Synthesis of an Aza-Analogue of Pyrethroid Cyphenothrin from (+)-3-Carene

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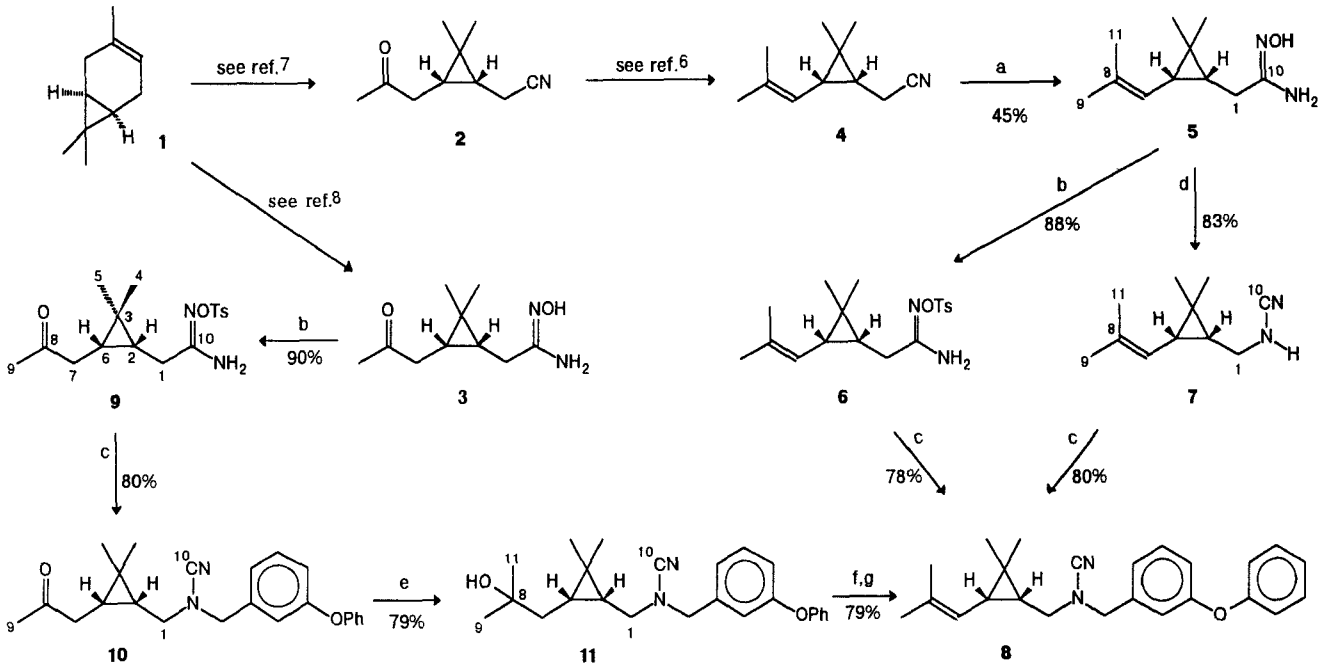
The preparation of *N*-cyano-*N*-(*m*-phenoxybenzyl)[(1*R*,3*S*)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylmethyl]amine (**8**) from monoterpene hydrocarbon (+)-3-carene is described.

Enzymatic hydrolysis of the ester linkage in pyrethroids is known to be one of the most important processes of destruction of these biologically active molecules in insects. Therefore, development of so-called non-ester pyrethroids is of special interest.[1,2]

Mono- and disubstituted chrysanthemylamines, described as volatile insecticides suitable for fumigant action,[3] represent a group of nitrogen-containing analogues of pyrethroid insecticides. *N*-Substituted chrysanthemylamines are synthesized either by metal hydride-induced reduction of the corresponding amides,[4] or by alkylation of primary and secondary amines with chrysanthemyl chloride.[5] These compounds might be also prepared by direct alkylation of chrysanthemylamine.[6]

Since the highest insecticidal activity among pyrethroid isomers has been reported for the 1*R*-isomers of cyclopropylcarboxylic acid derivatives,[1] synthesis of *N*-substituted derivatives of chrysanthemylamine in optically active form is of considerable interest. We have developed a synthetic route to *N*-cyano-*N*-(*m*-phenoxybenzyl)[(1*R*,3*S*)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylmethyl]amine (**8**) from natural monoterpene (+)-3-carene (**1**), using the known seco-derivatives **2**[7] and **3**[8] as intermediates. Direct alkylation of amines is known to be complicated by over-alkylation, so our synthetic pathway (Scheme) does not include the alkylation of simple amines but rather alkylation of *N*-cyano derivatives. Amide oximes are reported to react with *p*-toluenesulfonyl chloride to give *N*-substituted ureas as the products of Tiemann's rearrangement.[9] *N*-cyano amines being the stable intermediates in this reaction.[10] Both pathways of the synthesis shown in the Scheme are based on the formation of *N*-cyano amine derivatives.

The first pathway utilizes oxo nitrile **2**, which can be easily transformed into homochrysanthemyl nitrile **4** according to a known procedure.[7] The usual method for transformation of nitriles to the corresponding amide oximes is by reaction with NH_2OH.[9] Although further reaction of the amide oximes formed with an excess of NH_2OH may lead to formation of amides,[11] the reaction allowed us to prepare amide oxime **5**. Amide oxime **5** is



Scheme.

Reagents and conditions: [a] $NH_2OH{\times}HCl$, Na_2CO_3, EtOH, reflux, 15 h; [b] TsCl, Py, CH_2Cl_2, -10 °C, 2 h; [c] *m*-phenoxybenzyl chloride, H_2O, CH_2Cl_2, KOH, benzyltriethylammonium chloride, reflux, 2 h; [d] TsCl, Py, 20 °C → 70÷80 °C, 2h; [e] CH_3MgI, ether, reflux, 2 h; [f] $POCl_3$, Py, -5 °C, 24 h; [g] TsOH, toluene, reflux, 11 h.

The numbering scheme does not coincide with the numbering of the cyclic systems according to IUPAC.

easily transformed to the *N*-cyano derivative **7**. Compounds of type **7** are known to be easily alkylated to give the corresponding *N*-cyano-*N,N*-dialkyl derivatives.[12,13] Reaction of **7** with *m*-phenoxybenzyl chloride in a two-phase system in the presence of phase-transfer catalysis resulted in rapid alkylation, giving alkylated derivative **8**.

Compound **8** may also be prepared by using stable *O*-tosyl derivative **6** as an intermediate. Thus, if compound **6** is treated with *m*-phenoxybenzyl chloride in a two-phase system, a one-stage process involving rearrangement and subsequent alkylation occurs.

Because of low yield of amide oxime **5** (45%), we have devised another synthesis of compound **8**. In this second pathway, oxo amide oxime **3** was transformed to *O*-tosyl derivative **9**. Compound **9** was then alkylated affording derivative **10**. Reaction of **10** with MeMgI results in hydroxy derivative **11**. It should be pointed out that, in contrast to the Grignard reaction of oxo nitrile **2**,[6] the reaction of oxo *N*-cyano amine **10** was not accompanied by the addition of the methyl to the cyano group, and corresponding hydroxy derivative **11** was formed in good yield. Hydroxy derivative **11** was dehydrated with $POCl_3$ to give a mixture of the desired product **8** and its $\Delta^{8,9}$-isomer. The mixture was then treated with TsOH in toluene to give product **8**.

Compound **8** may be considered as an analogue of the well-known pyrethroid cyphenothrin.[1] Preliminary toxicological studies have shown that this compound demonstrates moderate toxicity toward house fly (LD_{50} = 5 µg/fly).

All the solvents used were reagent quality. Petroleum ether refers to that fraction which boils in the range 40–70 °C. Et_2O was freshly distilled. Removal of all solvents was carried out under reduced pressure and all commercial reagents were used without additional purification. Analytical TLC plates were Silufol (Silpearl on aluminium foil, Czechoslovakia). Preparative column chromatography was performed on SiO_2 ("KSK", Russia, 100–200 mesh, air dried and activated at 140 °C for 5 h). IR spectra were obtained for 1% solutions using a UR-20 spectrometer. A Polamat A polarimeter was used to measure optical rotation at 578 nm. Melting points were obtained using a Kofler melting point apparatus and are uncorrected. Microanalyses were obtained using a Hewlett Packard 185 analyser and a Carlo Erba 1106 analyser. Compounds **5**–**7** and **9** gave C, H, N analysis ± 0.33%. Mass spectra were obtained on a Finnigan MAT 8200 instrument using the electron impact ionization technique (50–150 °C, 70 eV). For some of the new compounds, precise mass determination for the molecular ion of a pure sample were obtained instead of combustion analyses. Purity was determined from constancy of melting point together with TLC and NMR data. ^1H and ^{13}C NMR specra were recorded at room temperature for 5–10% solutions using standard NMR software system on Bruker AC 200 and Bruker WP 200 SY instruments (^1H, 200.13 MHz; ^{13}C, 50.32 MHz) locked to the deuterium resonance of the solvent ($CDCl_3$). The chemical shifts were calculated relative to the solvent signal using as internal standard. δ_H 7.24 and δ_C 76.90 ppm.

(1*R*,3*S*)-2,2-Dimethyl-3-(2-oxopropyl)cyclopropanacetonitrile **(2)** was purchased from Janssen Chimica. (1*R*,3*S*)-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropanacetonitrile **(4)** was prepared from oxo nitrile **2** as described in Ref. 6. (1*R*,3*S*)-2,2-Dimethyl-3-(2-oxopropyl)cyclopropanacetamide oxime **(3)** was prepared from (+)-3-carene **(1)** as described in Ref. 8.

(1*R*,3*S*)-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropylacetamide Oxime (5):

Powdered Na_2CO_3 (2.0 g, 18.8 mmol) was added to a solution of nitrile **4** (3.0 g, 18.7 mmol) and $NH_2OH \cdot HCl$ (1.3 g, 18.7 mmol) in 95% aq EtOH (30 mL). The reaction mixture was stirred under reflux for 15 h, the solvent was evaporated at reduced pressure, and the residue was treated with 1 N HCl (15 mL) and extracted with Et_2O (2 × 10 mL). The aqueous phase was neutralized with 5% aq KOH (pH 7–8) and extracted with $CHCl_3$ (3 × 20 mL). The combined chloroform solutions were washed with brine (15 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure to give the crude product which was then chromatographed (eluent: 1 → 3% MeOH in Et_2O) affording amide oxime **5** as a viscous yellowish oil; yield: 1.6 g (45%); $[\alpha]^{26}$ – 9.9° (*c* = 6.48, $CHCl_3$).

MS: *m/z* (%) = 179 (28), 163 (40), 123 (92), 107 (88), 81 (100).

IR (CCl_4): *v* = 3600 (OH), 3505, 3400 (NH), 1665 (C=N), 1590 (NH), 1385 cm^{-1} (C–N).

^1H NMR ($CDCl_3$): δ = 0.93 (s, 3 H, 5-H_3), 1.04 (s, 3 H, 4-H_3), 1.29 (t, *J* = 9 Hz, 1 H, 6-H), 1.64 (s, 3 H, 9-H_3 or 11-H_3), 1.68 (s, 3 H, 11-H_3 or 9-H_3), 1.99 (dd, *J* = 15, 9 Hz, 1 H, 1-H_a), 2.16 (dd, *J* = 15, 6 Hz, 1 H, 1-H_b), 4.63 (br s, 2 H, NH_2), 4.88 (d, *J* = 8 Hz, 1 H, 7-H), 9.23 (br s, 1 H, NOH).

^{13}C NMR ($CDCl_3$): δ = 15.16 (q, C-5), 18.13 (q, C-11), 19.57 (s, C-3), 25.23 (d, C-6 or C-2), 25.55 (q, C-9), 26.32 (t, C-1), 26.45 (d, C-2 or C-6), 28.33 (q, C-4), 119.38 (d, C-7), 134.71 (s, C-8), 153.93 (s, C-10).

***N*-Cyano-[(1*R*,3*S*)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylmethyl]amine (7):**

A solution of TsCl (1 g, 5.3 mmol) in pyridine (5 mL) was added dropwise to a stirred solution of amide oxime **5** (1.0 g, 5.2 mmol) in pyridine (5 mL). The reaction mixture was stirred at r.t. for 1 h and then at 70–80 °C for 1 h, poured into water (50 mL) and extracted with Et_2O (4 × 20 mL). The combined ethereal extracts were dried (Na_2SO_4) and evaporated to leave the crude product which was then chromatographed (5 → 20% Et_2O in petroleum ether) to give *N*-cyano amine **7** as a colourless oil; yield: 0.8 g (83%); $[\alpha]^{21}$ + 48.5° (*c* = 2.39, $CHCl_3$).

MS: *m/z* (%) = 123 (43), 93 (42), 81 (45), 55 (32), 43 (100).

IR ($CHCl_3$): *v* = 3405 (NH), 2240 cm^{-1} (C≡N).

^1H NMR ($CDCl_3$): δ = 0.94 (s, 3 H, 5-H_3), 1.05 (s, 3 H, 4-H_3), 1.32 (t, *J* = 8 Hz, 1 H, 6-H), 1.60 (s, 3 H, 9-H_3 or 11-H_3), 1.64 (s, 3 H, 11-H_3 or 9-H_3), 2.94 (dd, *J* = 14, 8 Hz, 1 H, 1-Ha), 3.01 (dd, *J* = 14, 6.5 Hz, 1 H, 1-Hb), 4.48 (br s, 1 H, NH), 4.78 (d, *J* = 8.2 Hz, 1 H, 7-H).

^{13}C NMR ($CDCl_3$): δ = 15.03 (q, C-5), 18.19 (q, C-11), 20.22 (s, C-3), 25.34 (q, C-9), 25.85 (d, C-6 or C-2), 27.48 (d, C-2 or C-6), 28.12 (q, C-4), 43.41 (t, C-1), 116.66 (s, C-10), 117.90 (d, C-7), 135.70 (s, C-8).

***N*-Cyano-*N*-(*m*-phenoxybenzyl)[(1*R*,3*S*)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropylmethyl]amine (8):**

A mixture of 30% aq KOH (10 mL) and a solution of *N*-cyano amine **7** (1.5 g, 8.6 mmol), *m*-phenoxybenzyl chloride (1.9, 8.7 mmol), and benzyltriethylammonium chloride (0.1 g, 0.44 mmol) in CH_2Cl_2 (20 mL) was stirred under reflux for 2 h. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic extracts were washed with brine (40 mL) and dried (Na_2SO_4). The solvent was evaporated and the crude product was chromatographed (eluent: 1 → 5% Et_2O in petroleum ether) to give alkylated derivative **8** as a colourless oil; yield: 2.4 g (80%); $[\alpha]^{22}$ + 52.5° (*c* = 1.71, $CHCl_3$).

MS: *m/z* (%) = 360.2176 [$(M)^+$, 15, calc. for $C_{24}H_{28}N_2O$, 360.2202], 345 (5), 224 (5), 183 (29), 155 (3), 136 (7), 123 (100), 95 (10), 81 (18).

IR ($CHCl_3$): *v* = 2220 (C≡N), 1590 and 1495 cm^{-1} (C=C).

^1H NMR ($CDCl_3$): δ = 0.95 (s, 3 H, 5-H_3), 1.12 (s, 3 H, 4-H_3), 1.42 (t, *J* = 8 Hz, 1 H, 6-H), 1.65 (d, *J* = 1.5 Hz, 3 H, 11-H_3), 1.68 (d, *J* = 1.5 Hz, 3 H, 9-H_3), 2.88 (dd, *J* = 13, 8 Hz, 1 H, 1-Hb), 2.96 (dd, *J* = 13, 7 Hz, 1 H, 1-Ha), 4.13 (s, 2 H, $ArCH_2$), 4.75 (dqq, *J* = 8, 1.5, 1.5 Hz, 1 H, 7-H1), 6.70–7.50 (m, 9 H, ArH).

^{13}C NMR ($CDCl_3$): δ = 15.21 (q, C-5), 18.27 (q, C-11), 20.32 (s, C-3), 25.45 (q, C-9), 25.81 (d, C-6 or C-2), 25.98 (d, C-2 or C-6),

28.12 (q, C-4), 47.85 (t, C-1), 54.94 (t, ArCH$_2$), 117.64 (s, C-10), 117.95 (d, C-7), 135.72 (s, C-8); aromatic carbons, 118.05 (d), 118.21 (d), 118.75 (d), 122.48 (d), 123.29 (d), 129.55 (d), 129.94 (d), 136.86 (s), 156.49 (s), 157.45 (s).

A solution of $POCl_3$ (1.0 g, 6.5 mmol) in pyridine (25 mL) was added dropwise at −5 °C to a stirred solution of hydroxy derivative **11** (1.6 g, 4.2 mmol) in pyridine (20 mL) and the reaction mixture was stored at 0 °C overnight. The reaction mixture was poured into ice-cold water (50 mL). The resultant mixture was acidified with 10% aq HCl (pH 1–2) and extracted with Et_2O (3 × 30 mL). The combined ethereal extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated to give a mixture (1.4 g, 90%) of the desired product **8** and its $\Delta^{8,9}$-isomer. The mixture was then treated with TsOH (0.1 g, 0.6 mmol) in toluene (20 mL) for 11 h at reflux to give the desired unsaturated derivative **8** (1.2 g, 79% after purification by column chromatography).

Reaction of *p*-toluenesulfonate **6** (2.0 g, 5.7 mmol) with *m*-phenoxybenzyl chloride (1.3 g, 6.0 mmol) in the presence of benzyltriethylammonium chloride (0.07 g, 0.31 mmol) in a two-phase system (50 mL of CH_2Cl_2 and 50 mL of 30% aq KOH) was carried out as described above. The crude product was chromatographed to give *N*-cyano derivative **8**; yield: 1.6 g (78%).

(1*R*,3*S*)-2,2-Dimethyl-3-(2-methyl-1-propenyl)cyclopropylacetamide *O*-Tosyloxime (6):

A solution of TsCl (2.9 g, 15.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of amide oxime **5** (3.0 g, 15.5 mmol) and pyridine (1.5 g, 19.0 mmol) in CH_2Cl_2 (20 mL) at −10 °C and the stirring was continued for 2 h at the same temperature. The reaction mixture was washed successively with water (2 × 20 mL), 0.1 N aq HCl (10 mL) and brine (10 mL), and dried (Na_2SO_4). The solvent was removed at r.t. to give *p*-toluenesulfonate **6** as a yellowish solid; yield: 4.7 g (88%); mp 84–85 °C (Et_2O); $[\alpha]^{20}$ + 14.0° (*c* = 0.57, $CHCl_3$).

MS: *m/z* (%) = 196 (10), 172 [(TsOH)$^+$, 74], 136 (10), 123 (100), 121 (24), 108 (19), 107 (37), 93 (20), 91 (74), 81 (37), 79 (18), 77 (15), 65 (20).

IR ($CHCl_3$): ν = 3520 and 3400 (NH), 1650 (C=N), 1360, 1170 cm^{-1} (S=O).

^{1}H NMR ($CDCl_3$–CCl_4, 2:1 v/v): δ = 0.90 (s, 3H, 5-H$_3$), 1.06 (s, 3H, 4-H$_3$), 1.28 (t, *J* = 8.5 Hz, 1H, 6-H), 1.66 (d, *J* = 1.5 Hz, 3H, 9-H$_3$ or 11-H$_3$), 1.70 (d, *J* = 1.5 Hz, 3H, 11-H$_3$ or 9-H$_3$), 1.97 (dd, *J* = 15.5, 8.5 Hz, 1H, 1-Ha), 2.14 (dd, *J* = 15.5, 6.5 Hz, 1H, 1-Hb), 2.42 (s, 3H, ArCH$_3$), 4.85 (dqq, *J* = 8.5, 1.5, 1.5 Hz, 1H, 7-H), 4.87 (br s, 2H, NH$_2$), 7.26 (d, *J* = 8.0 Hz, 2H, ArH), 7.80 (d, *J* = 8.0 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$–CCl_4, 2:1 v/v): δ = 15.37 (q, C-5), 18.50 (q, C-11), 20.05 (s, C-3), 21.55 (q, ArCH$_3$), 25.64 (q, C-9), 25.82 (d, C-6 or C-2), 26.23 (d, C-2 or C-6), 26.30 (t, C-1), 28.59 (q, C-4), 119.34 (d, C-7), 135.54 (s, C-8), 159.57 (s, C-10); aromatic carbons 128.81 (d), 129.11 (d), 133.85 (s), 143.62 (s).

(1*R*,3*S*)-2,2-Dimethyl-3-(2-oxopropyl)cyclopropylacetamide *O*-Tosyloxime (9):

Reaction of amide oxime **3** (24.3, 0.124 mol) with TsCl (23.4 g, 0.123 mol) was carried out as described for the preparation of compound **6** and gave *p*-toluenesulfonate **9** as a white solid; yield: 38.9 g (90%); mp 96–97 °C (Et_2O); $[\alpha]^{22}$ −14.0° (*c* = 7.17, $CHCl_3$).

MS: *m/z* (%) = 172 [(TsOH)$^+$, 96], 108 (27), 107 (40), 91 (100), 89 (13), 79 (14), 77 (15), 65 (32).

IR (CCl_4): ν = 3495 and 3395 (NH), 1640 (C=N), 1600 (C=C), 1360, 1180 cm^{-1} (S=O).

^{1}H NMR ($CDCl_3$): δ = 0.80 (s, 3H, 5-H$_3$), 1.00 (s, 3H, 4-H$_3$), 1.80 (dd, *J* = 15.5, 8.5 Hz, 1H, 1-Hb), 2.13 (s, 3H, 9-H$_3$), 2.20 (dd, *J* = 15.5, 7.5 Hz, 1H, 1-Ha), 2.40 (s, 3H, ArCH$_3$), 2.61 (dd, *J* = 17.5, 4.5 Hz, 1H, 7-Ha), 5.44 (br s, 2H, NH$_2$), 7.29 (d, *J* = 8.0 Hz, 2H, ArH), 7.82 (d, *J* = 8.0 Hz, 2H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.49 (q, C-5), 16.40 (s, C-3), 21.15 (d, C-6 or C-2), 21.15 (q, ArCH$_3$), 22.15 (d, C-2 or C-6), 25.22 (t, C-1), 27.84 (q, C-4), 29.51 (q, C-9), 38.13 (t, C-7), 159.69 (s, C-10), 209.45 (s, C-8); aromatic carbons, 128.10 (d), 128.99 (d), 132.67 (s), 144.14 (s).

***N*-Cyano-*N*-(*m*-phenoxybenzyl)(1*R*,3*S*)-2,2-dimethyl-3-(2-oxopropyl)cyclopropylmethyl]amine (10):**

Alkylation of *p*-toluenesulfonate **9** (10.2 g, 29 mmol) with *m*-phenoxybenzyl chloride (6.2 g, 28.4 mmol) in the presence of benzyltriethylammonium chloride (0.1 g, 0.44 mmol) in a two-phase system (100 mL of CH_2Cl_2 and 100 mL of 30% aq KOH) was carried out as described above for the transformation of **7** to **8**. The crude product was chromatographed (eluent: 10 → 30% of Et_2O in petroleum ether) to give the *N*-cyano derivative **10** as a light yellow oil; yield: 8.2 g (80%); $[\alpha]^{25}$ −8.3° (*c* = 2.42, $CHCl_3$).

MS: *m/z* (%) = 362.1975 [(M)$^+$, 1.4, calc. for $C_{23}H_{26}N_2O_2$, 362.1994)], 200 (52), 149 (22), 91 (31), 44 (100), 43 (53).

IR ($CHCl_3$): ν = 2220 (C≡N), 1715 (C=O), 1590 and 1495 cm^{-1} (C=C).

^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 3H, 5-H$_3$), 1.07 (s, 3H, 4-H$_3$), 2.07 (s, 3H, 9-H$_3$), 2.24 (dd, *J* = 18, 8 Hz, 1H, 7-Hb), 2.35 (dd, *J* = 18, 7 Hz, 1H, 7-Ha), 2.80 (dd, *J* = 13, 8 Hz, 1H, 1-Hb), 2.90 (dd, *J* = 13, 7 Hz, 1H, 1-Ha), 4.09 (s, 2H, ArCH$_2$), 6.9–7.4 (m, 9H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.59 (q, C-5), 18.10 (s, C-3), 21.65 (d, C-6 or C-2), 22.98 (d, C-2 or C-6), 27.96 (q, C-4), 29.27 (q, C-9), 38.75 (t, C-7), 47.33 (t, C-1), 54.87 (t, ArCH$_2$), 117.37 (s, C-10), 207.30 (s, C-8); aromatic carbons 117.91 (d), 118.17 (d), 118.66 (d), 122.42 (d), 123.25 (d), 129.47 (d), 129.91 (d), 136.49 (s), 156.28 (s), 157.39 (s).

***N*-Cyano-*N*-(*m*-phenoxybenzyl)[(1*R*,3*S*)-2,2-dimethyl-3-(2-hydroxy-2-methylpropyl)cyclopropylmethyl]amine (11):**

A solution of keto derivative **10** (3.8 g, 10.5 mmol) in Et_2O (15 mL) was added dropwise to a solution of MeMgI (ca. 15 mmol, prepared from 0.6 g of Mg and 3.5 g of MeI) in Et_2O (50 mL). The reaction mixture was stirred under reflux for 2 h, cooled to r.t., and 0.1 N aq HCl (30 mL) was added dropwise to the resulting mixture. The organic phase was separated, and the aqueous phase was extracted with Et_2O (20 mL). The combined organic extracts were washed with brine (30 mL) and dried (Na_2SO_4). Evaporation of the solvent left the crude product which was then purified by column chromatography (eluent: 50 → 100% Et_2O in petroleum ether) to give the hydroxy derivative **11** as a yellowish viscous oil; yield: 3.3 g (85%); $[\alpha]^{22}$ + 6.1° (*c* = 1.63, $CHCl_3$).

MS: *m/z* (%) = 378.2315 [(M)$^+$, 7, calc. for $C_{24}H_{30}N_2O_2$, 378.2307], 377 (9), 363 (6), 320 (21), 319 (33), 224 (40), 211 (8), 183 (38), 181 (100), 96 (8), 81 (9), 59 (24), 43 (9).

IR ($CHCl_3$): ν = 3610 (OH), 2230 (C≡N), 1590 and 1485 cm^{-1} (C=C).

^{1}H NMR ($CDCl_3$): δ = 0.88 (s, 3H, 5-H$_3$), 1.06 (s, 3H, 4-H$_3$), 1.14 (s, 6H, 9-H$_3$ and 11-H$_3$), 1.26 (dd, *J* = 15, 8 Hz, 1H, 7-Hb), 1.39 (dd, *J* = 15, 4.5 Hz, 1H, 7-Ha), 2.25 (br s, 1H, OH), 2.72 (dd, *J* = 13, 8.2 Hz, 1H, 1-Hb), 2.95 (dd, *J* = 13, 6 Hz, 1H, 1-Ha), 4.09 (s, 2H, ArCH$_2$), 6.75–7.40 (m, 9H, ArH).

^{13}C NMR ($CDCl_3$): δ = 14.98 (q, C-5), 18.02 (s, C-3), 22.64 (d, C-6 or C-2), 22.95 (d, C-2 or C-6), 28.15 (q, C-4 and C-9), 29.37 (q, C-11), 37.60 (t, C-7), 47.73 (t, C-1), 54.98 (t, ArCH$_2$), 70.08 (s, C-8), 117.53 (s, C-10); aromatic carbons, 117.90 (d), 118.11 (d), 118.62 (d), 122.39 (d), 123.18 (d), 129.42 (d), 129.83 (d), 136.56 (s), 156.29 (s), 157.31 (s).

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