A CONVENIENT APPROACH TO THE *N*-SUBSTITUTED AMINO DIENES, *N*-BENZYL-5-ETHENYL-3,4-DIHYDROPYRIDIN-2-ONE AND *N*-CBZ-5-ETHENYL-1,2,3,4-TETRAHYDROPYRIDINE

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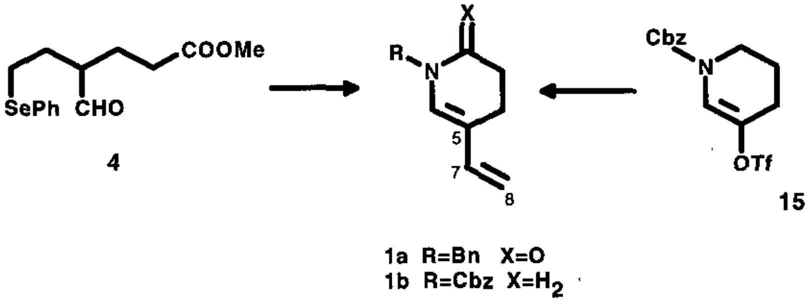
Abstract- A synthesis of *N*-substituted amino dienes (**1a**) and (**1b**) is described according to two different approaches. **1a** is obtained through condensation of methyl 4-formyl-6-selenophenylhexanoate (**4**) with benzylamine followed by oxidation and elimination; **1b** is formed by a Pd-catalyzed cross-coupling reaction utilizing vinyltributyltin. The preparation of **4** is also described.

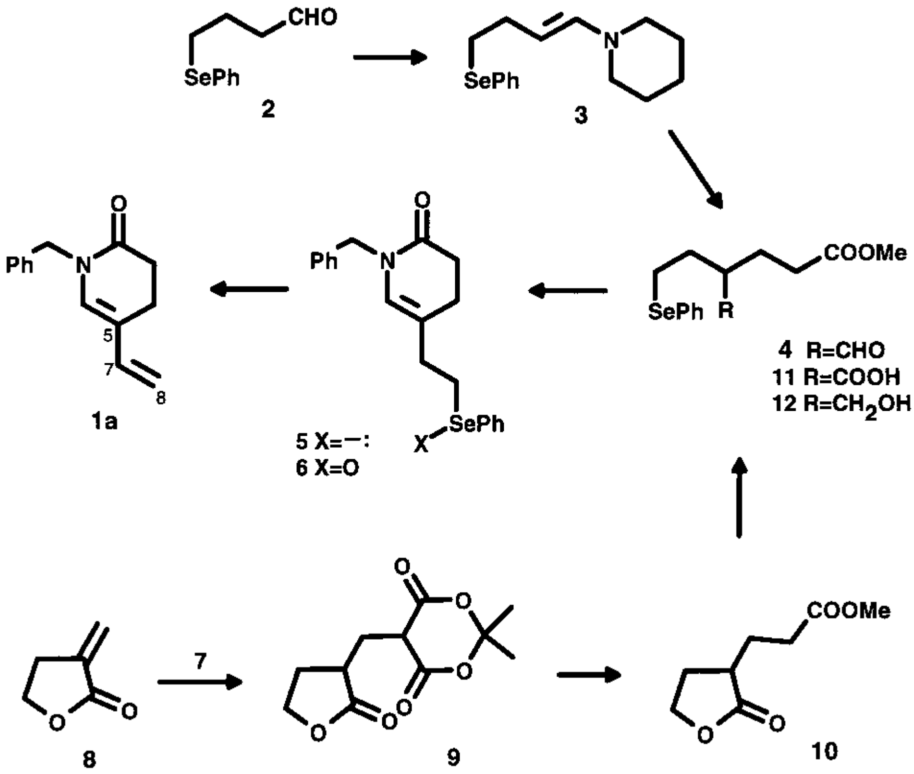
In connection with our program[1] on the synthesis of some indole alkaloids by [4+2]π cycloaddition, we required a convenient method for the preparation of the unknown amino dienes (**1a**) and (**1b**). A conventional approach has been devised to obtain the *N*-benzyl-5-ethenyl-3,4-dihydropiridin-2-one (**1a**): it is based on the formation of the key intermediate methyl 4-formyl-6-selenophenylhexanoate (**4**) in which the 2-selenophenylethylene group serves as the precursor of the vinyl appendage (Scheme I). For *N*-carbobenzyloxy-5-ethenyl-1,2,3,4-tetrahydropyridine (**1b**) a more direct access has been planned through a palladium mediated insertion of the vinyl appendage on the enol triflate (**15**). Here we give a brief report of the details of these preparations.

The synthesis of methyl 4-formyl-6-selenophenylhexanoate (**4**) was realized according to Scheme II. In a first approach the 4-selenophenylbutanal (**2**),[2] prepared through reduction of 4-selenophenylbutyric acid[3] followed by oxidation of the corresponding alcohol with sulfur trioxide-pyridine complex,[4] was converted into the formyl ester (**4**) by Michael addition of enamine (**3**) to methyl acrylate in acetonitrile.[5]



Scheme I

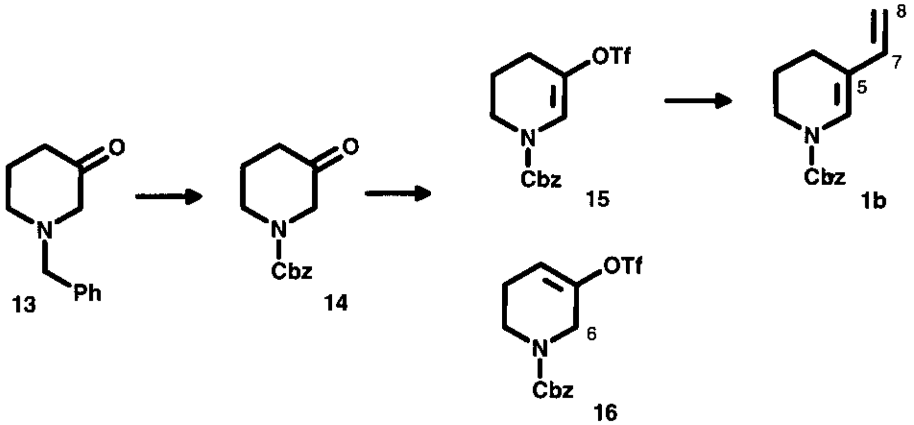
Since the yield of this conversion was unsatisfactory (55%), we turned our attention to explore an alternative approach in which the selenophenyl group is introduced on the preformed carbon frame as the last step. The Michael addition of isopropylidene malonate (Meldrum's acid) (**7**) to α-methylene-γ-butyrolactone (**8**) under phase-transfer conditions[6] gave the adduct (**9**) in 74% yield. The decarboxylation of **9** by heating in methanol-pyridine in the presence of a small amount of Cu powder that accelerated the conversion[7] afforded compound (**10**)[8] in 94% yield. Upon exposure to phenylselenolate,[3] **10** gave the methyl 4-carboxy-6-phenylselenohexanoate (**11**) in 81% yield. In a first attempt to reduce the COOH to CHO, **11** was treated with *N,N*-dimethylchloromethyleniminium chloride and $LiAlH(OtBu)_3$.[9] However the aldehyde (**4**) was obtained in only 8% yield. Therefore the carboxy function was reduced to hydroxymethyl by *N,N*-dimethylchloromethyleniminium chloride and $NaBH_4$.[10] In these conditions we obtained the alcohol (**12**) in 85% yield accompained by a small amount (4%) of the aldehyde (**4**). Subjection of **12** to Swern oxidation[11] at -78^0 C for 1 h gave **4** in 89% yield. The conversion of formyl ester (**4**) to unsaturated lactam (**5**) was realized by condensation with benzylamine in refluxing toluene. This reaction proceeded cleanly by distilling and draining off the toluene-water and toluene-methanol azeotropes. The presence of the double bond between positions 5 and 6 was demonstrated by the appearance of a broad singlet at δ 5.80 assignable to 6-H in the ^{1}H-nmr spectrum of **5**.



Scheme II

Oxidation of **5** by sodium metaperiodate in aqueous methanol gave the unstable selenoxide (**6**), that partially converted to 5-ethenyl-3,4-tetrahydropyridinone (**1a**) during the work-up of the reaction. Therefore **6** was not isolated but the crude reaction mixture was dissolved in toluene and heated for 30 min at 40^0 C to complete the oxidative elimination process, thus affording **1a** in 80% yield after purification. The ^{1}H-nmr spectrum contained two doublets at δ 4.91 (J=10.5 Hz) and δ 4.96 (J=17.5 Hz) assignable to 8-H_2 and a doublet of doublets at δ 6.21 (J=10.5 Hz, J=17.5 Hz) for 7-H; the singlet of 6-H was shifted to lower fields at δ 6.05. Accordingly the ^{13}C-nmr spectrum displayed sp^2 carbons at δ 118.72 (C-5), 110.64 (C-8), 134.59 (C-7) and 129.48 (C-6).

For the synthesis of *N*-Cbz-5-ethenyl-1,2,3,4-tetrahydropyridine (**1b**) we thought to realize the C-5 bond through a palladium catalyzed cross-coupling reaction using the enol triflate (**15**) as electrophile and the vinyltributyltin as nucleophile.[12] The commercially available *N*-benzyl-3-piperidone (**13**) was directly transformed into **14**[13] by heating with benzyl chloroformate in toluene at 60^0 C for 18 h. Following the Martin protocol,[14] by treatment with LDA in THF at -78^0 C and *N*-phenyltrifluoromethanesulfonimide, **14** was converted into a 95:5 mixture of enol triflates (**15**) and (**16**), easily separated by column chromatography. The ^{1}H-nmr spectrum of **15** showed a broad singlet at δ 7.35 for 6-H that had a correlation in the COSY spectra with the broad triplet signal at δ 2.48 due to 4-H_2. In the ^{1}H-nmr spectrum of triflate (**16**) the signal of 4-H appeared at δ 5.91 as a multiplet, and the signal of 6-H_2 appeared at δ 4.12 as a doublet because of a long-range coupling constant (J=1.8 Hz) with 4-H.



Scheme III

The reaction of triflate (**15**) with vinyltributyltin catalyzed by tris(dibenzylidenacetone)dipalladium in the presence of LiCl, tri-2-furylphosphine and aq. Na_2CO_3 afforded cleanly the desidered compound (**1b**) in 74% yield. The ^{1}H-nmr spectrum of **1b** showed at δ 6.32 a doublet of doublets (J=16.8 Hz, J=13.5 Hz) for 7-H and two doublets at δ 4.88 (J=13.5 Hz) and δ 4.99 (J=16.8 Hz) due to 8-H_2. The signal of 6-H appeared at δ 6.90 as a broad singlet, that correlates in the COSY with the signal at δ 2.19 due to 4–H_2. These amino dienes (**1a**) and (**1b**) have been obtained in 27% and 33% yields, respectively, as stable compounds which can be kept at room temperature for a long time.

EXPERIMENTAL

General Methods: Ir spectra were recorded on Perkin-Elmer 681 spectrophotometer for chloroform solutions. ^{1}H-Nmr and ^{13}C-nmr spectra were recorded on Bruker WP-80 (^{1}H, 80 MHz; ^{13}C, 20.1 MHz), Varian XL-200 (^{1}H, 200 MHz; ^{13}C, 50.2 MHz) and Bruker AC-300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz) spectrometers. EI mass spectra in the positive mode were determined on VG 70-70 EQ-HF instrument equipped with its standard source. Tlc data were obtained with Merck 60F-254 precoated silica gel on alumina sheets. Flash chromatography was carried out using Merck kiesegel 60, 230-400 mesh.

4-Selenophenylbutanal (**2**): 4-Selenophenylbutanol (5.12 g, 22.3 mmol), obtained by $LiAlH_4$ reduction of 4-selenophenylbutyric acid (78%), was dissolved in dry triethylamine (19.9 ml, 78.7 mmol) and the solution added to sulfur trioxide-pyridine complex (12.5 g, 78.7 mmol) in dimethyl sulfoxide (180 ml). After being stirred for 10 h at room temperature, the mixture was diluted with dichloromethane, basified with 10% $NaHCO_3$ solution and washed with water. The residue obtained after usual workup was purified by flash chromatography on silica gel (ether/hexane 1:4) to afford the aldehyde (**2**) (4.22 g, 83%) as a colorless oil: Ir 1740 cm^{-1}; ^{1}H-nmr (80 MHz, $CDCl_3$): δ 2.03 (2H, quint, J=6.4 Hz), 2.56 (2H, dt, J=6.4, 1.6 Hz), 2.90 (2H, t, J=6.4 Hz), 7.05-7.35 (3H, m), 7.36-7.70 (2H, m), 9.73 (1H, t, J=1.6 Hz); EIms: m/z 228 (30, Se^{80}), 157 (100), 77, 71; Anal. Calcd for $C_{10}H_{12}OSe$: C, 52.87; H, 5.33. Found: C, 52.18; H, 5.13.

Enamine (3): To a mixture of piperidine (1.4 ml, 14.1 mmol) and anhydrous K_2CO_3 (400 mg, 2.89 mmol) cooled to 0^0 C, aldehyde (**2**) (780 mg, 3.44 mmol) was added over a 1 h period. The reaction mixture was stirred for an additional 2 h at 0^0 C. The solids were filtered off, the solvent was removed, and then the resulting crude product was purified by distillation under reduced pressure to give 754 mg (74%) of **6** as a colorless liquid: bp 120-125^0 C (6 Torr); ^{1}H-nmr (200 MHz, $CDCl_3$): δ 1.34-1.68 (6H, m), 2.34 (2H, q, J=7.4 Hz), 2.72-2.81 (4H, m), 2.88 (2H, t, J=7.4 Hz), 4.34 (1H, q, J=7.4 Hz), 5.85 (1H, d, J=17.1 Hz), 7.25-7.56 (3H, m), 7.80-8.01 (2H, m); EIms: m/z 295 (18, Se^{80}), 157 (100), 124; Anal. Calcd for $C_{15}H_{21}NSe$: C, 61.22; H, 7.19; N, 4.76. Found: C, 61.57; H, 7.24, N, 4.61.

Methyl 4-Formyl-6-selenophenylhexanoate (4) from 3: To a solution of **3** (754 mg, 2.55 mmol) in dry acetonitrile (10 ml), cooled below 5^0 C, methyl acrylate (344 µl, 3.82 mmol) in acetonitrile (1 ml) was added over a 0.5 h period. The reaction mixture was allowed to warm to room temperature and stirred for 8 h. A reflux condenser was attached and the solution was heated at reflux for 24 h. Acetic acid (100 µl) and water (1 ml) were added to the reaction mixture, and the resulting solution was heated at reflux for 8 h. The mixture was allowed to cool to room temperature, the aqueous phase was saturated with NaCl, and the solution was extracted with ether. The organic extract was washed with 5% HCl, 5% $NaHCO_3$, and saturated aqueous NaCl. The organic phase was dried over Na_2SO_4 and concentrated to give **4** (460 mg, 55%) as colorless oil after purification on silica gel ($CHCl_3$/MeOH 95:5): R_f ($CHCl_3$/MeOH 95:5) 0.59; ^{1}H-nmr (300 MHz, $CDCl_3$): δ 1.67-1.86 (2H, m), 1.89-2.14 (2H, m), 2.19-2.41 (2H, m), 2.44-2.59 (1H, m), 2.80-2.99 (2H, m), 3.65 (3H, s), 7.15-7.35 (3H, m), 7.40-7.53 (2H, m), 9.55 (1H, br s); ^{13}C-nmr (50.2 MHz, $CDCl_3$): δ 23.88, 25.41, 29.56, 31.74 (4C), 51.43, 52.36, 127.81, 129.82, 133.52, 173.80, 203.83; EIms: m/z 314 (33, Se^{80}), 283 (11), 157 (100); Anal. Calcd. for $C_{14}H_{18}O_3Se$: C, 53.68; H, 5.80. Found: C, 54.01; H, 5.92.

Meldrum adduct (9): To a stirred solution of isopropylidene malonate (4.9 g, 34 mmol) in acetonitrile (35 ml) was added anhydrous K_2CO_3 (4.78 g, 34 mmol) and benzyltriethylammonium chloride (7.75 g, 34 mmol). The mixture was stirred for 20 min at room temperature, and then a solution of α-methylene-γ-butyrolactone (**8**) (5.0 g, 51 mmol) in acetonitrile (17 ml) was added. The resultant mixture was stirred for 10 h at 50^0 C. The mixture was cooled and water (30 ml) was added. The aqueous solution was washed with ether (30 ml) and acidified to pH 1-2 with 6N HCl. The crude product (**9**) (5.3 g, 64%) which precipitated as an amorphous solid, was isolated by filtration. The ether extraction of the filtrate gave, after purification on silica gel ($CHCl_3$/MeOH 95:5), an additional 800 mg (9.7%): R_f ($CHCl_3$/MeOH 95:5) 0.21; ir 1785, 1745 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$): δ 1.77 (3H, s), 1.86 (3H, s), 1.95-2.14 (1H, m), 2.23 (1H, ddd, J=14, 9, 6 Hz), 2.39-2.58 (2H, m), 3.10-3.25 (1H, m), 4.21 (1H, dt, J=12, 7.5 Hz), 4.38 (1H, dt, J=12, 3 Hz), 4.69 (1H, dd, J=9, 3 Hz); ^{13}C-nmr (50.2 MHz, $CDCl_3$): δ 26.61, 27.08, 29.02, 30.10, 35.93, 43.72, 67.41, 106.09, 165.93, 166.39, 180.40; EIms: m/z 184 (79), 167 (100), 140 (48); Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.49; H, 5.83. Found: C, 54.62; H, 5.91.

Methyl 3-(Tetrahydro-2-oxofuran-3-yl)propanoate (10): Five g (17.9 mmol) of **9** were dissolved in methanol/pyridine (1:10, 70 ml) containing 400 mg of Cu-powder, and the mixture was heated under reflux for 3 h.

After removal of Cu-powder by filtration, the solution was poured into 150 ml of water, acidified with 5% H_3PO_4, extracted with EtOAc to give, after purification on silica gel ($CHCl_3$/MeOH 3:1), 29 g of **10** (94%) as an oily compound: ^{1}H-Nmr (300 MHz, $CDCl_3$): δ 1.75 (1H, dt, J=8, 7.2 Hz), 1.81-1.98 (1H, m), 2.08 (1H, dt, J=7.2, 8 Hz), 2.30-2.41 (1H, m), 2.44 (2H, t, J=7.2 Hz), 2.48-2.61 (1H, m), 3.61 (3H,s), 4.12 (1H, td, J=11, 5.1), 4.29 (1H, td, J=11, 3 Hz); ^{13}C-nmr (75.4 MHz, $CDCl_3$): δ 25.96, 29.20, 31.91(3C), 38.88, 52.18, 66.98, 173.69, 179.33; EIms: m/z 172 (10), 140 (100), 113 (35); Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 56.03, H, 7.12.

Methyl 4-Carboxy-6-selenophenylhexanoate (11): A solution of 1.6 g (5.1 mmol) of diphenyl diselenide in 15 ml of dry dimethylformamide was deoxygenated by bubbling nitrogen through for 20 min. Sodium borohydride (430 mg, 11.3 mmol) was added, and then the temperature was slowly raised in an oil bath to 100^0 C. A solution of 1.55 g (9.0 mmol) of **10** in 4 ml of dimethylformamide was introduced, and then the oil bath temperature was raised to 120^0 C and kept at this temperature for 3 h. Usual work up and purification by flash cromatography ($CHCl_3$/MeOH 95:5) gave 2.4 g (81%) of **11** as an oil: R_f($CHCl_3$/MeOH 95:5) 0.21; ir 1730, 1680 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$): δ 1.74-2.16 (4H, m), 2.23-2.45 (2H, m), 2.33-2.67 (1H, m), 2.81-3.00 (2H, m), 3.65 (3H, s), 7.15-7.35 (3H, m) 7.40-7.61 (2H,m); ^{13}C-nmr (75.4 MHz, $CDCl_3$): δ 25.49, 27.17, 32.13, 32.86 (4C), 44.94, 53.24, 127.62, 129.67, 133.40, 174.01, 180.50; EIms: m/z 330 (2%, Se^{80}), 286, 241, 157 (100), 73: Anal.Calcd for $C_{14}H_{18}O_4Se$: C, 51.07; H, 5.51. Found: C, 51.89; H, 5.48.

Methyl 4-Hydroxymethyl-6-selenophenylhexanoate (12): Oxalyl chloride (977 mg, 7.7 mmol) was added to a solution of dimethylformamide (208 µl, 2.7 mmol) in dichloromethane (5 ml) at 0^0 C. After the solution was stirred for 1 h, the solvent was removed under a reduced pressure. To the residual white powder in acetonitrile (5 ml) and tetrahydrofuran (7 ml) was added a solution of acid (**11**) (900 mg, 2.7 mmol) and pyridine (218 µl, 2.7 mmol) in tetrahydrofuran (5 ml) at -30^0 C. The reaction mixture was stirred for 1 h, then, to the reaction mixture was added a suspension of $NaBH_4$ (205 mg, 5.41 mmol) in dimethylformamide (2 ml) at -78^0 C. The temperature was slowly raised to -30^0 C. After 2 h the reaction mixture was poured into water, acidified with 5% H_3PO_4 and extracted with EtOAc. The residue obtained from organic phase gave, after purification over silica gel (FC, $CHCl_3$/MeOH 95:5), 35 mg (4%) of **4** and 732 mg (85%) of **12**: R_f($CHCl_3$/MeOH 95:5) 0.31; ir 3650, 1730 cm^{-1}; ^{1}H-nmr (300 MHz, $CDCl_3$): δ 1.55-1.86 (5H, m), 2.32 (2H, t, J=7 Hz), 2.94 (2H, t, J=6.9 Hz), 3.54 (2H, bs), 3.68 (3H, s), 7.15-7.35

(3H, m), 7.40-7.55 (2H, m); EIms: 316 (11, Se^{80}), 286, 257, 159, 157 (100); Anal. Calcd. for $C_{14}H_{20}O_3Se$: C, 53.33; H, 6.40. Found: C, 53.08; H, 6.29.

Methyl 4-Formyl-6-selenophenylhexanoate (4) from 12: To a cold (-78° C) stirred solution of oxalyl chloride (392 mg, 3.1 mmol) in dichloromethane (5 ml) was added dropwise a solution of dimethyl sulfoxide (484 mg, 6.2 mmol) in dichloromethane (5 ml) over a period of 5 min. After the mixture was stirred at -78° C for 1 h, a solution of **12** (500 mg, 1.58 mmol) in dichloromethane (3 ml) was added to the mixture with stirring over a period of 5 min. After the reaction mixture was stirred at -78° C for 2 h, triethylamine (1.09 g, 10.8 mmol) was added, and the resulting mixture was warmed to room temperature. After addition of water (10 ml), the organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phase gave a residue which was purified by column chromatography on silica gel ($CHCl_3$/MeOH 95:5) to afford **4** (441 mg, 89%).

Dihydropyridinone (5): Compound (4) (200 mg, 0.64 mmol), benzylamine (70 mg, 0.65 mmol) and dry toluene (5 ml) were placed in a flask equipped with a Dean-Stark trap. The reaction mixture was heated at reflux for 6 h, and 2 ml of the toluene-water azeotrope was drained off. After addition of 7 ml of fresh toluene the reaction mixture was heated to reflux, and 4 ml of the toluene-methanol azeotrope was drained off. The remaining solvent was removed to give a crude product, which was purified by column chromatography on silica gel (hexane/ether 1:1) to give **5** (190 mg, 80%): R_f (hexane/ether 1:1) 0.16; ^{1}H-nmr (200 MHz, $CDCl_3$): δ 2.24 (2H, t, J=8 Hz), 2.38 (2H, t, J=7.5 Hz), 2.52 (2H, t, J=8 Hz), 2.93 (2H, t, J=7.5 Hz), 4.65 (2H, s), 5.80 (1H, br s), 7.15-7.45 (10H, m); ^{13}C-nmr (75.4 MHz, $CDCl_3$): δ 24.45, 26.60, 31.72, 34.97, 49.54, 118.73, 126.07, 127.56, 127.97, 128.23, 129.19, 129.60, 130.63, 133.56, 137.96, 169.18; EIms: m/z 371 (9, Se^{80}), 200, 157 (100), 110; Anal. Calcd for $C_{20}H_{21}NOSe$: C, 64.99; H, 5.72; N, 3.78. Found: C, 64.86; H, 5.68; N, 3.59.

***N*-Benzyl-5-ethenyl-3,4-dihydropyridin-2-one (1a):** To a solution of **5** (190 mg, 0.51 mmol) in methanol (10 ml), $NaIO_4$ (120 mg, 0.56) dissolved in water (4 ml) was added at -10° C. After 1 h the solution was poured into saturated aqueous $NaHCO_3$ and extracted with dichloromethane. The organic phase was dried over Na_2SO_4 and evaporated. The crude product mixture was directly dissolved in dry toluene (10 ml) and heated at 40° C for 30 min. Evaporation of the solvent and purification by column chromatography on silica gel (hexane/ether 1:1) gave **1a** as an oil (86 mg, 80%): R_f (hexane/ether 1:1) 0.33; ^{1}H-nmr (300 MHz, $CDCl_3$): δ 2.43 (2H, t, J=8 Hz), 2.51 (2H, t, J=8 Hz), 4.66 (2H, s), 4.91 (1H, d, J=10.5 Hz), 4.96 (1H, d, J=17.5 Hz), 6.05 (1H, br s), 6.21 (1H, dd, J=17.5, 10.5 Hz), 7.15-7.31 (5H, m); ^{13}C-nmr (75.4 MHz, $CDCl_3$): δ 19.91, 30.87, 49.30, 110.64, 118.72, 127.73, 128.82, 129.48, 134.59, 136.09, 168.96; EIms: m/z 213, 123 (100); Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.25; H, 6.98; N, 6.42.

***N*-Cbz-piperidin-3-one (14):** **13** (1.9 g, 10.0 mmol) was heated in toluene (25 ml) at 60° C in the presence of 1.6 ml (11.2 mmol) of benzyl chloroformate. After 18 h the reaction mixture was diluted with EtOAc, and washed with 5% $NaHCO_3$ solution to give, after evaporation and purification on silica gel (hexane/EtOAc 2:1), 1.8 g (81%) of **14** as an oil. ^{1}H-Nmr (300 MHz, $CDCl_3$): δ 1.99 (2H, quint, J=6.9 Hz), 2.48 (2H, t, J=6.9 Hz), 3.66 (2H, t, J=6.9 Hz), 4.08 (2H, s), 5.16 (2H, s), 7.38 (5H, s); EIms: m/z 233, 189, 94, 91 (100); Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.85; H, 6.48; N, 6.00. Found: C, 66.15; H, 6.52; N, 6.12.

Triflate (15): A solution of **14** (1 g, 4.48 mmol) in tetrahydrofuran (5 ml) was added to a solution of LDA (4.8 mmol) in tetrahydrofuran (5 ml) at -78° C. After 1 h a solution of *N*-phenyltrifluoromethanesulfonimide (1.9 g, 4.5 mmol) in tetrahydrofuran (5 ml) was added at -78° C. The reaction mixture was then warmed to 0° C and stirred for 3 h. Column chromatography on silica gel (hexane/ether 1:1) gave **15** as an oil (900 mg, 56%): ^{1}H-Nmr (300 MHz, $CDCl_3$): δ 1.91 (2H, quint, J=6.2 Hz), 2.48 (2H, br t, J=6.2 Hz), 3.61 (2H, t, J=6.2 Hz), 5.20 (2H, s), 7.12-7.45 (5H, m), 7.35 (1H, br s); EIms: m/z 365, 232, 188, 181, 142, 116, 91 (100); Anal. Calcd for $C_{14}H_{14}NO_5F_3S$: C, 46.00; H, 3.86; N, 3.84. Found: C, 46.55; H, 4.03; N, 3.69. The chromatography purification allowed the isolation of triflate (**16**) as an oil (47 mg, 3%): ^{1}H-Nmr (300 MHz, $CDCl_3$): δ 2.25-2.38 (2H, m), 3.61 (2H, t, J=6.5 Hz), 4.12 (2H, d, J=1.8 Hz), 5.17 (2H, s), 5.91 (1H, m), 7.48 (5H, s); EIms: m/z 233, 189, 94, 91 (100); Anal. Calcd for $C_{14}H_{14}NO_5F_3S$: C, 46.00; H, 3.86; N, 3.84. Found: C, 46.23; H, 3.98; N, 3.59.

***N*-Cbz-5-ethenyl-1,2,3,4-tetrahydropyridine (1b):** A flask which had been purged with nitrogen was charged with aq. $NaHCO_3$ (0.5 ml of a 2M solution), dimethylformamide (3 ml), **15** (100 mg, 0.281 mmol), LiCl (36 mg, 0.85 mmol), tri-2-furylphosphine (13 mg, 0.056 mmol) and tris(dibenzylideneacetone)dipalladium (26 mg, 0.028 mmol). After 10 min at room temperature vinyltributyltin (83 μl, 0.283 mmol) was added and the solution was stirred at room temperature for 2 h. Dilution of the reaction mixture with sat. aq. KF and hexane, filtration and separation of the organic phase was followed by drying over Na_2SO_4 and evaporation. Silica gel chromatography (hexane/ether 4:1) gave 51 mg (74%) of **1b** as an oil: R_f(hexane/ether 4:1) 0.48; ^{1}H-nmr (300 MHz, $CDCl_3$, 50° C): δ 1.80-1.93 (2H, m), 2.19 (2H, br t, J=6 Hz), 3.61 (2H, t, J=6.3 Hz), 4.88 (1H, d, J=13.5 Hz), 4.99 (1H, d, J=16.8 Hz), 6.32 (1H, dd, J=16.8, 13.5 Hz), 6.90 (1H, br s), 7.20-7.38 (5H, m); ^{13}C-nmr (75.4 MHz, $CDCl_3$, 50° C): δ 21.68, 30.22, 43.06, 68.28, 109.17, 127.02, 128.63 (2C), 128.77 (2C), 129.11, 129.61, 137.77, 155.94; EIms: m/z

243 (41), 199,108, 107, 91 (100); Anal. Calcd for $C_{15}H_{17}NO_2$: C, 59.24; H, 7.05; N, 5.76. Found: C, 59.65; H, 7.10; N, 5.81.

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