Supplementary Material (ESI) for Chemical Communications

Samarium diiodide-induced intramolecular pinacol coupling of dinitrones: Synthesis of *cis*-vicinal cyclic diamines

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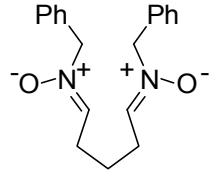
Supporting Information

General methods.
The ^{1}H NMR and ^{13}C were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS (δ=0) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16) for ^{13}C NMR. Tetrahydrofuran (THF) was distilled under argon from sodium-benzophenone, and CH_2Cl_2 was distilled from CaH_2. All reactions were performed under argon with anhydrous freshly distilled solvents. The *N*-benzylaldonitrones were synthesised following the procedure described by Dondoni and Merino[1] with *N*-benzylhydroxylamine and magnesium sulphate, whereas the ketonitrones were prepared by the method of Merino[2] using *N*-benzylhydroxylamine, magnesium sulphate and zinc chloride.
Samarium diiodide was prepared immediately before use by stirring vigorously under argon a suspension of samarium powder (567 mg, 3.8 mmol) and ICH_2CH_2I (843 mg, 3.0 mmol) in dry THF (30 mL) at room temperature for at least 2 h, during which time the colour changed from yellow to green and finally dark blue[3]. The diastereomeric ratio was determined by the ^{1}H NMR or ^{13}C NMR spectrum of the crude product.

General procedure for the intramolecular cyclisation of dinitrones
The dinitrone (0.3 mmol) was placed in a round bottomed flask fitted with a magnetic stirrer bar and flushed with argon. Dry THF (5 mL) and methanol (4.8 mmol, degassed) were then added and the solution was cooled to 0°C. SmI_2 (24 mL, 0.1 M in THF) was added dropwise in 30 minutes and the solution was left stirring approx. 12 h. The reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (10 mL). 5 mL of an aqueous solution of $NaHCO_3$ was added and the yellow mixture was extracted with AcOEt (3 × 20 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* to yield 1,2-diamine.
A solution of phosgene (20% in toluene, 160 μL, 0.3 mmol) was added dropwise to a solution of the crude diamine from above in CH_2Cl_2 (3 mL) and Et_3N (100 μL, 0.66 mmol) at -20°C. After addition the mixture was allowed to warm to room temperature over 30 min, 5 M NaOH (2 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL), dried with Na_2SO_4, and evaporated to give a red/brown viscous oil. The compounds were purified by flash chromatography using pentane:EtOAc as eluent.

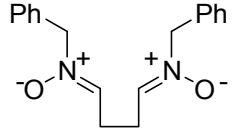
Nitrone **7a**:



To a well-stirred solution of glutaraldehyde (1.0 g, 10 mmol) in dichloromethane (40 mL), a solution of *N*-benzylhydroxylamine (2.7 g, 22 mmol) in dichloromethane (20 mL) and anhydrous magnesium sulphate (2.65 g, 22 mmol) were added and the mixture was stirred at room temperature for 2 h. The mixture was filtered and the filtrate evaporated to yield the crude product, which can be purified by trituration and washing with ethyl acetate to give the dinitrone as a white solid (2.4 g, 76% yield).

Mp = 147-148°C, R*f* = 0.26 (Ethyl Acetate 7/Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (quint, *J* = 7.6 Hz, 2H), 2.49 (q, *J* = 6.8 Hz, 4H), 4.85 (s, 4H), 6.70 (t, *J* = 6.0 Hz, 2H), 7.38 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 26.6 (2C), 69.5 (2C), 110.0 (2C), 129.2 (4C), 129.5 (4C), 133.0 (2C), 138.4 (2C).
IR (film, KBr), 3427, 2926, 1582, 1457, 1174, 1109 cm^{-1}.
HRMS: calcd for $C_{19}H_{22}N_2O_2$ [M^++Na]: 333.1579; found: 333.1579.

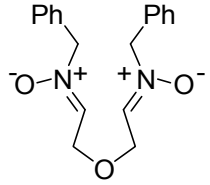
Nitrone **7b**:



A stream of ozone was bubbled through a solution of *trans,trans,cis*-1,5,9-cyclododecatriene (487 mg, 3 mmol) in CH_2Cl_2 (40 mL) at -78°C until the solution turned pale blue. Triphenylphosphine (820 mg, 3.1 mmol) was added slowly and the solution was allowed to warm up to room temperature over 4 h.

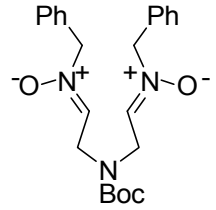
A solution of *N*-benzylhydroxylamine (2.3 g, 18.6 mmol) in dichloromethane (30 mL) and anhydrous magnesium sulphate (2.2 g, 18.6 mmol) were then added and the mixture was stirred at room temperature for 4 h. Filtration and evaporation of the filtrate gave a crude product, which was purified by trituration and washing with ethyl acetate to give the dinitrone as a yellow solid (1.8 g, 68% yield).
Mp = 156-157°C, R*f* = 0.34 (Ethyl Acetate 7/Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (t, *J* = 3.2 Hz, 4H), 4.82 (s, 4H), 6.73 (t, *J* = 5.6 Hz, 2H), 7.34-7.40 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5 (2C), 69.5 (2C), 129.2 (4C), 129.3 (4C), 129.5 (2C), 133.0 (2C), 137.5 (2C).
IR (film, KBr), 3064, 2997, 2894, 1602, 1581, 1495, 1456, 1428, 1153, 934 cm^{-1}.
HRMS: calcd for C18H20N2O2 [M^++Na]: 319,1422 ; found: 319.1427.

Nitrone **7c**:



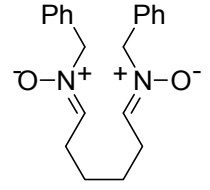
The dinitrone **7c** was synthesized following the same procedure as **7b**, using 2,5-dihydrofurane (350 mg, 5 mmol), triphenylphosphine (1.6 g, 6.0 mmol), a solution of *N*-benzylhydroxylamine (1.4 g, 11.0 mmol) in dichloromethane (20 mL) and anhydrous magnesium sulphate (1.3 g, 11.0 mmol). The corresponding dinitrone was obtained as a white solid (1.1 g, 78% yield).
Mp = decomposition, R*f* = 0.5 (Ethyl Acetate 7/Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.42 (d, *J* = 4.4 Hz, 4H), 4.86 (s, 4H), 6.76 (t, *J* = 4.4 Hz, 2H), 7.39 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.0 (2C), 69.4 (2C), 129.3 (4C), 129.5 (2C), 129.9 (4C), 132.3 (2C), 136.1 (2C).
IR (film, KBr), 3424, 3072, 3031, 2363, 1600, 1456, 1163, 903 cm^{-1}.
HRMS: calcd for $C_{18}H_{20}N_2O_3$ [M^++Na]: 335.1372 ; found: 335.1376.

Nitrone **7d**:



The desired *N*-Boc dialdehyde[4] (463.1 mg, 2.5 mmol) was reacted with a solution of *N*-benzylhydroxylamine (745 mg, 6.0 mmol) in dichloromethane (10 mL) and anhydrous magnesium sulphate (724.2 mg, 6.0 mmol). The corresponding dinitrone was obtained after flash chromatography as a white solid (100.2 mg, 10% yield).
Mp = 103-104°C, R*f* = 0.37 (Ethyl Acetate 4/ Methanol 1)
Mixture of rotamers: 1/1
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H), 4.12 (d, *J* = 4.8 Hz, 4H), 4.76 (s, 4H), 6.59 (br, 1H, rotamer), 6.77 (br, 1H, rotamer), 7.31 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.5 (3C), 45.2 (1C, rotamer), 46.3 (1C, rotamer), 69.5 (2C), 81.3 (1C), 129.2 (4C), 129.3(4C), 129.6 (2C), 132.7 (2C), 135.9 (1C, rotamer), 136.8 (1C, rotamer), 155.3 (1C).
IR (film, KBr), 3389, 2976, 1705, 1596, 1458, 1155, 1126 cm^{-1}.
HRMS: calcd for $C_{23}H_{29}N_3O_4$ [M^++Na]: 434.2056 ; found: 434.2054.

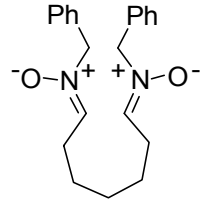
Nitrone **7e**:



To a stirred solution of $(COCl)_2$ (670 μL, 7.6 mmol) in dry CH_2Cl_2 (15 mL) was added at -78°C a solution of dry DMSO (720 μL, 10.2 mmol) in dry CH_2Cl_2 (15 mL) in 15 min. After 15 min, a solution of 1,6-hexanediol (300 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (15 mL) was then added in 15 min, and the resulting solution stirred for an additional 30 min at -78°C. Anhydrous Et_3N (2.8 mL, 20.3 mmol) was then added in 10 min, and the reaction mixture was stirred at -40°C for 1 h and at room temperature for 1 h. A solution of *N*-benzylhydroxylamine (700 mg, 5.6 mmol) in dichloromethane (10 mL) and anhydrous magnesium sulphate (614 mg, 5.6 mmol) were then added and the mixture was stirred at room temperature for 4 h. Filtration and evaporation of the filtrate gave a crude product, which was purified by trituration and washing with ethyl acetate to give the dinitrone as a white solid (577 mg, 70% yield).
Mp = 155-156°C, R*f* = 0.24 (Ethyl Acetate 7/Methanol 3)

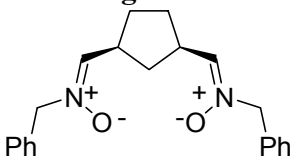
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (m, 4H), 2.47 (m, 4H), 4.86 (s, 4H), 6.62 (t, J = 6.0 Hz, 2H), 7.38 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6 (2C), 26.7 (2C), 69.5 (2C), 129.2 (4C), 129.5 (4C), 133.1 (2C), 138.8 (2C).
IR (film, KBr), 3429, 2917, 1593, 1457, 1168 cm^{-1}.
HRMS: calcd for $C_{20}H_{24}N_2O_2$ [M^++Na]:347.1735 ; found: 347.1728.

Nitrone **7f**:



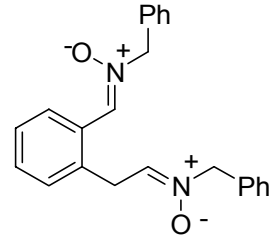
The dinitrone was synthesized following the same procedure for **7e,** using 1,7-heptanediol (335 mg, 2.5 mmol). The dinitrone was obtained as a white solid (480 mg, 56 % yield).
Mp = 148-149°C, R*f* = 0.38 (Ethyl Acetate 7/Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 2H), 1.49 (m, 4H), 2.45 (q, J = 6.8 Hz, 4H), 4.86 (s, 4H), 6.60 (t, J = 5.6 Hz, 2H), 7.38 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3 (2C), 26.7 (2C), 29.4, 69.5 (2C), 129.2 (4C), 129.5 (4C), 133.2 (2C), 139.1 (2C).
IR (film, KBr), 3062, 2995, 2919, 2854, 1582, 1495, 1457, 1429, 1213, 1172, 1110, 929 cm^{-1}.
HRMS: calcd for $C_{21}H_{26}N_2O_2$ [M^++Na]: 361.1879 ; found: 361.1892.

Nitrone **7g**:



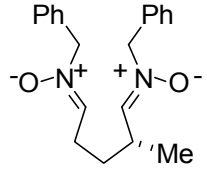
The dinitrone **7g** was synthesized following the same procedure as **7b**, using Norbonylene (470 mg, 5.0 mmol), triphenylphosphine (1.6 g, 6.0 mmol), a solution of *N*-benzylhydroxylamine (1.4 g, 11.0 mmol) in dichloromethane (20 mL) and anhydrous magnesium sulphate (1.3 g, 11.0 mmol). The corresponding dinitrone was obtained as a white solid (1.2 g, 72% yield).
Mp = 167-168°C, R*f* = 0.27 (Ethyl Acetate 7/ Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (dt, J = 9.6 Hz, J = 12.8 Hz, 1H), 1.55 (m, 2H), 2.07 (m, 2H), 2.38 (dt, J = 7.6 Hz, J = 12.8 Hz, 1H), 3.34 (m, 2H), 4.84 (s, 4H), 6.58 (d, J = 6.8 Hz, 2H), 7.33-7.41 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.5 (2C), 34.0, 37.0 (2C), 69.5 (2C), 129.1 (4C), 128.2 (2C), 129.4 (4C), 133.2(2C), 142.0 (2C).
IR (film, KBr), 3060, 3036, 2954, 2848, 1592, 1496, 1457, 1426, 1205, 1195, 1127 cm^{-1}.
HRMS: calcd for $C_{21}H_{24}N_2O_2$ [M^++Na]: 359.1735 ; found: 359.1724.

Nitrone **7h**:



To a solution of the dialdehyde[5] (600.0 mg, 4.0 mmol) in dichloromethane (15 mL) was added a solution of *N*-benzylhydroxylamine (1.2 g, 10.0 mmol) in dichloromethane (5 mL) and anhydrous magnesium sulphate (1.2 g, 10.0 mmol). The corresponding dinitrone was obtained after flash chromatography as a white solid (340.0 mg, 61% yield).
Mp = 145-146°C, R*f* = 0.26 (Ethyl Acetate 19/ Methanol 1)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (d, J = 6.4 Hz, 2H), 4.73 (s, 2H), 4.83 (s, 2H), 6.76 (t, J = 6.4 Hz, 1H), 7.20-7.39 (m, 11H), 7.48 (dd, J = 2.0 Hz, J = 8.0 Hz, 2H), 7.93 (s, 1H), 9.23 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.7, 69.9, 71.8, 128.0, 128.6, 128.8 (2C), 128.9 (2C), 129.2 (2C), 129.2, 129.4, 129.5, 129.6 (2C), 130.0, 130.5, 130.6, 131.8, 132.8, 135.3, 137.1.
IR (film, KBr), 3063, 3032, 1588, 1560, 1497, 1457, 1352, 1301, 1206, 1162, 941 cm^{-1}.
HRMS: calcd for $C_{23}H_{22}N_2O_2$ [M^++Na]: 381.1579 ; found: 381.1586.

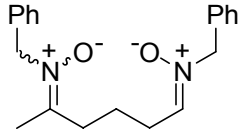
Nitrone **7i**:



The synthesis of the nitrone **7i** was realised following the same procedure as for **7b**, using (-)-*β*-citronellene (691 mg, 5.0 mmol), triphenylphosphine (1.6 g, 6.0 mmol), *N*-benzylhydroxylamine (1.4 g, 11.0 mmol) and anhydrous magnesium sulphate (1.3 g, 11.0 mmol). The corresponding dinitrone was obtained as a white sticky solid (1.1 g, 78% yield) after purification by chromatography on silica gel.

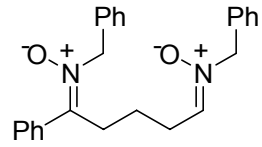
R*f* = 0.33 (Ethyl Acetate 7/ Methanol 3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (br, 3H), 1.60 (br, 1H), 1.73 (br, 1H), 2.53 (br, 2H), 3.25 (br, 2H), 5.02 (br, 4H), 6.59 (br, 1H), 6.81 (br, 1H), 7.27-7.4 (m, 10H).
IR (film, KBr), 3374, 3062, 2965, 1621, 1585, 1497, 1456, 1417, 1318, 1177, 1106, 912 cm^{-1}.
HRMS: calcd for $C_{20}H_{24}N_2O_2$ [M^++Na]: 347.1735 ; found: 347.1740.

Nitrone **7j** :



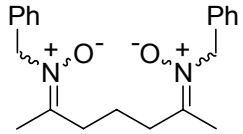
The synthesis of the ketoaldehyde was realised following the Swern oxidation described for **7e**, using $(COCl)_2$ (1.8 mL, 21.1 mmol), dry DMSO (1.8 mL, 25.4 mmol), 1,5-hexanediol (500 mg, 4.2 mmol) and anhydrous Et_3N (5.9 mL, 42.3 mmol). The reaction mixture was washed by water (10 mL) and the organic layer was washed once with brine, dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product. To a solution of the crude ketoaldehyde (271 mg, 2.37 mmol) in dichloromethane (10 mL), anhydrous zinc chloride (646 mg, 4.8 mmol), a solution of *N*-benzylhydroxylamine (650 mg, 5.2 mmol) in dichloromethane (4 mL) and anhydrous magnesium sulphate (573 mg, 5.2 mmol) were added sequentially. After 2.5 h at room temperature, the reaction was filtered, the filtrate evaporated and the residue was chromatographed on silica gel to give a yellow sticky powder (370 mg, 48% yield).
R*f* = 0.30 (Ethyl Acetate 1/ Methanol 1)
Mixture of isomers: Z/E ratio of 69/31
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (m, 2H, E isomer), 1.81 (m, 2H, Z isomer), 2.07 (s, 3H, Z isomer), 2.13 (s, 3H, E isomer), 2.40-2.55 (m, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 4.91 (s, 2H, E isomer), 5.09 (s, 2H, Z isomer), 6.58 (t, *J* = 5.6 Hz, 1H, E isomer), 6.85 (t, *J* = 4.8 Hz, 1H, Z isomer), 7.26-7.41 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (E isomer), 19.3 (Z isomer), 20.6 (E isomer), 22.8 (Z isomer), 26.5 (E isomer), 26.8 (Z isomer), 32.8 (Z isomer), 34.1 (E isomer), 64.0 (E isomer), 64.4 (Z isomer), 69.3 (E isomer), 69.5 (Z isomer), 127.9, 128.3, 128.4, 129.1, 129.1, 129.2, 129.2, 129.3, 129.4, 129.6, 133.0, 133.3, 133.8, 134.3, 134.5.
IR (film, KBr), 3208, 3030, 2937, 2360, 1653, 1604, 1496, 1455, 1142, 1029, 909, 732 cm^{-1}.

Nitrone **7k**:



A solution of 4-benzoylbutyric acid (1.0 g, 5 mmol) in THF (30 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (759 mg, 20 mmol) in THF (30 mL) at 0°C. The reaction mixture was then heated under reflux for 20 h. The reaction mixture was cooled, and excess of $LiAlH_4$ was destroyed by dropwise addition of ethyl acetate(40 mL). H_2O (25 mL) and then 1 *N* HCl (5 mL) were added, and the reaction mixture was filtered. The filtrate was evaporated and then coevaporated with toluene to give the diol as a thick liquid. The product was used without further purification. The diol is then oxidized following the preceding procedure, using $(COCl)_2$ (1.3 mL, 14.7 mmol), dry DMSO (1.3 mL, 17.6 mmol), 1-phenyl-1,5-heptanediol (530 mg, 2.9 mmol) and anhydrous Et_3N (4.1 mL, 29.4 mmol). To a solution of the crude ketoaldehyde (400 mg, 2.27 mmol) in dichloromethane (15 mL), anhydrous zinc chloride (691 mg, 5 mmol), a solution of *N*-benzylhydroxylamine (621 mg, 5 mmol) in dichloromethane (5 mL) and anhydrous magnesium sulphate (544 mg, 4.5 mmol) were added sequentially. After 72 h at 40°C, the reaction was filtered, the filtrate evaporated and the residue was chromatographed on silica gel to give a colourless instable powder (609 mg, 69% yield).
R*f* = 0.32 (Ethyl Acetate 4/ Methanol 1)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (t, *J* = 7.6 Hz, 2H), 2.65 (m, 2H), 3.02 (t, *J* = 7.6 Hz, 2H), 5.05 (s, 2H), 5.08 (s, 2H), 7.22-7.30 (m, 5H), 7.33 (m, 3H), 7.36 (m, 3H), 7.45-749 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 27.5, 34.0, 64.2, 68.2, 127.6, 128.4, 128.9, 128.9, 129.3, 129.5, 129.7, 130.6, 130.9, 132.9.
IR (film, KBr), 3483, 3062, 1653, 1636, 1497, 1455, 1156, 906 cm^{-1}.

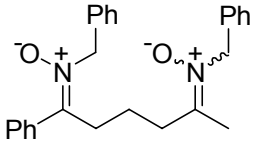
Nitrone **7l**:



To a solution of the diketone[6] (384.5 mg, 3.0 mmol) in dichloromethane (15 mL) was added anhydrous zinc chloride (818 mg, 6 mmol), a solution of *N*-benzylhydroxylamine (820 mg, 6.6 mmol) in dichloromethane (6 mL) and anhydrous magnesium sulphate (798 mg, 6.6 mmol). The corresponding dinitrone was obtained after flash chromatography as colourless oil (220 mg, 41% yield).

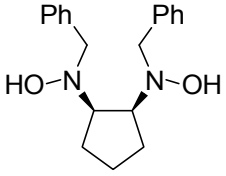
R*f* = 0.16 (Ethyl Acetate 1/ Methanol 1)
Mixture of isomers: ZZ, ZE and EE in ratio of 1/2/1
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (qu, *J* = 7.6 Hz, 1H), 1.90 (qu, *J* = 8.0 Hz, 1H), 2.02 (s, 1.5 H), 2.06 (s, 1.5 H), 2.12 (s, 1.5 H), 2.15 (s, 1.5 H), 2.27 (t, *J* = 7.6 Hz, 1H), 2.48 (t, *J* = 8.0 Hz, 1H), 2.56 (t, *J* = 7.6 Hz, 1H), 2.64 (t, *J* = 8.0 Hz, 1H), 5.03 (s, 1H), 5.04 (s, 1H), 5.06 (s, 1H), 5.08 (s, 1H), 7.30-7.38 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 18.5, 19.2, 19.4, 19.7, 22.1, 32.7, 33.0, 33.8, 34.3, 63.9, 64.4, 64.5, 64.7, 127.7, 127.7, 127.8, 127.9, 128.0, 128.4, 128.4, 128.5, 128.6, 128.7, 129.0, 129.1, 129.2, 129.2, 129.3, 133.7, 133.8, 134.2, 134.2.

Nitrone **7m**:



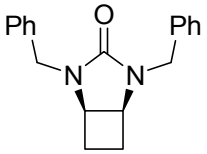
To a solution of the diketone[7] (140 mg, 0.74 mmol) in dichloromethane (5 mL) was added anhydrous zinc chloride (221 mg, 1.6 mmol), a solution of *N*-benzylhydroxylamine (274 mg, 2.2 mmol) in dichloromethane (2 mL) and anhydrous magnesium sulphate (196 mg, 1.6 mmol). The reaction mixture was heated 72 h at 40°C. The corresponding dinitrone was obtained after flash chromatography as a colourless oil (220 mg, 74% yield).
R*f* = 0.25 (Ethyl Acetate 1/ Methanol 1)
Mixture of isomers: Z/E ratio of 1/1
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (qu, *J* = 7.6 Hz, 1H), 1.84 (m, 1H), 2.01 (s, 1.5H), 2.06 (s, 1.5H), 2.42 (t, *J* = 8.0 Hz, 1H), 2.63 (t, *J* = 8.0 Hz, 1H), 2.88 (m, 1H), 4.90 (s, 1H), 4.96 (s, 1H), 5.05 (s, 1H), 5.07 (s, 1H), 7.11 (m, 1H), 7.20-7.31 (m, 8H), 7.34 (m, 2H), 7.37-7.42(m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 19.3, 20.0, 22.2, 32.9, 33.6, 34.1, 63.6, 64.2, 64.3, 64.5, 127.7, 127.9, 128.0, 128.0, 128.1, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 128.9, 129.2, 129.3, 129.7, 129.8, 133.9, 134.1, 134.2, 134.4, 134.6, 134.7.

Dihydroxylamine cyclopentane **8**:



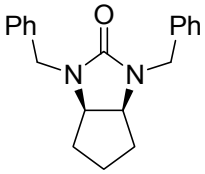
A stirred solution of the dinitrone (93.1 mg, 0.3 mmol) and methanol (121 μL, 3.0 mmol) in dry THF (8.4 mL) was cooled to 0°C under argon. A solution of SmI_2 (ca. 0.1M, 6.6 mL, 0.66 mmol) in THF was then added in 30 min. After 45 min, the reaction was judged to be complete by TLC, and the solution was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (2 mL). The yellow mixture was extracted with AcOEt (3 × 10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography with pentane-EtOAc to give the expected *N*-dihydroxydiamine as a colourless oil (71 mg, 76% yield).
R*f* = 0.56 (Pentane 9/Ethyl Acetate 1)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (m, 1H), 1.85 (m, 3H), 1.97 (m, 2H), 3.40 (s, 2H), 3.67 (d, *J* = 13.0 Hz, 2H), 4.01 (d, *J* = 13.0 Hz, 2H), 7.26-7.38 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8 (3C), 60.7(4C), 127.7 (2C), 128.6 (4C), 129.3 (4C), 137.5 (2C).
IR (film, KBr), 3344, 2957, 2867, 1496, 1453, 1051, 1029 cm^{-1}.
HRMS: calcd for $C_{19}H_{24}N_2O_2$ [M^++Na]: 335.1739; found: 335.1735.

Urea **9a**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9a** was obtained as a colourless oil (28 mg, 32 % yield) and as a single diastereoisomer.
R*f* = 0.34 (Pentane 4/Ethyl Acetate 1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (m, 2H), 2.10 (m, 2H), 3.93 (t, *J* = 4.8 Hz, 2H), 4.20 (d, *J* = 14.8 Hz, 2H), 4.64 (d, *J* = 14.8 Hz, 2H), 7.27-7.33 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5 (2C), 46.2 (2C), 53.3 (2C), 127.5 (2C), 128.5 (4C), 128.7 (4C), 137.9 (2C), 161.3.
IR (film, KBr), 3062, 3030, 2941, 1690, 1495, 1448, 1423, 1357, 1221, 752 cm^{-1}.
HRMS : calcd for $C_{19}H_{20}N_2O$ [M^++Na]: 315.1473; found: 315.1473.

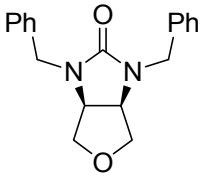
Urea **9b**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9b** was obtained as a white solid (61 mg, 66 % yield) and as a single diastereoisomer.
Mp = 121°C, R*f* = 0.39 (Pentane 4/Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37-1.45 (m, 2H), 1.52-1.60 (m, 2H), 1.68-1.79 (m, 2H), 3.77 (m, 2H), 4.09 (d, *J* = 15.4 Hz, 2H), 4.80 (d, *J* = 15.4 Hz, 2H), 7.24-7.35 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.0, 31.5 (2C), 46.4 (2C), 58.1 (2C), 127.5 (2C), 128.4 (4C), 128.8 (4C), 138.1 (2C), 160.2 (1C).
IR (film, KBr), 3438, 2915, 2362, 1676, 1451, 1249 cm^{-1}.
HRMS: calcd for $C_{20}H_{22}N_2O$ [M^++Na]: 329.1630 ; found: 329.1638.

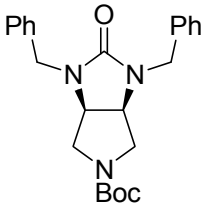
Urea **9c**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9c** was obtained as a white powder (48 mg, 52 % yield) and in a 5:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
Mp = 124-125°C, R*f* = 0.32 (Pentane 1/Ethyl Acetate 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (dt, *J* = 2.0 Hz, *J* = 9.6 Hz, 2H), 3.85 (d, *J* = 10.4 Hz, 2H), 3.93 (t, *J* = 2.0 Hz, 2H), 4.22 (d, *J* = 15.2 Hz, 2H), 4.74 (d, *J* = 15.2 Hz, 2H), 7.26-7.36 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.9 (2C), 58.4 (2C), 71.9 (2C), 127.8 (2C), 128.4 (4C), 1229.0 (4C), 137.3 (2C), 159.6.
IR (film, KBr), 3061, 2927, 1748, 1678, 1462, 1453, 1424, 1239, 1072, 920 cm^{-1}.
HRMS: calcd for $C_{19}H_{20}N_2O_2$ [M^++Na]: 331.1422 ; found: 331.1421.

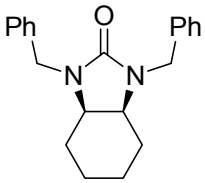
Urea **9d**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9d** was obtained as a colourless oil (56 mg, 59 % yield) and as a single diastereoisomer.
R*f* = 0.26 (Pentane 7/Ethyl Acetate 3).
Mixture of rotamers: 1/1

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9H), 3.11 (d, *J* = 10.4 Hz, 2H), 3.48 (br, 2H), 3.78 (s, 2H), 4.04 (br, 2H), 4.74 (br, 2H), 7.18-7.28 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.6 (3C), 46.8 (2C), 50.0 (2C), 56.2, 57.5, 80.3, 127.9 (4C), 128.5 (2C), 129.0 (4C), 137.0 (2C), 154.4, 159.5.
IR (film, KBr), 3501, 2976, 2930, 1693, 1450, 1417, 1365, 1245, 1169, 1109, 881, 753 cm^{-1}.
HRMS: calcd for $C_{24}H_{29}N_3O_3$ [M^++Na]: 430.2107 ; found: 430.2104.

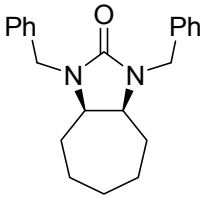
Urea **9e**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9e** was obtained as a colourless oil (41 mg, 43% yield) and in a 5:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
R*f* = 0.33 (Pentane 4/Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (m, 2H), 1.38 (m, 2H), 1.61 (m, 4H), 3.26 (t, *J* = 4.0 Hz, 2H), 4.08 (d, *J* = 15.4 Hz, 2H), 4.80 (d, *J* = 15.4 Hz, 2H), 7.24-7.34 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (2C), 25.5 (2C), 45.5 (2C), 52.7 (2C), 127.4 (2C), 128.4 (4C), 128.7 (4C), 138.1 (2C), 162.1.
IR (film, KBr), 2935, 2858, 1697, 1638, 1495, 1447, 1354, 1254, 1222, 955, 767 cm^{-1}.
HRMS: calcd for $C_{21}H_{24}N_2O$ [M^++Na]: 343.1786 ; found: 343.1782.

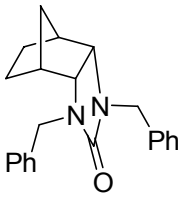
Urea **9f**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9f** was obtained as a colourless oil, (35 mg, 35% yield) and in a 3:1 diastereomeric ratio favouring the *cis* isomer.
Mixture of the 2 diastereoisomers, ratio cis/trans 3:1
R*f* = 0.27 (Pentane 4/Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14-1.27 (m, 2H), 1.34-1.55 (m, 3H), 1.58-1.74 (m, 5H), 2.02 (m, 2H, Trans), 3.06 (t, *J* = 3.6 Hz, 2H, Trans), 3.48 (t, *J* = 3.6 Hz, Cis), 3.97 (d, *J* = 15.2 Hz, 2H, Cis), 4.14 (d, *J* = 15.2 Hz, 2H, Trans), 4.70 (d, *J* = 15.2 Hz, 2H, Trans), 4.93 (d, *J* = 15.2 Hz, 2H, Cis), 7.24-7.34 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8 (2C, Cis), 26.1 (2C, Cis), 28.1 (2C), 30.4 (1C, Trans), 30.4 (1C, Cis), 45.3 (2C, Cis), 46.1 (2C, Trans), 56.7 (2C, Cis), 59.6 (2C, Trans), 127.5 (2C), 128.3 (4C), 128.7 (4C), 137.9 (2C), 160.6.
IR (film, KBr), 3028, 2920, 1685, 1495, 1448, 1354, 1255, 961, 745 cm^{-1}.
HRMS: calcd for $C_{22}H_{26}N_2O$ [M^++Na]: 357.1943 ; found: 357.1938.

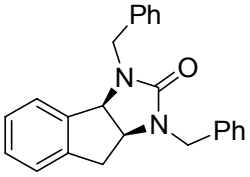
Urea **9g**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9g** was obtained as a colourless oil (52 mg, 52 % yield) and in a 4:1 diastereomeric ratio favouring the *endo* isomer.
Major stereoisomer
R*f* = 0.35 (Pentane 9/ Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 2H), 1.06 (dt, *J* = 1.6 Hz, *J* = 10.8 Hz, 1H), 1.38 (m, 2H), 1.64 (dt, *J* = 1.6 Hz, *J* = 10.4 Hz, 1H), 2.15 (m, 2H), 3.23 (d, *J* = 1.6 Hz, 2H), 4.17 (d, *J* = 15.0 Hz, 2H), 4.68 (d, *J* = 15.0 Hz, 2H), 7.22-7.34 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1 (2C), 31.4, 38.9 (2C), 46.7 (2C), 61.2 (2C), 127.5 (2C), 128.3 (4C), 128.7 (4C), 138.3 (2C), 160.9.
IR (film, KBr), 3470, 3029, 2957, 2873, 1690, 1495, 1449, 1357, 1291, 1240, 1152, 753 cm^{-1}.
HRMS: calcd for $C_{22}H_{24}N_2O$ [M^++Na]: 355.1786 ; found: 355.1794.

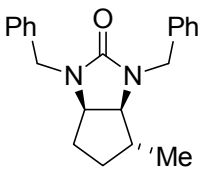
Urea **9h**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9h** was obtained as a colourless oil (61 mg, 58 % yield) and in a 4:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
R*f* = 0.30 (Pentane 9/ Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (dd, *J* = 11.6 Hz, *J* = 13.2 Hz, 1H), 2.60 (dd, *J* = 5.2 Hz, *J* = 13.2 Hz, 1H), 3.10 (ddd, *J* = 5.2 Hz, *J* = 10.8 Hz, *J* = 12.0 Hz, 1H), 3.96 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 4.60 (d, *J* = 15.2 Hz, 1H), 4.67 (d, *J* = 14.4 Hz, 1H), 4.82 (d, *J* = 15.2 Hz, 1H), 6.63 (d, *J* = 6.8 Hz, 1H), 7.01 (m, 1H), 7.09 (m, 2H), 7.24-7.44 (m, 11H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.1, 49.7, 49.9, 66.0, 67.6, 121.9, 126.5, 127.1, 127.2, 127.8, 127.9, 128.8 (4C), 128.9 (2C), 129.0 (2C), 137.2, 137.7, 139.9, 143.0, 167.2.
IR (film, KBr), 3307, 3029, 2927, 1701, 1496, 1455, 1354, 1142, 1056, 965, 747 cm^{-1}.
HRMS: calcd for $C_{24}H_{22}N_2O$ [M^++Na]: 377.1630 ; found: 377.1634.

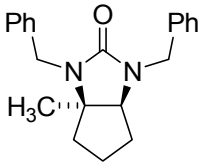
Urea **9i**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9i** was obtained as yellow oil (62 mg, 65 % yield) and in a 9:1 diastereomeric ratio favouring the *cis* isomer.
R*f* = 0.24 (Pentane 9/ Ethyl Acetate 1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (d, J = 6.8 Hz, 3H), 1.22 (m, 1H), 1.61-1.72 (m, 2H), 1.74-1.85 (m, 1H), 2.08 (m, 1H), 3.29 (dd, J = 2.0 Hz, J = 8.8 Hz, 1H), 3.76 (m, 1H), 4.06 (d, J = 14.8 Hz, 1H), 4.11 (, J = 14.8 Hz, 1H), 4.80 (d, J = 14.8 Hz, 1H), 4.82 (d, J = 14.8 Hz, 1H), 7.24-7.34 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 29.7, 30.8, 38.6, 46.4, 46.6, 58.1, 65.0, 127.5 (2C), 128.4 (4C), 128.7 (4C), 138.0 (2C), 159.8.
IR (film, KBr), 2955, 1689, 1495, 1450, 1357, 1244, 1075, 958, 815, 753 cm^{-1}.
HRMS: calcd for $C_{21}H_{24}N_2O$ [M^++Na]: 343.1786 ; found: 343.1787.

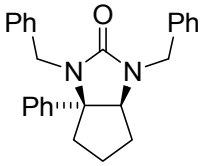
Urea **9j**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9j** was obtained as a white powder (40 mg, 42 % yield) and in a 7:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
Mp = 106-107°C, R*f* = 0.18 (Pentane 4/Ethyl Acetate 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 3H), 1.25 (m, 1H), 1.48-1.57 (m, 3H), 1.69-1.73 (m, 2H), 3.34 (t, J = 4.0 Hz, 1H), 4.07 (d, J = 15.4 Hz, 1H), 4.40 (d, J = 15.4 Hz, 1H), 4.48 (d, J = 16.0 Hz, 1H), 4.85 (d, J = 16.0 Hz, 1H), 7.23-7.37 (m, 10H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.1, 25.9, 31.5, 38.4, 44.3, 46.2, 65.4, 66.9, 127.2, 127.5, 128.0 (2C), 128.3 (2C), 128.6 (2C), 128.8 (2C), 138.1, 140.5, 159.8.
IR (film, KBr), 2959, 2864, 1736, 1676, 1495, 1467, 1449, 1418, 1354, 1026, 949 cm^{-1}.
HRMS: calcd for $C_{21}H_{24}N_2O$ [M^++Na]: 343.1786 ; found: 343.1786.

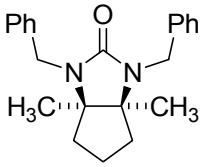
Urea **9k**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9k** was obtained as a colourless oil (48 mg, 44% yield) and in a 5:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
R*f* = 0.14 (Pentane 9/Ethyl Acetate 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46-1.70 (m, 3H), 1.83 (m, 2H), 1.88-1.96 (m, 1H), 3.49 (d, J = 15.6 Hz, 1H), 3.74 (d, J = 6.4 Hz, 1H), 4.08 (d, J = 14.8 Hz, 1H), 4.74 (d, J = 15.6 Hz, 1H), 5.01 (d, J = 14.8 Hz, 1H), 7.13 (m, 2H), 7.19-7.28 (m, 9H), 7.31-7.38 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8, 31.6, 35.0, 45.0, 46.5, 66.6, 72.5, 126.9 (2C), 127.2, 127.7, 127.9, 128.2, 128.5, 128.8 (2C), 128.8 (2C), 128.8 (2C), 137.8, 140.1, 143.0, 160.0.
IR (film, KBr), 3062, 3024, 2965, 2916, 1685, 1493, 1461, 1447, 1419, 1347, 1212, 747 cm^{-1}.
HRMS: calcd for $C_{26}H_{26}N_2O$ [M^++Na]: 405.1943 ; found: 405.1942.

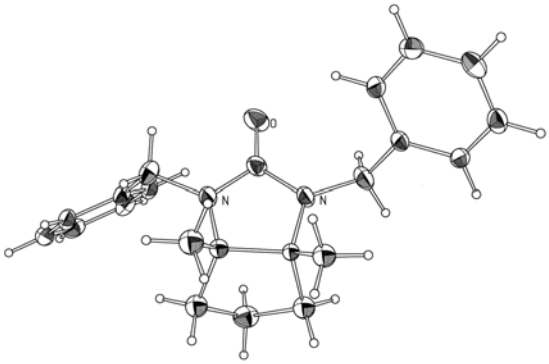
Urea **9l**:



Following the general procedure for the intramolecular cyclisation of dinitrones, compound **9l** was obtained as a colourless powder (28 mg, 28 % yield) and in a 4:1 diastereomeric ratio favouring the *cis* isomer.
Major stereoisomer
Mp = 112-113°C, R*f* = 0.22 (Pentane 4/Ethyl Acetate 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 6H), 1.27-1.34 (m, 4H), 1.73-1.78 (m, 2H), 4.33 (d, J = 15.6 Hz, 2H), 4.40 (d, J = 15.6 Hz, 2H), 7.16-7.18 (m, 2H), 7.21-7.25 (m, 4H), 7.29-7.31 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (2C), 22.0, 38.6 (2C), 44.3 (2C), 69.3 (2C), 127.1 (2C), 128.0 (4C), 128.6 (4C), 140.7 (2C), 159.8.
IR (film, KBr), 2966, 1669, 1494, 1442, 1416, 1353, 751 cm^{-1}.
HRMS: calcd for $C_{22}H_{26}N_2O$ [M^++Na]: 357.1943 ; found: 357.1940.

Supplementary Material (ESI) for Chemical Communications



X-ray crystal structure representation of the urea **9l**

1 A. Dondoni, S. Franco, F. Junquera, F. Merchán, P. Merino and T. Tejero, *Synth. Comm.*, **1994**, *24*, 2537.
2 S. Franco, F. L. Merchán, P. Merino and T. Tejero, *Synth. Comm.*, **1995**, *25*, 2275.
3 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, **1980**, *102*, 2693.
4 B. Garrigues, M. Lazrag, *Tetrahedron Lett.* **1986**, *27*, 1685.
5 J. L. Warnell and R. L. Shriner, *J. Am. Chem. Soc.*, **1957**, *79*, 3165.
6 R. A. Micheli, Z. G. Hajos, N. Cohan, D. R. Parrish, L. A. Portland, W. Sciamanna, M. A. Scott and P. A. Wehrli, *J. Org. Chem.*, **1975**, *40*, 675.
7 A. Nishinaga, K. Rindo and T. Matsuura, *Synthesis*, **1986**, 1038.