Supporting information

General: All NMR experiments were done on a Varian Unity 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C), and chemical shifts are given in ppm relative to TMS. For the photo-initiated radical cyclizations a micro photochemical reaction assembly as designed by J. H. Penn and R. D. Orr[1] from Aldrich was used. A borosilicate glass immersion well was employed to exclude wavelengths lower than 300 nm. Except for the radical cyclizations (performed under an argon atmosphere), all reactions were carried out under an atmosphere of dry nitrogen. Coupling constants were measured using J doubling[2] and are all given in Hz. The letters *e* and *z* stands for entgegen and zusammen and refer to the orientation of methylene protons relative to neighbouring methine protons. The assignment of pyrrolidine stereochemistry was based on NOE difference and noesy experiments. Cis-trans ratios were determined by integration in crude ^{1}H NMR spectra.

Solvents: Anhydrous solvents were used in all reactions. Drying was accomplished by refluxing over sodium (THF, diethyl ether, toluene) or calcium hydride (dichloromethane, benzene) before distillation.

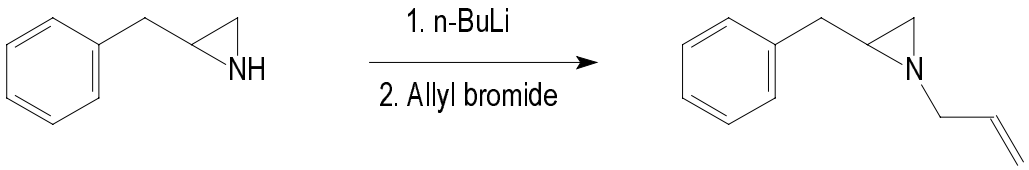
Materials: 2-Benzyl-aziridine,[3] 2-isobutyl-aziridine,[3,4] 2-hexyl-aziridine[4] and 2-phenoxymethyl-aziridine[4] were prepared according to or in analogy with literature procedures. The α-phenylselanyl ketones were prepared according to Engman.[5] All other chemicals were purchased from Lancaster or Aldrich. Tri-*n*-butyltin hydride was distilled from lithium aluminium hydride before use.

---

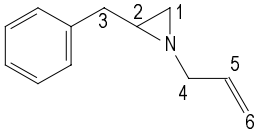
[1] Penn, J. H.; Orr, R. D. *J. Chem. Ed.* **1989**, *66*, 86.
[2] McIntyre, R.; Freeman, R. *J. Magn. Reson.* **1992**, *96*, 425. del Rio-Portilla, F.; Blechta, V.; Freeman, R. *J. Magn. Reson.* **1994**, *A 111*, 132.
[3] Brois, S. J. *J. Org. Chem.* **1962**; *27*; 3532.
[4] Hassner, A.; Galle, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 3733.
[5] Engman, L.; *Tetrahedron Lett*. **1985**, *26*, 6385.

Typical procedure for allylation of aziridines:

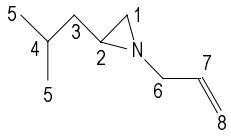
***N*-Allyl-2-benzyl-aziridine (1a): (method A)**



To 2-benzyl-aziridine (2.33 g, 17.5 mmol) in dry THF (100 mL) at –78 ^{o}C was added *n*-butyllithium (9.1 mL 2.5 M, 22.75 mmol) in hexane. The reaction mixture was left for 15 min at –78 ^{o}C and allyl bromide (6.35 g, 52.5 mmol) was added rapidly to the suspension of the amide salt. The reaction mixture was then allowed to reach room temperature overnight. Diethyl ether was added and the organic phase washed with three portions of brine. The organic phase was evaporated *in vacuo*, and the crude material purified on silica gel (40% ethyl acetate in pentane) to yield 2.54 g (84%) of the title compound.



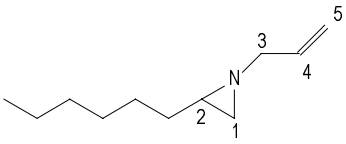
^{1}H NMR ($CDCl_3$) δ 1.32 (d, J = 6.3, 1H, *H-1z*), 1.62 (ddt, J = 3.6, 6.5, 6.2, 1H, *H-2*), 1.71 (d, J = 3.5, 1H, *H-1e*), 2.61 (dd, J = 6.3, 14.3, 1H, *H-3/H'-3*), 2.82 (tdd, J = 1.4, 5.8, 14.0, 1H, *H-4/H'-4*), 2.84 (dd, J = 6.2, 14.4, 1H, *H'-3/H-3*), 2.91 (tdd, J = 1.4, 5.8, 14.0, 1H, *H'-4/H-4*), 5.07 (tdd, J = 1.2, 1.9, 10.3, 1H, *H-6z*), 5.17 (qd, J = 1.7, 17.2, 1H, *H-6e*), 5.87 (tdd, J = 5.7, 10.4, 17.2, 1H, *H-5*), 7.19-7.34 (m, 5H, *Ph*).
^{13}C NMR ($CDCl_3$) δ 33.5, 39.4, 40.4, 63.3, 116.2, 126.2, 128.4, 128.7, 135.4, 139.6.



***N*-Allyl-2-isobutyl-aziridine (1b):** ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 1.4, 6.7, 6H, *H-5*), 1.14-1.40 (several multiplets, 4H, *H-1z, H-2, H-3 and H'-3*), 1.51 (d, J = 3.2, 1H, *H-1e*), 1.74 (m, 1H, *H-4*), 2.81 (tdd, J = 1.6, 5.8, 13.7, 1H, *H-6/H'-6*), 2.88 (tdd, J =

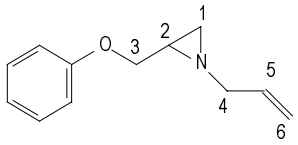
1.7, 6.0, 13.7, 1H, *H'-6/H-6*), 5.09 (dm, J = 10.4, 1H, *H-8z*), 5.18 (qd, J = 1.6, 17.1, 1H, *H-8e*), 5.92 (tdd, J = 5.8, 10.3, 17.2, 1H, *H-7*).

^{13}C NMR ($CDCl_3$) δ 22.3 (*CH_3*), 23.0 (*CH_3*), 27.1, 33.7, 38.1, 42.2, 63.6(*C-6*), 116.1 (*C-8*), 135.7 (*C-7*).



***N*-Allyl-2-hexyl-aziridine (1c):** ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 3H, *CH_3*), 1.21-1.50 (several peaks, 12H, *alkyl chain, H-2, H-1z*), 1.54 (d, J = 3.3, 1H, *H-1e*), 2.82 (tdd, J = 1.5, 6.0, 13.8, 1H, *H-3/H'-3*), 2.88 (tdd, J = 1.5, 5.8, 13.8, 1H, *H'-3/H-3*), 5.10 (tdd, J = 1.2, 1.9, 10.4, 1H, *H-5z*), 5.19 (qd, J = 1,7, 17.2, 1H, *H-5e*), 5.93 (tdd, J = 5.9, 10.4, 17.2, 1H, *H-4*).

^{13}C NMR ($CDCl_3$) δ 14.0 (*CH_3*), 22.6, 27.4, 29.1, 31.8, 33.0, 33.5, 39.5 (*C-2*), 63.5 (*C-3*), 116.1 (*C-5*), 135.6 (*C-4*).

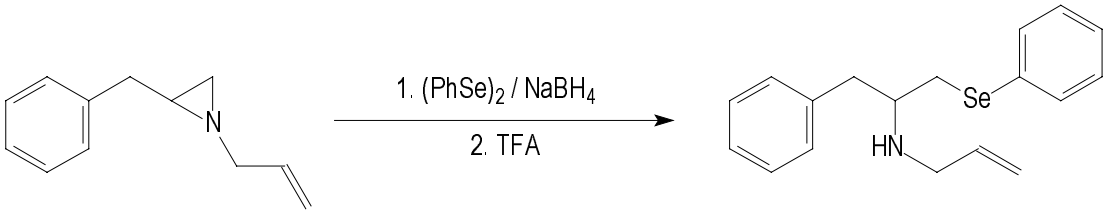


***N*-Allyl-2-phenoxymethyl-aziridine (1d):** 54% Yield. ^{1}H NMR ($CDCl_3$) δ 1.44 (d, 6.5, 1H, *H-1z*), 1.80 (d, J = 3.4, 1H, *H-1e*), 1.86 (m, 1H, *H-2*) 2.90 (tdd, J = 1.4, 5.8, 14.0, 1H, *H-4/H'-4*), 2.98 (tdd, J = 1.4, 5.6, 13.9, 1H, *H'-4/H-4*), 3.95 (m, 2H, *H-3 and H'-3*), 5.14 (tdd, J = 1.4, 1.8, 10.4, 1H, *H-6z*), 5.27 (qd, J = 1.7, 17.2, 1H, *H-6e*), 5.94 (tdd, J = 5.7, 10.4, 17.2, 1H, *H-5*), 6.89-6.96 (m, 3H, *Ph*), 7.23-7.30 (m, 2H, *Ph*).

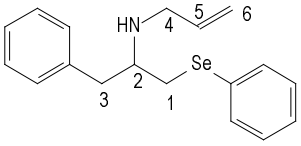
^{13}C NMR ($CDCl_3$) δ 31.6 (*C-1*), 37.4 (*C-2*), 62.9 (*C-4*), 70.1 (*C-3*), 114.6 (*C-Ph*), 116.4 (*C-6*), 120.8 (*C-Ph*), 129.4 (*C-Ph*), 135.0 (*C-5*), 158.7 (*C-Ph*).

Typical procedure for ring opening of allylated aziridines with benzeneselenol:

***N*-Allyl-2-amino-3-phenylpropyl phenyl selenide (2a):**

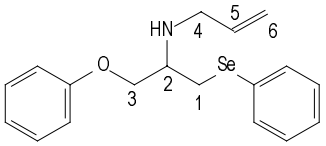


Diphenyl diselenide (392 mg, 1.26 mmol) was dissolved in THF (6.5 mL) and the solution titrated with $NaBH_4$ in water until colourless. *N*-Allyl-2-benzyl-aziridine (145 mg, 0.84 mmol) was then added to this solution followed by trifluoroacetic acid (110 μL, 1.43 mmol). The reaction was left for one hour, an aqueous NaOH solution (20 mL 1 M) was added, and the water/THF mixture extracted with ether. The organic phase was washed once with water, once with brine, and dried over KOH pellets and evaporated *in vacuo*. Flash chromatography on silica gel (50% ethyl acetate in pentane) afforded 245 mg (86%) of the title compound.



^{1}H NMR ($CDCl_3$) δ 2.80 (dd, 7.1, 13.8, 1H, *H-3/H'-3*), 2.88 (dd, J = 6.2, 13.8, 1H, *H'-3/H-3*), 2.94 (m, 1H, *H-1/H'-1*), 3.02 (m, 1H, *H-2*), 3.03 (m, 1H, *H'-1/H-1*), 3.21 (dddd, J = 1.3, 1.6, 6.0, 14.0, 1H, *H-4/H'-4*), 3.25 (dddd, J = 1.3, 1.6, 6.0, 14.0, 1H, *H'-4/H-4*), 5.03 (tdd, J = 1.3, 1.7, 10.2, 1H, *H-6z*), 5.08 (qd, J = 1.7, 17.2, 1H, *H-6e*), 5.79 (tdd, J = 6.1, 10.2, 17.2, 1H, *H-5*), 7.14 (m, 1H, *Ph*), 7.16 (m, 1H, *Ph*), 7.20-7.24 (several multiplets, 4H, *Ph*), 7.26 (m, 1H, *Ph*_), 7.28 (m, 1H, *Ph*), 7.42-7.46 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 33.1 (*C-1*), 40.6 (*C-3*), 49.7 (*C-2*), 54.2 (*C-4*), 115.9 (*C-6*), 116.3 (*C-Ph*), 128.4 (*C-Ph*), 130.4 (*C-Ph*), 132.6 (*C-Ph*), 136.7 (*C-5*), 138.6 (*C-Ph*).



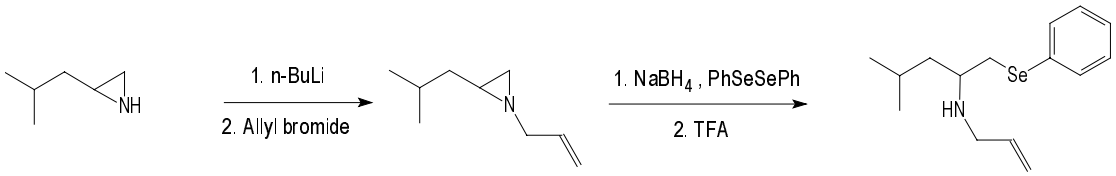
***N*-Allyl-2-amino-3-phenoxypropyl phenyl selenide (2d):** 83% Yield. ^{1}H NMR ($CDCl_3$) δ 1.73 (broad s, 1H, *N-H*) 3.13-3.24 (several multiplets, 3H, *H-1, H'-1 and H-2*), 3.29 (m, 2H, *H-4 and H'-4*), 4.02 (m, 2H, *H-3/H'-3*), 5.06 (tdd, J = 1.3, 1.7, 10.2, 1H, *H-6z*), 5.14 (qd, J = 1.7, 17.2, 1H, *H-6e*), 5.86 (tdd, J = 6.1, 10.2, 17.2, 1H, *H-5*), 6.85 (m, 1H, *Ph*), 6.87 (m, 1H, *Ph*), 6.94 (m, 1H, *Ph*), 7.19-7.31 (several multiplets, 5H, *Ph*), 7.49-7.54 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 30.3 (*C-1*), 49.9 (*C-4*), 56.1 (*C-2*), 69.1 (*C-3*), 114.5 (*C-Ph*), 116.1 (*C-6*), 120.9 (*C-Ph*), 126.9 (*C-Ph*), 129.1 (*C-Ph*), 129.4 (*C-Ph*), 130.1 (*C-Ph*), 132.6 (*C-Ph*), 136.6 (*C-5*), 158.5 (*C-Ph*).

Typical one-pot procedure for allylation and aziridine ring opening:

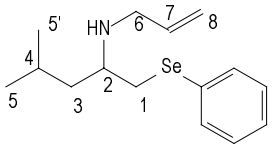
***N*-Allyl-2-amino-4-methylpentyl phenyl selenide (2b):**

Some of the low molecular weight aziridines were allylated and ring opened *in situ* without workup.



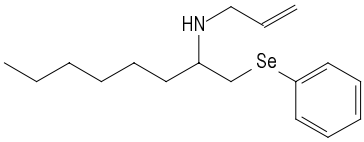
To 2-isobutyl-aziridine (200 mg, 2.02 mmol) in dry THF (12 mL) at –78 ^{o}C was added *n*-butyllithium (2.22 mL 1 M, 2.22 mmol) in hexane. The reaction mixture was left for 15 min at –78 ^{o}C and allyl bromide (0.188 mL, 2.22 mmol) was added rapidly to the suspension of the amide salt. The cooling bath was removed and the reaction mixture was refluxed for 1 h. In another flask, sodium borohydride was added to diphenyl diselenide (0.946 mg, 3.03 mmol) in ethanol until the solution turned colourless. At room temperature, this solution was then added to the aziridine solution, followed by trifluoroacetic acid (0.468 mL, 6.06 mmol). After 1 h, diethyl ether was added and the organic phase extracted three times with water. The organic phase was dried over KOH pellets and evaporated *in vacuo*. The crude material was

purified on silica gel (50% ethyl acetate in pentane with small amounts (<1%) of NMe_3 as a silica deactivator) to yield 280 mg (47 %) of the title compound.



^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 2.6, 1H, *H-5/H'-5*), 0.86 (d, J = 2.6, 1H, *H'-5/H-5*), 1.37 (m, 2H, *H-3*), 1.62 (broad s, 1H, *N-H*) 1.64 (nonet, J = 6.5, *H-4*), 2.80 (ddtd, J = 5.2, 5.7, 6.6, 10.9, 1H, *H-2*), 2.98 (dd, J = 5.7, 12.2, 1H, *H-1/H'-1*), 3.10 (dd, J = 5.2, 12.2, 1H, *H'-1/H-1*), 3.17 (dddd, J = 1.3, 1.5, 6.1, 13.8, 1H, *H-6/H'-6*), 3.21 (dddd, J = 1.3, 1.6, 6.0, 13.8, 1H, *H'-6/H-6*), 5.04 (tdd, J = 1.3, 1.8, 10.2, 1H, *H-8z*), 5.10 (tdd, J = 1.6, 1.8, 17.1, 1H, *H-8e*), 5.84 (tdd, J = 6.1, 10.2, 17.1, 1H, *H-7*), 7.21-7.27 (several multiplets, 3H, *Ph*), 7.49-7.55 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 22.7 (*C-5*), 22.8 (*C-5*), 24.9 (*C-4*), 34.3 (*C-1*), 43.9 (*C-3*), 49.4 (*C-6*), 54.2 (*C-2*), 115.9 (*C-8*), 126.8 (*C-Ph*), 129.0 (*C-Ph*), 130.5 (*C-Ph*), 132.9 (*C-Ph*), 136.8 (*C-7*).

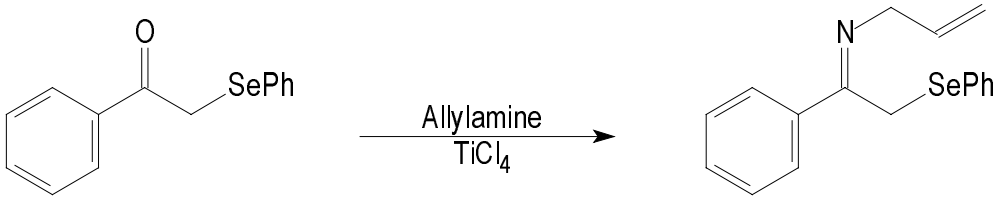


***N*-Allyl-2-aminooctyl phenyl selenide (2c):** 45 % Yield (over two steps). ^{1}H NMR ($CDCl_3$) δ 0.87 (m, 3H, CH_3), 1.18 – 1.34 (several multiplets, 8H, $CH_2CH_2CH_2CH_2$) 1.49 (several multiplets, 3H, *H-3, H'-3 and N-H*), 2.73 (dtd, J = 5.2, 6.1, 6.2, 1H, *H-2*), 2.97 (dd, J = 6.2, 12.2, 1H, *H-1/H'-1*), 3.11 (dd, J = 5.2, 12.2, 1H, *H'-1/H-1*), 3.18 (ddd, J = 1.3, 1.6, 6.0, 2H, *H-4 and H'-4*), 5.04 (tdd, J = 1.2, 1.8, 10.2, 1H, *H-6z*), 5.11 (tdd, J = 1.6, 1.8, 17.2, 1H, *H-6e*), 5.85 (tdd, J = 1.6, 10.2, 17.1, 1H, *H-5*), 7.21-7.27 (several multiplets, 3H, *Ph*), 7.49-7.55 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 22.5 (CH_2), 25.7 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 33.8 (*C-1*), 34.3 (*C-3*), 49.5 (*C-4*), 56.2 (*C-2*), 115.8 (*C-6*), 126.7 (*C-Ph*), 128.9 (*C-Ph*), 130.4 (*C-Ph*), 132.7 (*C-Ph*), 136.9 (*C-5*).

Typical procedure for *in situ* preparation of *N*-allyl-2-iminoalkyl phenyl selenides:

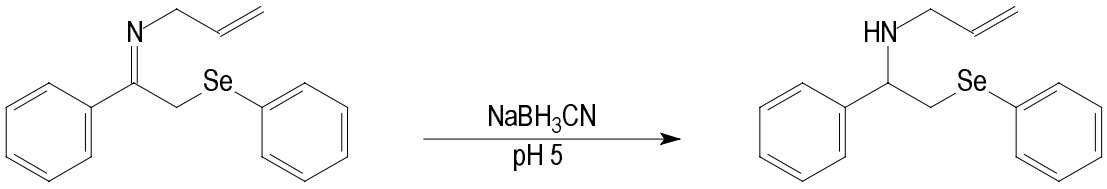
***N*-Allyl-2-imino-2-phenylethyl phenyl selenide:**



A solution of $TiCl_4$ (0.49 g, 2.6 mmol) in dry toluene (7 mL) was added dropwise at 0 ^oC during 10 min to a solution of phenyl-2-phenylselanylethanone (1.3 g, 4.72 mmol) and allylamine (1.08 g, 18.9 mmol) in dry diethyl ether (20 mL). The reaction mixture was left overnight at room temperature. The thick, white suspension that formed was poured into a separatory funnel containing diethyl ether and ice-cold aqueous 1M NaOH. The phases were separated and the ether layer washed three times with water. After drying (KOH) and evaporation of the solvent, the crude product was taken to the next step without further purification.

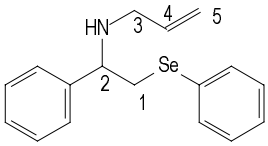
Typical procedure for reduction of *N*-allyl-2-iminoalkyl phenyl selenides:

***N*-Allyl-2-amino-2-phenylethyl phenyl selenide (5b):**



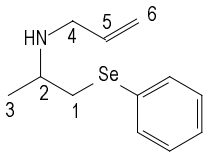
The *in situ* generated imine (1.43 g, 4.57 mmol) in methanol (20 mL) was charged together with a small amount of bromocresol green into a flask and the mixture was cooled to –50 ^oC. $NaBH_3CN$ (0.574 g, 9.14 mmol) was added and the reaction mixture titrated with HCl in MeOH until the indicator changed colour to yellow. The reaction was left for 3 h and then allowed to warm to room temperature. Water was added, the crude product was extracted with 3 portions of diethyl ether, and the combined organic extracts washed three times with water. After drying ($MgSO_4$) and evaporation *in vacuo*, the residue was chromatographed on silica gel (CH_2Cl_2 and

then 50% ethyl acetate in CH_2Cl_2) to give 0.845 g (58% over two steps) of the title compound.



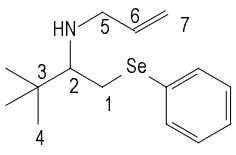
^{1}H NMR ($CDCl_3$) δ 1.94 (broad s, 1H, *N-H*), 2.98 (dddd, J = 1.2, 1.4, 6.7, 14.2, 1H, *H-3/H'-3*), 3.09 (dd, J = 9.3, 12.4, 1H, *H-1/H'-1*), 3.12 (, J = 1.5, 1.8, 5.2, 14.2, 1H, *H'-3/H-3*), 3.23 (dd, J = 4.5, 12.4, 1H, *H'-1/H-1*), 3.77 (dd, J = 4.5, 9.3, 1H, *H-2*), 5.04 (dddd, J = 1.2, 1.4, 1.8, 10.2, 1H, *H-5z*), 5.09 (dtd, J = 1.5, 1.7, 17.2, 1H, *H-1e*), 5.83 (dddd, J = 5.3, 6.6, 10.3, 17.2, 1H, *H-4*), 7.23-7.33 (several multiplets, 8H, *Ph*), 7.49-7.52 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 36.5 (*C-1*), 50.0 (*C-3*), 61.3 (*C-2*), 115.8 (*C-5*), 127.0 (*C-Ph*), 127.1 (*C-Ph*), 127.5 (*C-Ph*), 128.5 (*C-Ph*), 128.5 (*C-Ph*), 129.1 (*C-Ph*), 132.9 (*C-Ph*), 136.8 (*C-4*), 142.8 (*C-Ph*).



***N*-Allyl-2-aminopropyl phenyl selenide (5a):** ^{1}H NMR ($CDCl_3$) δ 1.13 (d, J = 6.2, 3H, *H-3*), 2.86 (pd, J = 6.2, 5.8, 1H, *H-2*), 2.94 (dd, J = 6.2, 12.2, 1H, *H-1/H'-1*), 3.00 (dd, J = 5.7, 12.1, 1H, *H'-1/H-1*), 3.14 (dddd, J = 1.3, 1.6, 6.2, 13.9, 1H, *H-4/H'-4*), 3.23 (dddd, J = 1.3, 1.6, 5.8, 13.9, 1H, *H'-4/H-4*), 5.04 (tdd, J = 1.3, 1.8, 10.2, 1H, *H-6z*), 5.11 (tdd, J = 1.6, 1.8, 17.2, 1H, *H-6e*), 5.84 (tdd, J = 5.8, 6.2, 10.2, 17.1, 1H, *H-5*), 7.19-7.25 (several multiplets, 3H, *Ph*), 7.48-7.52 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 20.5 (*C-3*), 35.8 (*C-1*), 49.5 (*C-4*), 51.7 (*C-2*), 115.5 (*C-6*), 126.6 (*C-Ph*), 128.8 (*C-Ph*), 130.1 (*C-Ph*), 132.5 (*C-Ph*), 136.6 (*C-5*).



***N*-Allyl-2-amino-3,3-dimethylbutyl phenyl selenide (5c):** 37% Yield (over two steps). ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9H, *H-4*), 0.97 (broad s, 1H, *N-H*), 2.30 (dd, J =

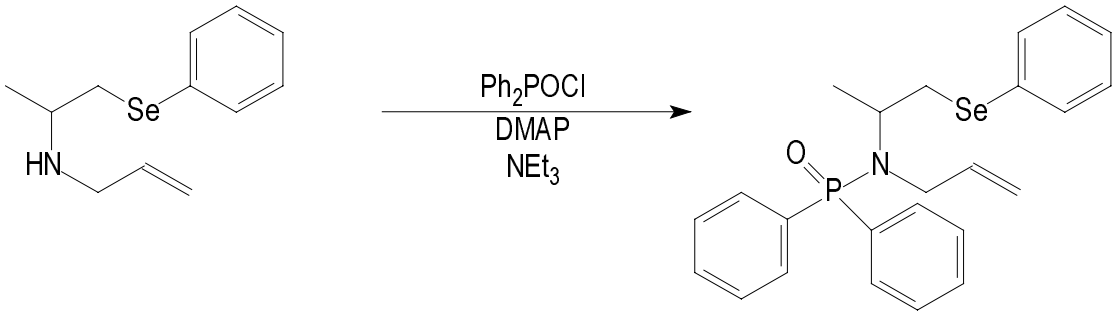
3.5, 9.0, 1H, *H-2*), 2.76 (dd, J = 9.0, 12.1, 1H, *H-1/H'-1*), 3.12 (dddd, J = 1.3, 1.6, 6.1, 13.7, 1H, *H-5/H'-5*), 3.15 (dd, J = 3.5, 12.1, 1H, *H'-1/H-1*), 3.29 (dddd, J = 1.3, 1.6, 6.0, 13.7, 1H, *H'-5/H-5*), 4.93 (tdd, J = 1.3, 2.0, 10.2, 1H, *H-7z*), 5.04 (tdd, J = 1.6, 2.0, 17.1, 1H, *H-7e*), 5.79 (tdd, J = 6.0, 10.2, 17.1, 1H, *H-6*), 7.11-7.19 (several multiplets, 3H, *Ph*), 7.39-7.43 (several multiplets, 2H, *Ph*).

^{13}C NMR ($CDCl_3$) δ 26.9 (*C-4*), 32.0 (*C-1*), 36.1 (*C-3*), 53.7 (*C-5*), 66.1 (*C-2*), 115.4 (*C-7*), 126.7 (*C-Ph*), 129.0 (*C-Ph*), 131.2 (*C-Ph*), 132.4 (*C-Ph*), 137.3 (*C-6*).

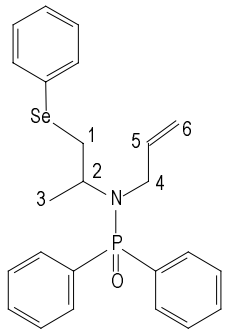
Typical procedure for *N*-protection of *N*-allyl-2-aminoalkyl phenyl selenides:

The procedure is typical for all protecting groups used. Compounds described in Table 1 were obtained in 80-100% yield. Because of the presence of rotamers, the ^{1}H NMR spectra of these materials were exceedingly complex.

***N*-Allyl-*N*-diphenylphosphinoyl-2-aminopropyl phenyl selenide:**

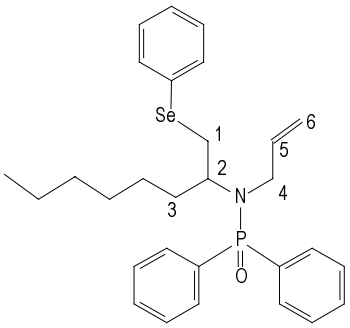


To a solution of *N*-allyl-2-aminopropyl phenyl selenide (300 mg, 1.18 mmol) in dry dichloromethane (6 mL) was added DMAP (29 mg, 0.24 mmol) and triethylamine (0.362 mL, 2.60 mmol). The reaction mixture was cooled to 0 ^{o}C, diphenylphosphinic chloride (450 μL, 2.36 mmol) was added dropwise and the flask was left overnight at room temperature. More dichloromethane was added, the solution was extracted three times with water and dried over $MgSO_4$. After evaporation of the solvent and flash chromatography on silica gel (ethyl acetate), 474 mg (88%) of the title compound was isolated.



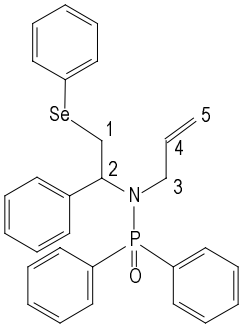
^{1}H NMR δ 1.38 (d, J = 7.0, 3H, *H-3*), 3.00 (dd, J = 9.2, 12.3, 1H, *H-1/H'-1*), 3.37 (dd, J = 5.8, 12.3, 1H, *H'-1/H-1*), 3.59-3.69 (several multiplets, 3H, *H-2*, *H-4 and H'-4*), 4.93 (qd, J = 1.6, 17.1, 1H, *H-1e*), 4.95 (dqd, J = 0.6, 1.5, 10.4, 1H, *H-6z*), 5.88 (dddd, J = 6.2, 6.6, 10.3, 17.0, 1H, *H-5*), 7.15-7.20 (several multiplets, 3H, *Ph*), 7.34-7.51 (several multiplets, 8H, *Ph*), 7.82-7.90 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 19.6 (2 signals), 33.9 (2 signals), 45.9 (2 signals), 52.9 (2 signals), 116.3 (*C-5*), 126.7 (*C-Ph*), 128.3 (2 signals, *C-Ph*), 128.5 (2 signals, *C-Ph*), 129.0 (*C-Ph*), 129.9 (*C-Ph*), 131.2 (*C-Ph*), 131.5 (*C-Ph*), 131.7 (3 signals, *C-Ph*), 132.3 (*C-Ph*), 132.4 (*C-Ph*), 132.8 (*C-Ph*), 138.2 (2 signals, *C-6*).



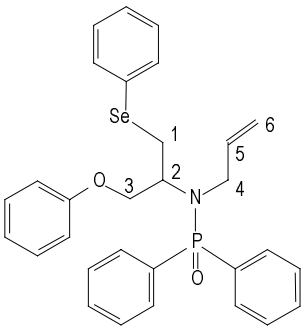
***N*-Allyl-*N*-diphenylphosphinoyl-2-aminooctyl phenyl selenide:** 55% Yield. ^{1}H NMR δ 0.86 (m, 3H, *CH_3*), 1.07-1.38 (several multiplets, 8H, *CH_2*), 1.73 (m, 2H, *CH_2-3*), 3.08 (m, 1H, *H-1/H'-1*), 3.33-3.45 (several multiplets, 2H, *H'-1/H-1 and H-2*), 3.63 (m, 2H, *H-4 and H'-4*), 4.91 (qd, J = 1.4, 17.1, 1H, *H-6e*), 4.93 (m, 1H, *H-1z*), 5.93 (tdd, J = 6.3, 10.3, 17.0, 1H, *H-5*), 7.16-7.21 (several multiplets, 3H, *Ph*), 7.33-7.47 (several multiplets, 8H, *Ph*), 7.84-7.95 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 14.0 (*CH_3*), 22.5, 26.7, 28.9, 31.5, 33.1 (2 signals, *C-1*), 33.3 (2 signals, *C-3*), 46.7 (2 signals, *C-4*), 57.5 (2 signals, *C-2*), 116.5 (*C-6*), 126.6 (*C-Ph*), 128.2 (*C-Ph*), 128.3 (*C-Ph*), 128.9 (*C-Ph*), 130.4 (*C-Ph*), 131.2 (*C-Ph*), 131.5 (2 signals, *C-Ph*), 131.6 (*C-Ph*), 132.1 (*C-Ph*), 132.4 (*C-Ph*), 132.5 (*C-Ph*), 132.6 (*C-Ph*), 132.9 (*C-Ph*), 137.9 (2 signals, *C-7*).



***N*-Allyl-*N*-diphenylphosphinoyl-2-amino-2-phenylethyl phenyl selenide:** 71% Yield. ^{1}H NMR δ 3.33 (tddd, J = 1.1, 7.9, 11.8, 16.5, 1H, *H-3/H'-3*), 3.54 (ddddd, J = 1.8, 1.9, 4.8, 10.4, 16.5, 1H, *H-3/H'-3*), 3.60 (ddd, J = 0.4, 5.8, 12.3, 1H, *H-1/H'-1*), 3.76 (dd, J = 10.4, 12.2, 1H, *H'-1/H-1*), 4.77 (dddd, J = 1.2, 1.4, 2.0, 17.2, 1H, *H-5e*), 4.84 (dt, J = 5.7, 10.4, 1H, *H-2*), 4.87 (dddd, J = 0.6, 1.4, 1.7, 10.2, 1H, *H-5z*), 5.67 (dddd, J = 4.8, 8.0, 10.2, 17.2, 1H, *H-4*), 7.14-7.21 (several multiplets, 3H, *Ph*), 7.25-7.49 (several multiplets, 13H, *Ph*), 7.78-7.87 (several multiplets, 4H, *Ph*).

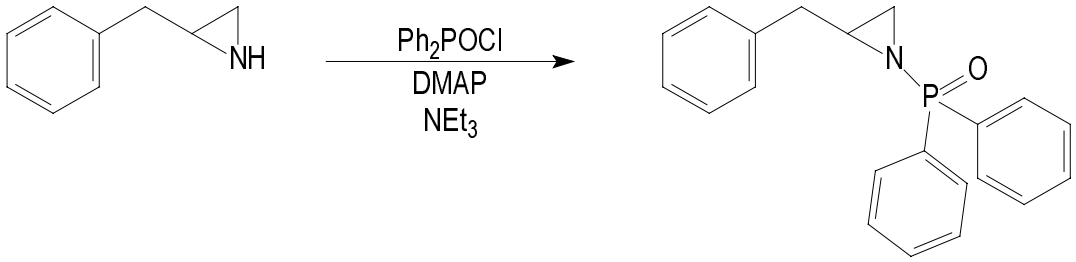
^{13}C NMR δ 31.1 (2 signals, *C-1*), 46.7 (2 signals, *C-3*), 60.0 (2 signals, *C-2*), 116.2 (*C-5*), 126.6 (*C-Ph*), 127.5 (*C-Ph*), 128.0 (*C-Ph*), 128.1 (2 signals, *C-Ph*), 128.2 (*C-Ph*), 128.7 (*C-Ph*), 128.8 (*C-Ph*), 130.0 (2 signals, *C-Ph*), 131.0 (*C-Ph*), 131.1 (*C-Ph*), 131.4 (2 signals, *C-Ph*), 131.5 (2 signals, *C-6*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 132.4 (*C-Ph*), 132.6 (*C-Ph*), 137.2 (2 signals, C-*7*), 137.7 (2 signals, *Ph*).



***N*-Allyl-*N*-diphenylphosphinoyl-2-amino-3-phenoxypropyl phenyl selenide:** 82% Yield. ^{1}H NMR δ 3.40 (m, 2H, *H-1 and H'-1*), 3.72 (m, 2H, *H-4 and H'-4*), 3.91 (m, 1H, *H-2*), 4.30 (m, 2H, *H-3 and H'-3*), 4.93 (m, 2H, *H-6z and H-6e*), 5.84 (tdd, J = 6.6, 9.9, 17.5, 1H, *H-5*), 6.79-6.83 (several multiplets, 2H, *Ph*), 6.94 (m, 1H, *Ph*), 7.16-7.21 (several multiplets, 3H, *Ph*), 7.22-7.27 (several multiplets, 2H, *Ph*), 7.33-7.50 (several multiplets, 8H, *Ph*), 7.85-7.93 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 28.9 (*C-1*), 48.0 (2 signals, *C-4*), 56.5 (2 signals, *C-2*), 68.4 (2 signals, *C-3*), 114.4 (*C-Ph*), 117.0 (*C-6*), 120.9 (*C-Ph*), 128.3 (2 signals, *C-Ph*), 128.5 (2 signals, *C-Ph*) 129.1 (*C-Ph*), 129.4 (*C-Ph*), 129.8 (*C-Ph*), 131.2 (*C-Ph*), 131.8 (*C-Ph*), 132.1 (*C-Ph*), 132.4 (*C-Ph*), 132.5 (*C-Ph*), 132.6 (*C-Ph*), 137.4 (*C-5*), 158.1 (*C-Ph*).

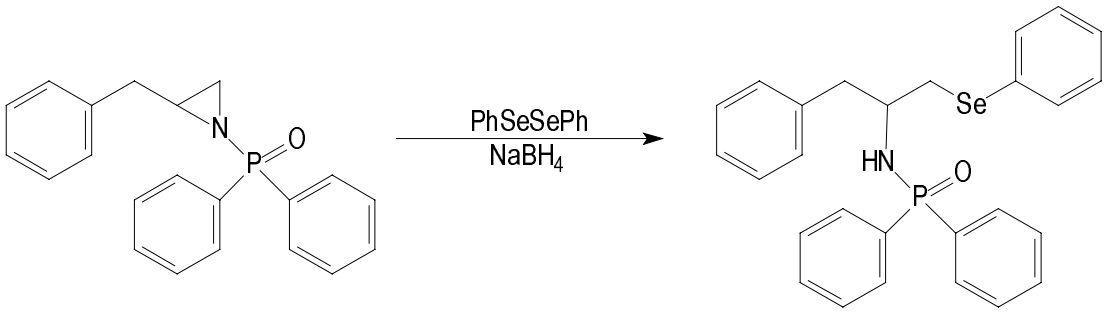
Alternative route to N-protected *N*-allyl-2-aminoalkyl phenyl selenides: *N*-Diphenylphosphinoyl-2-benzyl-aziridine:



To a solution of 2-benzyl-aziridine (205 mg, 1.54 mmol) in dry dichloromethane (8 mL) was added triethylamine (0.215 mL, 1.54 mmol). The reaction mixture was cooled to 0 ^{o}C and diphenylphosphinic chloride (0.294 mL, 1.54 mmol) was added dropwise. The reaction mixture was kept at 0 ^{o}C for 1 h and at room temperature for 4 h. Extra dichloromethane was added, the solution was extracted three times with aqueous $NaHCO_3$, once with water and dried with $MgSO_4$. After evaporation of the solvent, flash chromatography on silica gel (50% ethyl acetate in pentane) 461 mg (87%) of the title compound was isolated. ^{1}H NMR data were in good agreement with literature.[6]

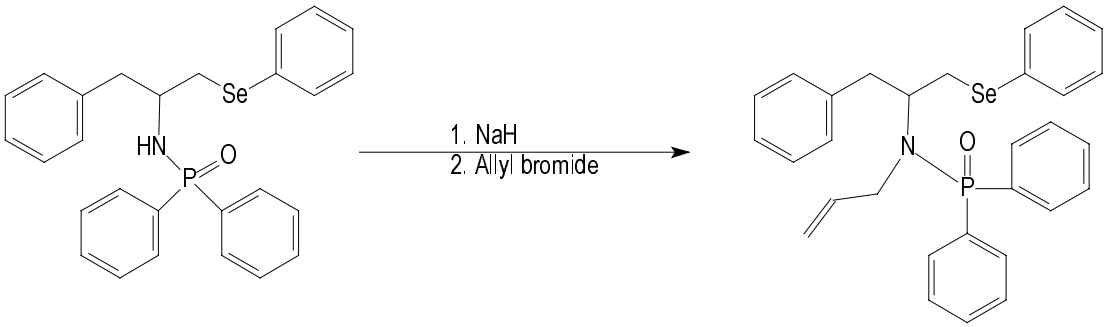
[6] Cantrill, A. A.; Osborn; H. M. I.; Sweeney, J. *Tetrahedron* **1998**, *54*, 2181.

_N_-Diphenylphosphinoyl-2-amino-3-phenylpropyl phenyl selenide:



Diphenyl diselenide (1.47 g, 4.70 mmol) was dissolved in ethanol (50 mL) and $NaBH_4$ added portionwise until the solution was decolourized. *N*-Diphenylphosphinoyl-2-benzyl-aziridine (1.045 g, 3.13 mmol) in THF was then added and the reaction mixture left overnight at room temperature. After dilution with diethyl ether, the solution was washed three times with water and dried over $MgSO_4$. Flash chromatography (ethyl acetate) afforded 0.814 g (53%) of the title compound. ^{1}H NMR data were in good agreement with literature.[7]

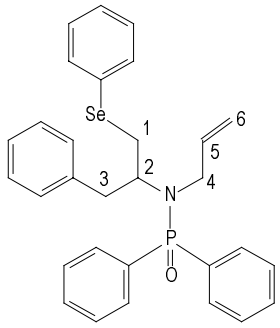
_N_-Allyl-_N_-diphenylphosphinoyl-2-amino-3-phenylpropyl phenyl selenide:



NaH (60% in mineral oil; 133 mg, 3.32 mmol) was washed three times with pentane and suspended in dry DMF (15 mL). *N*-Diphenylphosphinoyl-2-amino-3-phenylpropyl phenyl selenide (814 mg, 1.66 mmol) in dry DMF (10 mL) was then added. Finally, allyl bromide (210 μL, 2.49 mmol) was syringed into the solution and the reaction left overnight at room temperature. Water was added and the reaction mixture extracted with diethyl ether. After drying ($MgSO_4$), evaporation and flash

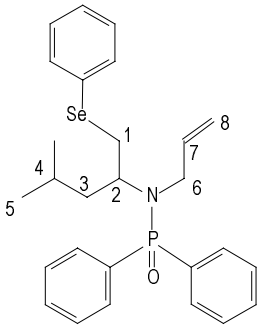
[7] See ref. 6.

chromatography (50% ethyl acetate in pentane), 739 mg (84%) of the title compound was isolated.



^{1}H NMR δ 3.09 (ddd, J = 1.1, 6.6, 12.8, 1H, *H-1/H'1*), 3.11 (m, 2H, *H-3 and H'-3*), 3.34 (ddd, J = 0.6, 8.1, 12.8, 1H, *H'-1/H-1*), 3.67 (m, 1H, *H-2*), 3.70 (m, 2H, *H-4 and H'-4*), 5.01 (m, 2H, *H-6z and H-6e*), 6.79 (tdd, J = 6.6, 9.9, 17.4, 1H, *H-5*), 6.86-6.92 (several multiplets, 4H, *Ph*), 7.10-7.24 (several multiplets, 2H, *Ph*), 7.28-7.37 (several multiplets, 8H, *Ph*), 7.39-7.48 (several multiplets, 2H, *Ph*), 7.68-7.75 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 31.0 (2 signals, *C-1*), 40.7 (2 signals, *C-3*), 47.5 (2 signals, *C-4*), 59.5 (2 signals, *C-2*), 116.8 (*C-6*), 126.4 (*C-Ph*), 126.4 (*C-Ph*), 128.3 (2 signals, *C-Ph*), 128.4 (3 signals, *C-Ph*), 129.0 (*C-Ph*), 129.3 (*C-Ph*), 130.1 (*C-Ph*), 131.2 (*C-Ph*), 131.5 (2 signal, *C-Ph*), 132.4 (*C-Ph*), 132.5 (*C-6*), 132.6 (*C-Ph*), 132.8 (*C-Ph*), 138.1 (2 signals, C-*7*), 138.9 (*Ph*).



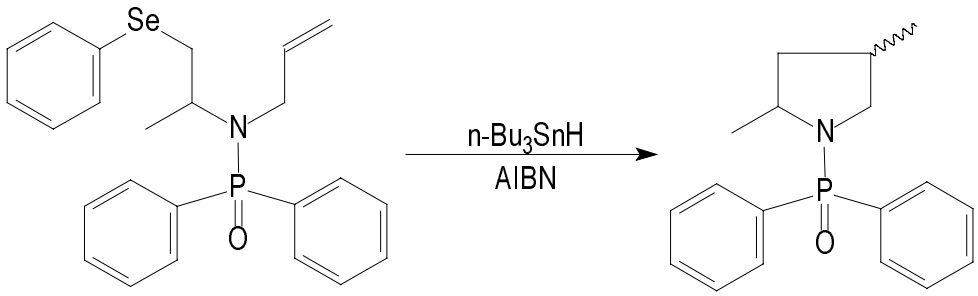
***N*-Allyl-*N*-diphenylphosphinoyl-2-amino-4-methylpentyl phenyl selenide:** 79% Yield. ^{1}H NMR δ 0.69 (d, J = 5.8, 3H, *H-5/H'-5*), 0.70 (d, J = 5.8, 3H, *H'-5/H-5*), 1.33-1.73 (several multiplets, 3H, *H-3 and H-4*), 3.08 (ddd, J = 0.8, 7.7, 12.2, 1H, *H-1/H'-1*), 3.39 (dd, J = 6.8, 12.2, 1H, *H'-1/H-1*), 3.49 (m, 1H, *H-2*), 3.64 (m, 2H, *H-6 and H'-6*), 4.92 (qd, J = 1.4, 17.0, 1H, *H-8e*), 4.94 (qd, J = 1.4, 10.2, 1H, *H-8z*), 5.92

(tdd, J = 6.7, 10.2, 17.0, 1H, *H-7*), 7.18-7.23 (several multiplets, 3H, *Ph*), 7.35-7.49 (several multiplets, 8H, *Ph*), 7.88-7.94 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 22.3 (*C-5 and C'5*), 24.6 (*C-4*), 33.2 (2 signals, *C-1*), 42.4 (2 signals, *C-3*), 46.8 (2 signals, *C-6*), 55.5 (2 signals, *C-2*), 116.5 (*C-8*), 126.7 (*C-Ph*), 128.2 (2 signals, *C-Ph*), 128.3 (2 signals, *C-Ph*), 128.9 (*C-Ph*), 130.2 (*C-Ph*), 131.1 (*C-Ph*), 131.5 (2 signal, *C-Ph*), 131.6 (2 signals, C-*Ph*), 131.7 (*C-Ph*), 132.3 (*C-Ph*), 132.5 (2 signals, *C-Ph*), 132.6 (2 signals, *C-Ph*), 133.0 (*C-Ph*), 137.9 (2 signals, *C-7*).

Typical procedure for radical cyclization (for yields and cis/trans ratios, see Table 2):

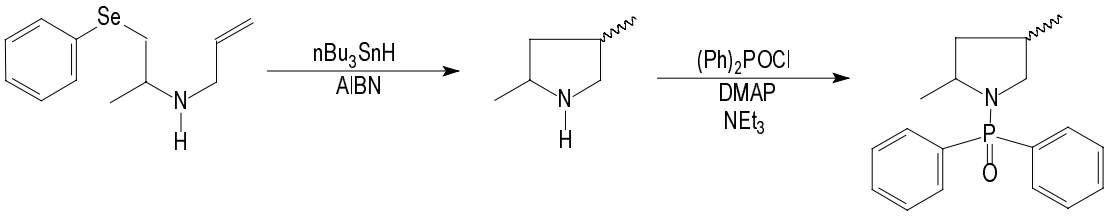
***N*-Diphenylphosphinoyl-2,4-dimethylpyrrolidine:**



N-Allyl-*N*-diphenylphosphinoyl-2-aminopropyl phenyl selenide (215 mg, 0.47 mmol) and AIBN (11.6 mg, 0.07 mmol) were dissolved in dry benzene (10 mL) and argon was bubbled through the solution for five minutes. Freshly distilled tri-*n*-butyltin hydride (190 μL, 0.71 mmol) was then added and the solution irradiated overnight at 15 ^{o}C. The solvent was evaporated *in vacuo* and the product subjected to flash chromatography (ethyl acetate) to yield 110 mg (78%) of the title compound.

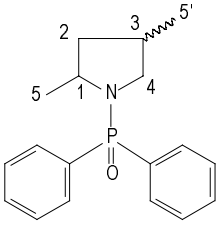
Typical procedure for radical cyclization of unprotected *N*-allyl-2-aminoalkyl phenyl selenide with subsequent protection (for yields and cis/trans ratios, see Table 2):

***N*-Diphenylphosphinoyl-2,4-dimethylpyrrolidine:**



N-Diphenylphosphinoyl-*N*-allyl-2-aminopropyl phenyl selenide (162 mg, 0.67 mmol) and AIBN (11.6 mg, 0.10 mmol) were dissolved in dry benzene (10 mL) and argon was bubbled through the solution for five minutes. Freshly distilled tri-*n*-butyltin hydride (270 μL, 1.01 mmol) was added and the solution irradiated overnight at 15 ^{o}C. To the reaction mixture was added triethylamine (205 μL, 1.47 mmol), DMAP (16.4 mg, 0.2 mmol) and finally, dropwise, diphenylphosphinic chloride (256 μL, 1.34 mmol). The solution was left overnight and then extracted with three portions of water. Drying ($MgSO_4$), evaporation and flash chromatography (ethyl acetate with small amounts (<1%) of NMe_3 as a silica deactivator), gave 118 mg (59%) of the title compound.

Radical cyclizations at elevated temperature were performed as described above, but initiation was effected by heating at reflux for 12 h without irradiation.

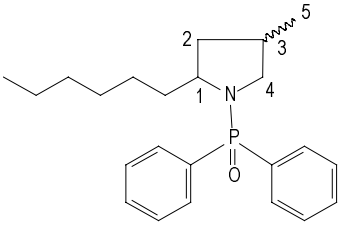


***N*-Diphenylphosphinoyl-2,4-*cis*-dimethylpyrrolidine:** ^{1}H NMR δ 0.96 (d, J = 6.4, 3H, *Me-5*), 0.97 (d, J = 5.9, 3H, *Me-6*), 1.10 (ddd, J = 7.5, 10.4, 12.3, 1H, *H-2/H'-2*), 2.22 (m, 1H, *H-3*), 2.32 (dddd, J = 1.3, 7.2, 7.5, 12.3, 1H, *H'-2/H-2*), 2.71 (td, J = 10.3, 12.3, 1H, *H-4/H'-4*), 3.26 (dddd, J = 1.3, 6.7, 8.8, 10.4, 1H, *H'-4/H-4*), 3.78 (qdd, J = 6.3, 7.3, 8.9, 1H, *H-1*), 7.37-7.52 (several multiplets, 6H, *Ph*), 7.81-7.95 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 17.0 (*C-6*), 23.4 (2 signals, *C-5*), 35.1 (2 signals, *C-3*), 43.8 (2 signals, *C-2*), 54.4 (2 signals, *C-4*), 54.6 (2 signals, *C-1*), 128.0 (*C-Ph*), 128.2 (*C-Ph*), 128.3 (*C-Ph*), 128.4 (*C-Ph*), 131.3 (2 signals, *C-Ph*), 131.4 (2 signals, *C-Ph*), 131.9 (*C-Ph*), 132.0 (*C-Ph*), 132.1 (2 signals, *C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 133.2 (*C-Ph*), 133.3 (*C-Ph*).

***N*-Diphenylphosphinoyl-2,4-*trans*-dimethylpyrrolidine:** ^{1}H NMR δ 1.00 (d, J = 6.5, 3H, *Me-5*), 1.01 (d, J = 6.5, 3H, *Me-6*), 1.69 (m, 2H, *H-2 and H'-2*), 2.43 (m, 1H, *H-3*), 2.69 (ddd, J = 7.9, 8.1, 9.5, 1H, *H-4/H'-4*), 3.28 (ddd, J = 4.8, 7.3, 9.4, 1H, *H'-4/H-4*), 3.82 (m, 1H, *H-1*), 7.37-7.49 (several multiplets, 6H, *Ph*), 7.83-7.94 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 17.7 (*C-6*), 23.0 (2 signals, *C-5*), 32.3 (2 signals, *C-3*), 42.5 (2 signals, *C-2*), 54.1 (2 signals, *C-4*), 54.4 (2 signals, *C-1*), 128.0 (*C-Ph*), 128.2 (2 signals, *C-Ph*), 128.3 (*C-Ph*), 131.3 (2 signals, *C-Ph*), 131.4 (2 signals, *C-Ph*), 131.7 (*C-Ph*), 132.0 (*C-Ph*), 132.1 (2 signals, *C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 133.0 (*C-Ph*), 133.3 (*C-Ph*).

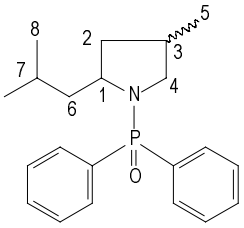


***N*-Diphenylphosphinoyl-*cis*-2-hexyl-4-methylpyrrolidine:** ^{1}H NMR δ 0.82 (t, J = 7.2, 3H, *Me*), 0.95 (d, J = 6.4, 3H, *Me-5*), 0.97-1.41 (several multiplets, 11H, *alkyl chain and H-2/H'-2*), 2.22 (m, 1H, *H-3*), 2.28 (ddd, J = 1.2, 7.6, 12.0, 1H, *H'2/H-2*), 2.65 (td, J = 10.6, 13.5, 1H, *H-4/H'-4*), 3.28 (dddd, J = 1.2, 6.6, 9.4, 10.4, 1H, *H'-4/H-4*), 3.67 (ddddd, J = 3.8, 7.2, 9.6, 9.9, 10.4, 1H, *H-1*), 7.36-7.49 (several multiplets, 6H, *Ph*), 7.79-7.86 (several multiplets, 2H, *Ph*), 7.88-7.95 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 13.8 (*C-Me*), 16.8 (*C-5*), 22.3 (*CH_2*), 25.21 (*CH_2*), 28.7 (*CH_2*), 31.4 (*CH_2*), 35.2 (2 signals, *C-3*), 37.1 (2 signals, *CH_2*), 41.1 (2 signals, *C-2*), 54.9 (2 signals, *C-4*), 58.5 (2 signals, *C-1*), 127.9 (*C-Ph*), 128.0 (*C-Ph*), 128.2 (*C-Ph*), 128.3 (*C-Ph*), 131.2 (2 signals, *C-Ph*), 131.3 (2 signals, *C-Ph*), 132.0 (*C-Ph*), 132.1 (*C-Ph*), 132.3 (*C-Ph*), 131.4 (*C-Ph*), 133.3 (*C-Ph*), 133.4 (*C-Ph*).

***N*-Diphenylphosphinoyl-*trans*-2-hexyl-4-methylpyrrolidine:** ^{1}H NMR δ 0.81 (t, J = 7.3, 3H, *Me*), 1.01 (d, J = 6.6, 3H, *Me-5*), 0.79-1.41 (several multiplets, 10H, *alkyl chain*), 1.60 (ddd, J = 7.5, 10.0, 12.2, 1H, *H-2/H'-2*), 1.80 (ddd, J = 1.8, 6.3, 12.1, 1H, *H'-2/H-2*), 2.36 (m, 1H, *H-3*), 2.71 (ddd, J = 8.0, 8.5, 9.4, 1H, *H-4/H'-4*), 3.24 (ddd, J = 5.0, 7.4, 9.4, 1H, *H'-4/H-4*), 3.62 (m, 1H, *H-1*), 7.37-7.51 (several multiplets, 6H, *Ph*), 7.81-7.95 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 13.8 (*C-Me*), 16.8 (*C-5*), 22.3 (*CH_2*), 26.13 (*CH_2*), 28.5 (*CH_2*), 31.4 (*CH_2*), 32.4 (2 signals, *C-3*), 36.3 (2 signals, *CH_2*), 39.2 (2 signals, *C-2*), 53.8 (2 signals, *C-4*), 59.0 (2 signals, *C-1*), 127.9 (*C-Ph*), 128.0 (*C-Ph*), 128.2 (2 signals, *C-Ph*), 131.1 (2 signals, *C-Ph*), 131.3 (2 signals, *C-Ph*), 131.4 (*C-Ph*), 132.7 (*C-Ph*), 131.1 (*C-Ph*), 132.0 (2 signals, *C-Ph*), 132.2 (2 signals, *C-Ph*), 132.3 (2 signals, *C-Ph*), 133.0 (*C-Ph*), 133.3 (*C-Ph*).



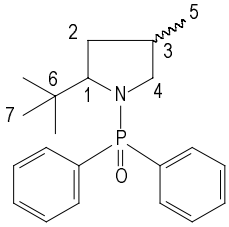
***N*-Diphenylphosphinoyl-*cis*-2-(2-methylpropyl)-4-methylpyrrolidine:** ^{1}H NMR δ 0.35 (d, J = 6.5, 3H, *H-8/H'-8*), 0.66 (d, J = 6.5, 3H, *H'-8/H-8*), 0.92 (d, J = 6.3, 3H, *H-5*), 1.05 (m, 1H, *H-2/H'-2*), 1.06 (m, 1H, *H-6/H'-6*), 1.26 (m, 1H, *H-7*), 1.28 (ddd, J = 3.8, 11.1, 13.3,1H, *H'-6/H-6*), 2.22 (m, 1H, *H-3*), 2.29 (dddd, J = 1.1, 7.2, 7.6, 12.1, 1H, *H'-2/H-2*), 2.62 (td, J = 10.5, 14.6, 1H, *H-4/ H'-4*), 3.26 (dddd, J = 1.2, 6.3, 9.5, 10.5, 1H, *H'-4*/*H-4*), 3.63 (m, 1H, *H-1*), 7.33-7.49 (several multiplets, 6H, *Ph*), 7.76-7.82 (several multiplets, 2H, *Ph*), 7.87-7.93 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 17.0 (*C-5*), 20.6 (*C-8*), 23.9 (*C-8*), 24.9 (*C-7*), 35.6 (2 signals, *C-3*), 41.5 (2 signals, *C-2*), 47.1 (2 signals, *C-6*), 54.3 (2 signals, *C-4*), 57.0 (2 signals, *C-1*), 128.0 (*C-Ph*), 128.1 (*C-Ph*), 128.3 (*C-Ph*), 128.4 (*C-Ph*), 131.3 (2 signals, *C-Ph*), 131.5 (2 signals, *C-Ph*), 131.8 (*C-Ph*), 132.0 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 132.5 (*C-Ph*), 132.6 (*C-Ph*), 133.1 (*C-Ph*), 133.3 (*C-Ph*).

***N*-Diphenylphosphinoyl-*trans*-2-(2-methylpropyl)-4-methylpyrrolidine:** ^{1}H NMR δ 0.35 (d, J = 6.5, 3H, *H-8/H'-8*), 0.70 (d, J = 6.5, 3H, *H'-8/H-8*), 1.01 (d, J = 6.5, 3H, *H-5*), 1.14 (m, 1H, *H-6/H'-6*), 1.23 (m, 1H, *H-7*), 1.36 (ddd, J = 3.6, 10.9, 12.8, 1H,

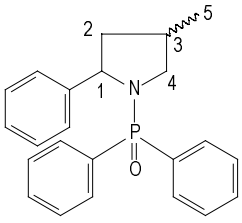
H'-6/H-6), 1.61 (dddd, J = 0.9, 7.4, 10.3, 12.2, 1H, *H-2/H'-2*), 1.77 (ddd, J = 0.8, 6.2, 12.3, 1H, *H'-2/H-2*), 2.37 (m, 1H, *H-3*), 2.73 (ddd, J = 8.2, 9.1, 9.5, 1H, *H-4/H'-4*), 3.24 (ddd, J = 5.3, 7.5, 9.5, 1H, *H'-4/H-4*), 3.66 (m, 1H, *H-1*), 7.36-7.47 (several multiplets, 6H, *Ph*), 7.84-7.98 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 17.5 (*C-5*), 20.3 (*C-8*), 23.4 (*C-8*), 25.1 (*C-7*), 32.2 (2 signals, *C-3*), 39.2 (2 signals, *C-2*), 45.3 (2 signals, *C-6*), 53.0 (2 signals, *C-4*), 57.2 (2 signals, *C-1*), 127.7 (*C-Ph*), 127.8 (*C-Ph*), 127.9 (*C-Ph*), 128.0 (*C-Ph*), 130.9 (2 signals, *C-Ph*), 131.1 (2 signals, *C-Ph*), 131.4 (*C-Ph*), 131.6 (*C-Ph*), 131.7 (*C-Ph*), 131.8 (*C-Ph*), 131.9 (*C-Ph*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.7 (*C-Ph*), 133.0 (*C-Ph*).



***N*-Diphenylphosphinoyl-*trans*-2-(1,1-dimethyl)ethyl-4-methylpyrrolidine:** ^{1}H NMR δ 0.81 (s, 9H, *H-7*), 0.83 (d, J = 6.7, 3H, *H-5*), 1.46 (ddd, J = 8.5, 9.0, 13.1, 1H, *H-2/H'-2*), 2.07 (ddd, J = 1.7, 7.9, 13.1, 1H, *H'-2/H-2*), 2.41 (m, 1H, *H-3*), 2.74 (ddd, J = 5.3, 10.7, 13.5, 1H, *H-4/ H'-4*), 3.33 (ddd, J = 8.5, 9.9, 10.6, 1H, *H'-4/H-4*), 3.85 (ddd, J = 0.6, 1.8, 8.6, 1H, *H-1*), 7.38-7.51 (several multiplets, 6H, *Ph*), 7.76-7.83 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 20.3 (*C-5*), 27.6 (*C-7*), 33.9 (2 signals, *C-3*), 36.2 (2 signals, *C-6*), 36.9 (2 signals, *C-2*), 55.9 (2 signals, *C-4*), 68.1 (2 signals, *C-1*), 128.0 (2 signals, C-*Ph*), 128.1 (*C-Ph*), 128.2 (*C-Ph*), 131.3 (3 signals, *C-Ph*), 131.4 (*C-Ph*), 131.5 (*C-Ph*), 131.8 (*C-Ph*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 132.4 (*C-Ph*), 133.6 (*C-Ph*), 133.8 (*C-Ph*).



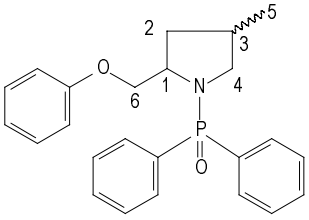
***N*-Diphenylphosphinoyl-*cis*-4-methyl-2-phenylpyrrolidine:** ^{1}H NMR δ 0.99 (d, J = 6.4, 3H, *H-5*), 1.47 (ddd, J = 9.1, 11.5, 12.5, 1H, *H-2/H'-2*), 2.40 (m, 1H, *H-3*), 2.51 (dddd, J = 1.4, 6.7, 7.3, 12.5, 1H, *H'-2/H-2*), 2.95 (ddd, J = 10.5, 10.8, 14.7, 1H, *H-*

4/H'-4), 3.62 (dddd, J = 1.4, 6.6, 10.6, 11.4, 1H, *H'-4/H-4*), 4.61 (ddd, J = 7.3, 9.1, 13.0, 1H, *H-1*), 6.91-6.95 (several multiplets, 2H, *Ph*), 7.00-7.11 (several multiplets, 5H, *Ph*), 7.19 (m, 1H, *Ph*), 7.37-7.46 (several multiplets, 3H, *Ph*), 7.48-7.55 (several multiplets, 2H, *Ph*), 7.89-7.96 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 16.0 (*C-5*), 35.9 (2 signals, *C-3*), 46.6 (2 signals, *C-2*), 56.2 (2 signals, *C-4*), 62.5 (2 signals, *C-1*), 125.7 (*C-Ph*), 126.0 (*C-Ph*), 127.7 (*C-Ph*), 127.4 (*C-Ph*), 127.7 (*C-Ph*), 128.1 (*C-Ph*), 128.2 (*C-Ph*), 130.0 (*C-Ph*), 130.8 (2 signals, *C-Ph*), 131.3 (2 signals, *C-Ph*), 131.9 (*C-Ph*), 132.0 (2 signals, *C-Ph*), 132.1 (*C-Ph*), 133.2 (*C-Ph*), 145.6 (2 signals, C-*Ph*).

***N*-Diphenylphosphinoyl-*trans* -4-methyl-2-phenylpyrrolidine:** ^{1}H NMR δ 1.03 (d, J = 6.5, 3H, *H-5*), 1.88 (ddd, J = 2.3, 6.1, 12.3, 1H, *H-2/H'-2*), 2.02 (ddd, J = 8.0, 10.3, 12.2, 1H, *H'-2/H-2*), 2.47 (m, 1H, *H-3*), 3.03 (ddd, J = 8.5, 9.5, 11.1, 1H, *H-4/H'-4*), 3.47 (ddd, J = 4.5, 7.3, 9.5, 1H, *H'-4/H-4*), 4.71 (ddd, J = 2.3, 8.0, 10.9, 1H, *H-1*), 7.05-7.20 (several multiplets, 7H, *Ph*), 7.26 (m, 1H, *Ph*), 7.37-7.46 (several multiplets, 3H, *Ph*), 7.61-7.68 (several multiplets, 2H, *Ph*), 7.88-7.95 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 17.0 (*C-5*), 32.1 (2 signals, *C-3*), 44.7 (2 signals, *C-2*), 54.4 (2 signals, *C-4*), 62.4 (2 signals, *C-1*), 125.8 (*C-Ph*), 126.2 (*C-Ph*), 127.6 (*C-Ph*), 127.7 (*C-Ph*), 127.8 (*C-Ph*), 128.2 (*C-Ph*), 128.4 (*C-Ph*), 130.7 (*C-Ph*), 131.1 (2 signals, *C-Ph*), 131.4 (2 signals, *C-Ph*), 131.8 (*C-Ph*), 132.0 (*C-Ph*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 133.1 (*C-Ph*), 145.5 (2 signals, C-*Ph*).



***N*-Diphenylphosphinoyl-*cis*-4-methyl-2-phenoxymethylpyrrolidine:** ^{1}H NMR δ 1.00 (d, J = 6.6, 3H, *H-5*), 1.54 (ddd, J = 7.1, 10.4, 12.8, 1H, *H-2/H'-2*), 2.27 (m, 1H, *H-3*), 2.37 (dtd, J = 1.1, 7.9, 12.8, 1H, *H'-2/H-2*), 2.77 (dd, J = 10.5, 12.8, 1H, *H-4/H'-4*), 3.33 (dddd, J = 1.2, 6.7, 9.1, 10.5, 1H, *H'-4/H-4*), 3.70 (dd, J = 7.2, 9.6, 1H, *H-6/H'-6*), 3.86 (dd, J = 4.1, 9.6, 1H, *H'-6/H-6*), 4.04 (ddddd, J = 4.1, 6.9, 7.1, 7.9, 9.9, 1H, *H-1*), 6.65-6.69 (several multiplets, 2H, *Ph*), 6.90 (m, 1H, *Ph*), 7.16-7.23

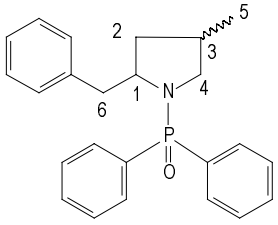
(several multiplets, 2H, *Ph*), 7.36-7.52 (several multiplets, 6H, *Ph*), 7.80-7.93 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 16.8 (*C-5*), 35.1 (2 signals, *C-3*), 38.4 (2 signals, *C-2*), 55.5 (2 signals, *C-4*), 56.9 (2 signals, *C-1*), 70.7 (2 signals, *C-6*), 114.4 (*C-Ph*), 120.6 (*C-Ph*), 128.2 (*C-Ph*), 128.4 (2 signals, C-*Ph*), 128.6 (*C-Ph*), 129.3 (*C-Ph*), 131.6 (3 signals, C-*Ph*), 131.7 (2 signals, *C-Ph*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 132.4 (*C-Ph*), 132.9 (2 signals, C-*Ph*), 158.5 (C-*Ph*).

***N*-Diphenylphosphinoyl-*trans*-4-methyl-2-phenoxymethylpyrrolidine:** ^{1}H NMR δ 1.03 (d, J = 6.6, 3H, *H-5*), 1.69 (ddd, J = 7.9, 10.5, 12.7, 1H, *H-2/H'-2*), 2.21 (ddd, J = 1.6, 6.4, 12.6, 1H, *H'-2/H-2*), 2.49 (m, 1H, *H-3*), 2.74 (ddd, J = 7.5, 8.6, 9.3, 1H, *H-4/H'-4*), 3.29 (ddd, J = 4.0, 7.4, 9.3, 1H, *H'-4/H-4*), 3.72 (dd, J = 8.6, 9.8, 1H, *H-6/H'-6*), 3.87 (dd, J = 4.0, 9.9, 1H, *H'-6/H-6*), 4.04 (m, 1H, *H-1*), 6.61-6.66 (several multiplets, 2H, *Ph*), 6.88 (m, 1H, *Ph*), 7.14-7.20 (several multiplets, 2H, *Ph*), 7.38-7.54 (several multiplets, 6H, *Ph*), 7.80-7.94 (several multiplets, 4H, *Ph*).

^{13}C NMR δ 17.6 (*C-5*), 32.4 (2 signals, *C-3*), 37.7 (2 signals, *C-2*), 55.0 (2 signals, *C-4*), 57.2 (2 signals, *C-1*), 69.4 (2 signals, *C-6*), 114.4 (*C-Ph*), 120.6 (*C-Ph*), 128.3 (*C-Ph*), 128.5 (2 signals, C-*Ph*), 128.6 (*C-Ph*), 129.3 (*C-Ph*), 131.3 (C-*Ph*), 131.7 (3 signals, *C-Ph*), 131.8 (*C-Ph*), 132.1 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (2 signals, C-*Ph*), 132.6 (*C-Ph*), 133.0 (C-*Ph*), 158.5 (C-*Ph*).

Radical cyclizations in Table 1 were performed as described in the above section. Cyclized compounds were generally isolated in 60-92 % yields.



***N*-Diphenylphosphinoyl-*cis*-2-bensyl-4-methylpyrrolidine:** 81% Yield (cis/trans = 24/1). ^{1}H NMR δ 0.94 (d, J = 6.5, 3H, *H-5*), 1.21 (ddd, J = 7.2, 10.4, 12.5, 1H, *H-2/H'-2*), 2.04 (td, J = 7.0, 12.5, 1H, *H'-2/H-2*), 2.20 (m, 1H, *H-3*), 2.47 (dd, J = 10.2, 12.9, 1H, *H-4/H'-4*), 2.70 (ddd, J = 10.4, 10.7, 13.4, 1H, *H-6/H'-6*), 2.75 (dd, J = 4.0, 13.0, 1H, *H'-4/H-4*), 3.33 (dd, J = 6.8, 9.2, 10.5, 1H, *H'-6/H-6*), 3.87 (m, 1H, *H-1*),

6.77-6.81 (several multiplets, 2H, *Ph*), 7.11-7.22 (several multiplets, 3H, *Ph*), 7.41-7.57 (several multiplets, 6H, *Ph*), 7.83-7.90 (several multiplets, 2H, *Ph*), 7.93-8.00 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 17.1 (*C-5*), 35.2 (2 signals, *C-3*), 40.9 (2 signals, *C-2*), 43.8 (2 signals, *C-6*), 55.0 (2 signals, *C-4*), 60.3 (2 signals, *C-1*), 126.0 (*C-Ph*), 128.2 (*C-Ph*), 128.3 (C-*Ph*), 128.4 (*C-Ph*), 128.5 (*C-Ph*), 128.6 (*C-Ph*), 129.1 (*C-Ph*), 131.6 (2 signals, C-*Ph*), 131.7 (2 signals, *C-Ph*), 131.9 (*C-Ph*), 132.2 (*C+-Ph*), 132.3 (*C-Ph*), 132.5 (*C-Ph*), 132.6 (C-*Ph*), 133.2 (2 signals, C-*Ph*), 138.6 (C-*Ph*).

***N*-Diphenylphosphinoyl-*trans*-2-bensyl-4-methyl pyrrolidine:** ^{1}H NMR δ 1.01 (d, J = 6.6, 3H, *H-5*), 1.46 (m, 1H, *H-2*/*H'-2*), 1.80 (dd, J = 6.4, 12.3, 1H, *H'-2*/*H-2*), 2.44 (m, 1H, *H-3*), 2.52 (dd, J = 10.8, 13.1, 1H, *H-6*/*H'-6*), 2.73-2.81 (several multiplets, 2H, *H'-6*/*H-6 and H-4*/*H'-4*), 3.34 (ddd, J = 4.6, 7.6, 9.4, 1H, *H'-4*/*H-4*), 3.82 (m, 1H, *H-1*), 6.77-6.81 (several multiplets, 2H, *Ph*), 7.11-7.22 (several multiplets, 3H, *Ph*), 7.41-7.57 (several multiplets, 6H, *Ph*), 7.83-7.90 (several multiplets, 2H, *Ph*), 7.93-8.00 (several multiplets, 2H, *Ph*).

^{13}C NMR δ 17.7 (*C-5*), 32.3 (2 signals, *C-3*), 38.6 (2 signals, *C-2*), 43.0 (2 signals, *C-6*), 54.2 (*C-4*), 61.2 (*C-1*), 126.0 (*C-Ph*), 128.2 (*C-Ph*), 128.3 (C-*Ph*), 128.4 (*C-Ph*), 128.5 (*C-Ph*), 128.6 (*C-Ph*), 129.1 (*C-Ph*), 131.6 (2 signals, C-*Ph*), 131.6 (2 signals, *C-Ph*), 131.7 (*C-Ph*), 132.2 (*C-Ph*), 132.3 (*C-Ph*), 132.4 (*C-Ph*), 132.6 (C-*Ph*), 132.7 (C-*Ph*), 139.1 (C-*Ph*).