found: 335.1878.

3-(7-(1-Benzyl-4-ethyl)-indolyl)-butanoic acid (12). A mixture of **11** (1.03 g, 3.05 mmol) and KOH (672 mg, 12 mmol) were heated in *tert*-butanol (15 mL) and H_2O (0.75 mL) for 3.5 h at 90°C. The mixture was poured into ice (100 mL) and dilute hydrochloric acid (10 mL), extracted with tert-butyl methyl ether, the combined organic layers were washed with brine and dried over $MgSO_4$. The solvents were removed in vacuo, and flash chromatography (dichloromethane/methanol 200:1) afforded **12** (830 mg, 85 %) as a colourless solid (mp. 44°C). *^1H NMR* (200 MHz, $CDCl_3$): δ 7.25-7.15 (m, 3 H); 7.13 (d, 3.4 Hz, 1 H); 7.0-6.9 (m, 4 H); 6.63 (d, 3.4 Hz, 1 H); 5.73 (d, 17.3 Hz, 1 H); 5.53 (d, 17.3 Hz, 1 H); 3.84 (m, 1H); 2.95 (q, 7.7 Hz); 2.66 (dd, 15.7/5.5 Hz, 1 H); 2.49 (dd, 15.7/8.9 Hz, 1 H); 1.37 (t, 7.7 Hz, 3 H); 1.10 (d, 6.8 Hz, 3 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 178.7 (Cq), 138.9 (Cq), 134.6 (Cq), 132.8 (Cq), 131.1 (CH), 129.8 (Cq), 128.8 (CH, 2 C), 127.5 (Cq), 127.4 (CH), 125.8 (CH, 2 C), 119.6 (CH), 118.4 (CH), 100.1 (CH), 53.3 (CH_2), 43.0 (CH_2), 29.6 (CH), 25.9 (CH_2), 22.0 (CH_3), 14.5 (CH_3); *IR* ($CHCl_3$): 3500-2500 (br), 3010 (m), 2980 (m), 2940 (m), 1710 (s), 1500 (m), 1455 (m), 1410 (m), 1300 (m), 915 (w), 825 (w), 725 (m), 700 (m) cm^{-1}; *MS*: m/z 322 (M^++1, 20), 321 (M^+, 100), 263 (18), 262 (95), 234 (12), 172 (10), 91 (95); *Anal.* calcd. for $C_{21}H_{23}NO_2$: C 78.47, H 7.21, N 4.36, found: C 78.38, H 7.17, N 4.34.

2-Benzyl-4-ethyl-8-methyl-7,8-dihydro-1H-1-aza-as-indacen-6-one (13b). The acid **12** (283 mg, 0.88 mmol) was added to pre-warmed polyphosphoric acid (15 mL) and heated for 3.5 h at 85°C with stirring. The mixture was cautiously hydrolyzed with ice, then extracted with dichloromethane and the combined organic phases concentrated under reduced pressure. Flash chromatography (dichloromethane/methanol 200:1) gave **13b** (154 mg, 58 %) as a light-brown solid (mp. 182-184°C). *^1H NMR* (200 MHz, $CDCl_3$): δ 8.31 (br, NH), 7.4-7.2 (m, 6 H), 6.49 (d, 2 Hz, 1 H), 4.22 (s, 2 H), 3.59 (m, 1 H), 2.96 (dd, 18.5/7.5 Hz, 1 H), 2.90 (q, 7.7 Hz, 2 H), 2.32 (dd, 18.5/2.5 Hz, 1 H), 1.43 (d, 7.5 Hz, 3 H), 1.35 (t, 7.7 Hz, 3 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 205.9 (Cq), 142.4 (Cq), 141.1 (Cq), 137.9 (Cq), 136.1 (Cq), 133.6 (Cq), 131.6 (Cq), 131.2 (Cq), 129.0 (CH, 2 C), 128.9 (CH, 2 C), 127.1 (CH), 112.9 (CH), 101.7 (CH), 45.7 (CH_2), 34.9 (CH_2), 30.7 (CH), 26.1 (CH_2), 21.1 (CH_3), 14.4 (CH_3); *IR* ($CHCl_3$): 3500-3200 (br), 3460 (w), 3000 (w), 2960 (m), 2920 (m), 1680 (s), 1610 (m), 1540 (m) cm^{-1}; *MS*: m/z 303 (M^+, 100), 288 (72), 260 (7), 154 (6), 131 (7), 91 (17).

2-Benzyl-4-ethyl-6,8-dimethyl-1,6,7,8-tetrahydro-1-aza-as-indacene (15). A suspension of dichlorotitanocene (112 mg, 0.45 mmol) in dry tetrahydrofuran (3 mL) was cooled to -78°C and treated with 1.6 M methyllithium solution (diethyl ether) under argon and with protection against light. A solution of **13b** (30 mg, 0.14 mmol) in dry tetrahydrofuran (2 mL) was added to the dimethyltitanocene solution at room temperature, and the mixture was heated to reflux for 17 h in the dark. Then the reaction mixture was poured into sat. ammonium chloride solution, extracted with dichloromethane and concentrated in vacuo. Palladium-on-charcoal (5%, 1 mg) and dry methanol (3 mL) were added to the residue, and the mixture was stirred at room temperature for 4 h under a hydrogen atmosphere (H_2-balloon). The catalyst was filtered off, and the filtrate was concentrated and purified by preparative thin layer chromatography (dichloromethane/petroleum ether 1:1) to afford **15** (12 mg, 40 %) as a nearly colourless oil. *^1H NMR* (400 MHz, $CDCl_3$): δ 7.7 (s, br, NH), 7.35-7.25 (m, 5 H), 6.79 (s, 1 H), 6.45 (dt, 2.1/1 Hz, 1 H), 4.14 (s, 2 H), 3.34 (m, 1 H), 3.18 (m, 1 H), 2.88 (qd, 7.5/2.4 Hz, 2 H), 2.55 (ddd, 12.3/7.5/7.5 Hz, 1 H), 1.38 (d, 6.9 Hz, 3 H), 1.34 (d, 6.9 Hz, 3 H), 1.33 (t, 7.5 Hz, 3 H), 1.3-1.2 (m, 1 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 142.5 (Cq), 138.9 (Cq), 136.2 (Cq), 134.4 (Cq), 132.9 (Cq), 128.8 (CH, 2 C), 128.7 (CH, 2 C), 127.0 (Cq), 126.7 (CH), 114.0 (CH), 100.1 (CH), 44.7 (CH_2), 38.9 (CH), 37.1 (CH), 34.8 (CH_2), 26.5 (CH_2), 21.1 (CH_3), 20.8 (CH_3), 15.1 (CH_3); *IR* ($CHCl_3$): 3450 (w), 2980 (m), 2940 (m), 2920 (m), 2860 (w), 1600 (m), 1440 (m), 1090 (m) cm^{-1}; *MS* : m/z 303 (M^+, 90), 302 (12), 289 (24), 288 (100), 274 (9). 258 (6), 197 (15), 182 (12), 168 (9), 91 (15); *exact mass* calcd. for $C_{22}H_{25}N$: 303.2016, found: 303.2001.

1-(4-Ethyl-2-hydroxy-phenyl)-ethan-1-one (17). A solution of the phenol **16** (6.1 g, 50 mmol) in dry dichloromethane (25 mL) was treated with 0.15 ml (3 mol%) trifluoromethanesulphonic acid and dropwise with a solution of acetyl chloride (4.0 mL, 56 mmol) in dichloromethane (10 mL). After stirring at room temperature for 30 min, the mixture was diluted with 35 mL dichloromethane and washed with water and $NaHCO_3$-solution. Then the solvent was evaporated and the residue kept under vacuum until no loss of weight was observed any more. The raw material was pure enough to be subjected to the Fries rearrangement. To this end, the acetate (6.96 g, 41.9 mmol) was mixed with small portions of $AlCl_3$ (7.3 g, 55 mmol) - *Caution*: HCl-evolution. The mixture was then heated in a prewarmed oil bath at 140°C for 15 min. After cooling, the glassy substance was suspended with 15 mL of conc. hydrochloric acid, 20 mL of water and 20 mL of dichloromethane. The layers were separated and the aqueous layer was extracted with tert-butyl methyl ether. The combined organic layers were washed with $NaHCO_3$-solution and brine, dried over $MgSO_4$ and concentrated. The residue was distilled (Kugelrohr, 0.3 bar, 75°C) to give 6.3 g (76 %) of **17** as a colourless oil. *^{1}H NMR* (400 MHz, $CDCl_3$): δ 7.52 (d, 2 Hz, 1 H); 7.32 (dd, 8.5/2 Hz, 1 H); 6.91 (d, 8.5 Hz, 1 H); 2.64 (s, 3 H); 2.61 (q, 7.5 Hz, 2 H); 1.23 (t, 7.5 Hz, 3 H); *IR* ($CHCl_3$): 3500-3100 (br), 3028 (m), 2970 (m), 2935 (w), 2876 (w), 1643 (vs), 1618 (m), 1592 (m), 1486 (s), 1371 (s), 1299 (s), 961 (m), 838 (m), 635 (m) cm^{-1}; *MS*: m/z 164 (M^+, 40), 149 (100), 131 (20), 91 (10), 77 (20); *exact mass* calcd. for $C_{10}H_{12}O_2$: 164.0837, found: 164.0837.

4-Ethyl-2-(1-hydroxy-1-methyl-but-3-enyl)-phenol (18). A solution of the ketone **17** (3.47 g, 20.9 mmol) in dry tetrahydrofuran (50 mL) was cooled to 0°C under an argon atmosphere, before 22.5 mL (45 mmol) of a 2 M allylmagnesium chloride solution (Aldrich) were added within 5 min. The reaction mixture was heated at 65°C for 20 min, then cooled and quenched with 10 mL ammonium chloride solution and 50 mL brine. After extraction with tert-butyl methyl ether, the organic layers were combined, dried over $MgSO_4$ and concentrated followed by flash chromatography (petroleum ether/ tert-butyl methyl ether 10:1) to give **18** (4.32 g, 96 %) as a colourless oil. *^{1}H NMR* (400 MHz, $CDCl_3$): δ 8.86 (br, 1 H); 6.99 (dd, 8/2 Hz, 1 H); 6.85 (d, 2 Hz, 1 H); 6.80 (d, 8 Hz, 1 H); 5.81 (m, 1 H); 5.23 (d, 10 Hz, 1 H); 5.22 (d, 17 Hz, 1 H); 2.85 (dd, 14/7 Hz, 1 H); 2.63 (s, 1 H); 1.56 (q, 7.5 Hz, 2 H); 2.54 (m, 1 H); 1.62 (s, 3 H); 1.20 (t, 7.5 Hz, 3 H); *IR* ($CHCl_3$): 3600-3550 (br), 3550-3200 (br), 2970 (m), 2935 (w), 2875 (w), 1495 (s), 1378 (m), 1235 (s), 1070 (m), 1034 (m), 831 (m), 665 (m) cm^{-1}; *MS* : m/z 206 (M^+, 1), 205 (2), 188 (M^+-H_2O, 25), 173 (188-CH_3, 100), 159 (50), 91 (30); *exact mass* calcd. for $C_{13}H_{18}O_2$: 206.1307, found: 206.1307.

4-Ethyl-2-(1-methyl-but-3-enyl)-phenol (19a) and 1-Ethyl-3-(1-methyl-but-3-enyl)-4-triethylsilyloxy-benzene (19b). A solution of the alcohol **18** (4.07 g, 19.6 mmol) in dry dichloromethane (90 mL) was cooled to 0°C and treated with 3.45 mL (21.5 mmol) triethylsilane under argon. Then 16 mL (210 mmol) trifluoroacetic acid were slowly added with external cooling. After the exothermic reaction had ceased, the mixture was stirred at room temperature for 30 min, then neutralized with dilute NaOH-solution/ice. After concentrating the organic layer and purifying the residue by flash chromatography (petroleum ether/tert-butyl methyl ether 20:1), two products **19a** (1.76 g, 47 %) and **19b** (2.09 g, 35 %) were obtained as colourless oils. **19a**: *^{1}H NMR* (400 MHz, $CDCl_3$): δ 6.99 (d, 2 Hz, 1 H); 6.90 (dd, 8/2 Hz, 1 H); 6.67 (d, 8 Hz, 1 H); 5.78 (ddt, 17/10/7 Hz, 1 H); 5.04 (d, 17 Hz, 1 H); 4.99 (d, 10 Hz, 1 H); 4.58 (s, 1 H); 3.12 (m, 1 H); 2.57 (q, 7.5 Hz, 2 H); 2.43 (m, 1 H); 2.29 (m, 1 H); 1.26 (d, 7 Hz, 3 H); 1.21 (t, 7.5 Hz, 3 H); *IR* ($CHCl_3$): 3616 (m), 2967 (m), 2932 (m), 2874 (w), 1641 (w), 1505 (m), 1456 (w), 1431 (w), 1323 (w), 1255(m), 1181 (m), 914 (m) cm^{-1} *MS*: m/z 190 (M^+, 10), 149 (M^+-C_3H_5, 10), 133 (5), 115 (5), 91 (10), 77 (8); *exact mass* calcd. for $C_{13}H_{18}O$ 190.1358, found 190.1358; *Anal.* calcd. C: 82.06 H: 9.53, found C: 81.76 H: 10.02. **19b**: *^{1}H NMR* (400 MHz, $CDCl_3$): δ 6.97 (d, 2 Hz, 1 H); 6.87 (dd, 8/2 Hz, 1 H); 6.69 (d, 8 Hz, 1 H); 5.76 (dddd, 15.5/10/7.5/6 Hz, 1 H); 5.01 (dq, 15/1.5, 1 H); 4.90 (d, 10 Hz, 1 H); 3.21 (m, 1 H); 2.57 (q, 7.5 Hz, 2 H); 2.40 (m, 1 H); 2.20 (m, 1 H); 1.21 (t, 7.5 Hz, 3 H); 1.19 (d, 7 Hz, 3 H); 1.01 (t, 8 Hz, 9 H); 0.78 (q, 8 Hz, 6 H); *IR* ($CHCl_3$): 2964 (m), 2937 (w), 2879 (m), 1641 (w), 1495 (m), 1449 (w), 1416 (w), 1267 (m), 1018 (m), 926 (m), 730 (m) cm^{-1} ; *MS*: m/z 304 (M^+, 15), 263 (M^+-C_3H_5, 100), 235 (10), 115 (20), 87 (25), 59 (20); *exact mass* calcd. for $C_{19}H_{32}OSi$: 304.2222, found: 304.2222.

4-Ethyl-2-(1-methyl-but-3-enyl)-6-nitro-phenol (20). *Preparation starting from 19a:* To a solution of **19a** (1.68 g, 8.58 mmol) in hexane (20 mL), was dropwise added 65 % nitric acid (0.8 mL, 11.3 mmol). The yellow-coloured mixture was stirred at room temperature for 2 h, then H_2O (30 mL) was added, the layers were separated and the aqueous layer extracted with tert-butyl methyl ether. After drying ($MgSO_4$) the organic layers from the nitrations of **19a** and **19b** were combined, concentrated and purified by flash chromatography (petroleum ether/tert-butyl methyl ether 20:1) to yield **20** (2.48 g, 69 %) as a yellow oil. *Preparation starting from 19b:* A solution of **19b** (2.02 g, 6.64 mmol) in glacial acetic acid was treated with 65 % nitric acid (0.7 mL, 10 mmol) and stirred at room temperature for 2 h, before the mixture was neutralized with a cold dilute sodium hydroxide solution. After extraction (tert-butyl methyl ether) and drying ($MgSO_4$) the organic layer was combined with that from nitration of **19a**. *^{1}H NMR* (200 MHz, $CDCl_3$): δ 10.93 (s, 1 H); 7.78 (d, 2 Hz, 1 H); 7.30 (d, 2 Hz, 1 H); 5.73 (ddt, 17/10/7 Hz, 1 H); 5.00 (d, 17 Hz, 1 H); 4.97 (d, 10 Hz, 1 H); 3.37 (m, 1 H); 2.62 (q, 7.5 Hz, 2 H); 2.50-2.25 (m, 2 H); 1.24 (d, 7 Hz, 3 H); 1.23 (t, 7.5 Hz, 3 H); *^{13}C-NMR* (50.3 MHz, $CDCl_3$): δ 151.3 (Cq), 137.4 (Cq), 136.5 (CH), 135.4 (Cq), 135.2 (CH), 133.3 (Cq), 120.7 (CH), 116.3 (CH_2), 40.6 (CH_2), 32.0 (CH), 27.9 (CH_2), 19.7 (CH_3), 15.2 (CH_3); *IR* ($CHCl_3$): 3600-3100 (br), 2971 (m), 2936 (w), 2878 (w), 1625 (m), 1542 (s), 1467 (m), 1432 (m), 1326 (m), 1272 (m), 1239 (m), 918 (m), 688 (m) cm^{-1}; *MS* : 235 (M^+, 20), 194 (M^+-C_3H_5, 100), 176 (10), 146 (50), 131 (75), 91 (15), 77 (20); *exact mass* calcd. for $C_{13}H_{17}NO_3$: 253.1208, found: 235.1208

4-Ethyl-2-(1-methyl-but-3-enyl)-6-nitro-phenyl-trifluoromethanesulphonate (21). A solution of the phenol **20** (2.323 g, 9.9 mmol) in dry dichloromethane (40 mL) was cooled to -50°C under argon atmosphere, and 2,4,6-collidine (1.57

mL, 11.9 mmol), followed by a solution of freshly distilled trifluoromethanesulphonic anhydride (1.95 mL, 11.9 mmol) in dichloromethane (5 mL) were added within 5 min. After stirring at -50°C for 20 min, H_2O (20 mL) and dilute hydrochloric acid (5 mL) were added. Extraction (dichloromethane), followed by concentration of the combined organic layers and flash chromatography (petroleum ether/tert-butyl methyl ether 50:1) afforded **21** (3.25 g, 88 %) as an orange-yellow syrup. *^{1}H NMR* (400 MHz, $CDCl_3$): δ 7.68 (d, 2 Hz, 1 H); 7.42 (d, 2 Hz, 1 H); 5.69 (ddt, 17/10/7 Hz, 1 H); 5.03 (d, 10 Hz, 1 H); 4.99 (d, 17 Hz, 1 H); 3.31 (m, 1 H); 2.75 (q, 7.5 Hz, 2 H); 2.34 (m, 2 H); 1.29 (d, 6.5 Hz, 3 H); 1.29 (t, 7.5 Hz, 3 H); *^{13}C NMR* (50.3 MHz, $CDCl_3$): δ 145.6 (Cq), 143.1 (Cq), 142.9 (Cq), 135.2 (Cq), 135.1 (CH), 132.2 (CH), 123.4 (CH), 121.6 (Cq), 117.4 (CH_2), 41.9 (CH_2), 32.5 (CH), 28.3 (CH_2), 20.6 (CH_3), 14.8 (CH_3); *IR* (CCl_4): 2976 (m), 2938 (w), 2879 (w), 1644 (w), 1548 (s), 1441 (m), 1413 (m), 1355 (m), 1248 (m), 1219 (s), 1177 (m), 1137 (s), 1098 (m), 920 (m), 857 (s), 637 (m) cm^{-1}; *MS* : m/z 367 (M^+, 5), 326 (M^+-C_3H_5, 90), 263 (25), 217 (85), 193 (326-SO_2CF_3, 100), 189 (50), 176 (40), 161 (35), 131 (35); *exact mass* calcd. for $C_{14}H_{16}NO_5F_3S$: 367.0701, found: 367.0701.

5-Ethyl-1,3-dimethyl-7-nitro-1H-indene (23). A mixture of the triflate **21** (736 mg, 2 mmol), $Cl_2Pd(PPh_3)_2$ (70 mg, 5 mol%), LiCl (253 mg, 6 mmol), triethylamine (1 mL), H_2O (1 mL) and acetonitrile (25 mL) was heated to 70°C within 30 min and kept at that temperature for 1 h (argon atmosphere). After addition of H_2O (50 mL), extraction (tert-butyl methyl ether), washing (brine) and drying ($MgSO_4$) the combined organic layers, the solvents were removed in vacuo, and the residue was adsorbed to silica gel and purified by flash chromatography (petroleum ether/tert-butyl methyl ether 50:1) to give **23** (0.361 mg, 83 %) as a yellow syrup. *^{1}H NMR* (400 MHz, $CDCl_3$): δ 7.79 (br, 1 H); 7.35 (br, 1 H); 6.27 (m, 1 H); 4.10 (m, 1 H); 2.78 (q, 7.5 Hz, 2 H); 2.14 (t, 1.5 Hz, 3 H); 1.31 (t, 7.5 Hz, 3 H); 1.24 (d, 7 Hz, 3 H); *^{13}C NMR* (67.5 MHz, $CDCl_3$): δ 148.7 (Cq), 144.7 (Cq), 144.5 (Cq), 141.7 (Cq), 138.9 (CH), 135.9 (Cq), 124.0 (CH), 119.1 (CH), 44.5 (CH), 28.5 (CH_2), 15.4 (CH_3), 14.3 (CH_3), 12.7 (CH_3); *IR* (CCl_4): 2971 (m), 2937 (w), 2874 (w), 1530 (s), 1361 (m), 1343 (s), 1073 (w), 879 (m) cm^{-1}; *MS* : m/z 217 (M^+, 100), 200 (75), 170 (55), 155 (60), 141 (55), 128 (50), 115 (50), 77 (25); *exact mass* calcd. for $C_{13}H_{15}NO_2$: 217.1103, found: 217.1103; *Anal.* calcd.: C 71.87, H 6.96, N 6.45; found: C 71.35, H 6.99, N 6.69.

6-Ethyl-1-methyl-3-methylen-4-nitro-indane (22). A mixture of the triflate **21** (750 mg, 2.04 mmol), $Pd(OAc)_2$ (25 mg, 5.5 mol%), triphenylphosphine (60 mg, 11 mol%), tetraethylammonium chloride (352 mg, 2.1 mmol), acetonitrile (25 mL), H_2O (1 mL) and triethylamine (1 mL) were stirred for 15 min at room temperature and then for 40 min at 50°C and subsequently worked up as described for **23**. The products **23** (less polar, 144 mg, 32 %) and **22** (more polar, 187 mg, 42 %) were separated by flash chromatography (petroleum ether/tert-butyl methyl ether 20:1). **22:** *^{1}H NMR* (200 MHz, $CDCl_3$): δ 7.37 (br, 1 H); 7.25 (br, 1 H); 5.46 (t, 2 Hz, 1 H); 5.29 (t, 2 Hz, 1 H); 3.20 (m, 1 H); 3.04 (ddt, 15/8/2 Hz, 1 H); 2.69 (q, 7.5 Hz, 2 H); 2.44 (ddt, 15/5.5/2 Hz, 1 H); 1.29 (d, 7 Hz, 3 H); 1.25 (t, 7.5 Hz, 3 H); *^{13}C NMR* (67.5 MHz, $CDCl_3$): δ 155.0 (Cq), 145.8 (Cq), 145.7 (Cq), 143.8 (Cq), 129.3 (Cq), 127.6 (CH), 121.5 (CH), 110.0 (CH_2), 43.0 (CH_2), 36.5 (CH), 28.3 (CH_2), 20.4 (CH_3), 15.1 (CH_3); *IR* (CCl_4): 2970 (m), 2934 (w), 2874 (w), 1532 (s), 1459 (w), 1365 (m), 881 (m) cm^{-1}; *MS*: m/z 217 (M^+, 70), 200 (18), 189 (20), 172 (100), 158 (35), 143 (40), 128 (50), 115 (45), 91 (25); *exact mass* calcd. for $C_{13}H_{15}NO_2$: 217.1103, found: 217.1103.

4-Ethyl-6,8-dimethyl-1,8-dihydro-1-aza-as-indacene (29). A solution of the indene **23** (60 mg, 0.28 mmol) in dry tetrahydrofuran (5 mL) was cooled to -50°C and treated dropwise with 0.85 mL (0.85 mmol) of a 1 M vinylmagnesium bromide-solution (Aldrich) under argon atmosphere. After stirring for 25 min at -50°C, the mixture was quenched with sat. ammonium chloride solution (10 mL). The layers were separated, the aqueous layer was extracted (tert-butyl methyl ether) and the combined organic layers were washed (brine), dried ($MgSO_4$) and concentrated. Flash chromatography (petroleum ether/ tert-butyl methyl ether 20:1) afforded **29** (8 mg, 14 %) as a darkening oil. *^{1}H NMR* (200 MHz, $CDCl_3$): δ 8.05 (s, br, NH); 7.19 (dd, 3/2.5 Hz, 1 H); 7.00 (s, 1 H); 6.66 (dd, 3/2 Hz, 1 H); 6.01 (m, 1 H); 3.61 (m, 1 H); 3.01 (q, 7.5 Hz, 2 H); 2.22 (t, 2 Hz, 3 H); 1.41 (t, 7.5 Hz, 3 H); 1.38 (d, 7 Hz, 3 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 140.5 (Cq), 139.3 (Cq), 134.8 (Cq), 132.9 (CH), 132.0 (Cq), 129.0 (Cq), 125.6 (Cq), 123.3 (CH), 110.8 (CH), 101.6 (CH), 41.8 (CH), 26.6 (CH_2), 16.1 (CH_3), 15.1 (CH_3), 13.4 (CH_3); *IR* (FT, CCl_4): 3495 (w), 2965 (m), 2928 (w), 2868 (w), 1454 (w), 1362 (w), 1216 (w) cm^{-1}; *MS* : m/z 211 (M^+, 100), 196 (60), 182 (55), 172 /30), 158 (25), 59 (75); *exact mass* calcd. for $C_{15}H_{17}N$: 211.1361, found: 211.1361.

4-Ethyl-6,8-dimethyl-1,6-dihydro-1-aza-as-indacene (28). Preparation from **22** analogous to **29**, giving **28** (10 %) as a darkening oil. *^{1}H NMR* (400 MHz, $CDCl_3$): δ 8.38 (s, br, NH); 7.20 (dd, 3/2.5 Hz, 1 H); 7.07 (s, 1 H); 6.63 (dd, 2/3 Hz, 1 H); 6.06 (m, 1 H); 3,48 (m, 1 H); 2.98 (q, 7.5 Hz, 2 H); 2.45 (t, 2 Hz, 3 H); 1.37 (t, 7.5 Hz, 3 H); 1.32 (d, 7 Hz, 3 H); *IR* (CCl_4): 3501 (m), 2967 (s), 2930 (m), 2871 (m), 1629 (w), 1516 (w), 1455 (m), 1400 (m), 1368 (m), 1309 (m), 1263 (m), 1090 (m), 1023 (m), 893 (m), 865 (m), 721 (s) cm^{-1}; *MS* : m/z 211 (M^+, 100), 196 (65), 182 (60), 167 (20); *exact mass* calcd. for $C_{15}H_{17}N$: 211.1361, found: 211.1361.

(±)-*cis*-Trikentrin A (rac 1). A mixture of **29** (10 mg, 0.05 mmol), palladium-on-charcoal (10 %, 0.5 mg) and dry methanol (3 mL) were stirred for 22 h at room temperature under a hydrogen atmosphere (H_2-balloon). The catalyst was filtered off, and the filtrate was concentrated and purified by preparative thin-layer-chromatography (petroleum ether/ tert-butyl methyl ether 4:1) to afford **rac 1** (8 mg, 80 %) as a slowly darkening oil. *^1H NMR* (400 MHz, $CDCl_3$): δ 8.10 (s, br, NH); 7.16 (dd, 3/2.5 Hz, 1 H); 6.84 (br, 1 H); 6.60 (dd, 3/2 Hz, 1 H); 3.45 (m, 1 H); 3.23 (m, 1 H); 2.94 (qd, 7.5/2.5 Hz, 2 H); 2.61 (dt, 12.5/7.5 Hz, 1 H); 1.50 (d, 7 Hz, 3 H); 1.38 (d, 7 Hz, 3 H); 1.37 (t, 7.5 Hz, 3 H); 1.32 (dt, 12.5/9 Hz, 1 H); *^{13}C NMR* (50.32 MHz, $CDCl_3$): δ 143.0 (Cq), 135.0 (Cq), 132.4 (Cq), 126.9 (Cq), 122.8 (CH), 114.0 (CH), 101.3 (CH), 44.7 (CH_2), 38.9 (CH), 37.2 (CH), 26.5 (CH_2), 21.0 (CH_3), 20.8 (CH_3), 15.0 (CH_3); *IR* (FT, CCl_4): 3500 (m), 2960 (s), 2929 (m), 2869 (m), 1456 (w), 1400 (m), 1374 (w), 1359 (w), 1216 (w), 1072 (w), 1063 (w), 898 (w), 863 (w) cm^{-1}; *MS* : m/z 213 (M^+, 60), 198 (100), 184 (15), 169 (20), 154 (10); exact mass calcd. for $C_{15}H_{19}N$: 213.1517, found: 213.1517.

REFERENCES AND NOTES

1. Capon, R. J.; MacLeod, J. K.; Scammels, P. J. *Tetrahedron* **1986**, *42*, 6545-6550.
2. Herb, R.; Carrol, A. R.; Yoshida, W. Y.; Scheuer, P. J.; Paul, V. J. *Tetrahedron* **1990**, *46*, 3089-3092.
3. Total syntheses: Muratake, H.; Natsume, M. *Tetrahedron Lett.* **1989**, *30*, 5771-5772. Kanematsu, K.; Yasukouchi, T. *Tetrahedron Lett.* **1989**, *30*, 6559-6562. McLeod, J. K.; Monahan, L. C. *Austr. J. Chem.* **1990**, *43*, 329-337. Muratake, H.; Watanabe, M.; Goto, K.; Natsume, M. *Tetrahedron* **1990**, *46*, 4179-4192. Boger, D. L.; Zhang, M. *J. Am. Chem. Soc.* **1991**, *113*, 4230-4234. Muratake, H.; Mikawa, A.; Natsume, M. *Tetrahedron Lett.* **1992**, *33*, 4595-4598 (herbindoles). Muratake, H.; Seino, T.; Natsume, M. *Tetrahedron Lett.* **1993**, *34*, 4815-4818.
4. Heck, R. F. *Org. React.* **1982**, *27*, 345-390.
5. a) Monse, B. *Palladium-katalysierte Wege zu selektiv substituierten Indolen*, Universität Bonn 1990. b) Wiedenau, P. *Studien zur Synthese der Trikentrine*, Universität Bonn 1991. c) Wiedenau, P. *Synthese des (±)-cis-Trikentrin A*, Technische Universität Berlin 1994.
6. Bosco, M.; Dalpozzo, R.; Bartoli, G.; Palmieri, G.; Petrini, M. *J. Chem. Soc. Perk. Trans. 2* **1991**, 657-661.
7. Kikugawa, Y.; Miyake, Y. *Synthesis* **1981**, 461-462.
8. Youn, I. K.; Yon, G. H.; Pak, C. S. *Tetrahedron Lett.* **1986**, *27*, 2409-2410. Hudlicky, T.; Sinai-Zingde, G.; Natchus, M. G. *Tetrahedron Lett.* **1987**, *28*, 5287-5290.
9. Petasis, N. A.; Bzowej, E. I.. *J. Am. Chem. Soc.* **1990**, *112*, 6392-6394.
10. For the use of triflates in Heck type reactions see e.g.: Rice, J. E.; Cai, Z. W. *J. Org. Chem.* **1993**, *58*, 1415-1424. Gribble, G. W.; Conway, S. C. *Syn. Comm.* **1992**, 2129-2141. Overman, L. E.; Laschat, S.; Narjes, F. *Tetrahedron* **1994**, *50*, 347-358. Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478-5486. O-he, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201-2208.
11. Effenberger, F.; Klenk, H. *Chem.Ber.* **1974**, *107*, 175-182.
12. Henecka, H. in Houben-Weyl *Methoden der Organischen Synthese* **1973**, *Vol. VII/2a*, 379-389.
13. Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633-651.
14. Stang, P. J.; Hanack, M.; Subramaniam, L. R. *Synthesis* **1982**, 115-118.
15. Jeffery, T. *Tetrahedron Lett.* **1994**, *35*, 3051-3054.
16. Grigg, R.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakun, T. *Tetrahedron* **1990**, *46*, 4003-4018.

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