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Supporting Information for:

Nitrogen Assistance in the Intramolecular Nickel-Promoted Tandem Cyclisation-Quenching Processes

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Synthesis of starting materials.

Allylamine, benzylamine, 2-(1-cyclohexenyl)ethylamine, 4-bromo-1-butene, butylbromide, 2,3-dibromopropene, 2-bromoaniline, 2,3-dichloropropene are commercial products and were used as received or distilled if required.

3-Bromocyclohexene and 3-bromocyclooctene are obtained by allylic bromination of the corresponding cycloalkenes with NBS and dibenzoylperoxide according to a published procedure¹. 1-Cyclohexenylmethanol was obtained from cyclohexenone according to a previously described method². 2,4-Dibromo-1-butene was obtained by bromination (PPh_3Br_2) of 3-bromo-3-buten-1-ol. This bromoalcohol was obtained from Aldrich or synthesized by hydrobromination of 3-buten-1-ol³.

Synthesis of secondary amines

Method A: A solution of the corresponding allyl halide (50 mmol) and benzylamine (250 mmol) in dichloromethane (50 ml) was stirred at rt under argon for 2

¹ Greenwood, F.L.; Kellert, M.D. *J. Am. Chem. Soc.* **1953**, *75*, 4842-4851.

² Pagès, L.; Llebaria, A.; Camps, F.; Molins, E.; Miravittles, C.; Moretó, J.M. *J. Am. Chem. Soc.* **1992**, *114*, 10499-10461

³ Cousseau, J. *Synthesis*, **1980**, 805-806.

days. After dilution with dichloromethane, the mixture was washed with saturated aqueous sodium carbonate solution. The organic layer was dried and evaporated to dryness. The excess of benzylamine was removed by distillation at 0.5 mm Hg, and the remaining amine was obtained as an oil that was used without further purification or distilled at low pressure if required.

Method B: A solution of the primary amine (100 mmol) and Et₃N (100 mmol) in Et₂O (25 mL) is added dropwise over an ice cooled solution of the corresponding halide (100 mmol) in Et₂O (25 mL) under argon. After stirring for 12 h at rt, the reaction mixture is filtered and the solids washed with Et₂O. The combined ethereal solutions are evaporated to dryness and the resulting oil is distilled at reduced pressure or chromatographed to furnish the amine.

Method C: A mixture of benzylamine (250mmol), anh. K₂CO₃ (60 mmol) and the halide (50 mmol) is heated under argon at 70°C for 12 h. The reaction mixture is filtered and the solid washed with dichloromethane. The filtrate is washed with saturated aqueous Na₂CO₃, dried, and evaporated. Distillation of the resulting oil afforded the corresponding amine.

***N*-Benzyl-2-cyclohexenylamine**

From benzylamine and 3-bromocyclohexene in 71% yield according to the general procedure A .

¹HNMR (300 MHz): 1.40-2.05 (7H, m), 3.21 (1H, bb), 3.81 and 3.88 (2H, AB system, *J* = 13.1 Hz, NCH₂Ar), 5.75 (2H, bb), 7.20-7.40 (5H, m).¹³CNMR (75.4 MHz): 20.1 (CH₂), 25.2 (CH₂), 29.3 (CH₂), 50.8 (NCH₂Ar), 52.2 (CH), 126.7 (ArCH), 128.0 (ArCH), 128.2 (ArCH), 128.8 and 129.8 (=CH), 140.6 (q).

***N*-Benzyl-2-bromoallylamine**^{4,5}

Obtained from benzylamine and 2,3-dibromopropene in 55 % yield according to method A.

bp: 65-70 °C / 0.04 Torr

¹HNMR (200 MHz): 1.82 (1H, bs), 3.47 (2H, s), 3.74 (2H, s, NCH₂Ar), 5.60 (1H, s), 5.80 (1H, s), 7.22-7.40 (5H, m). ¹³CNMR (50.3 MHz): 51.5 (CH₂), 56.6 (CH₂), 117.9 (=CH₂), 128.1 (ArCH), 128.3 (ArCH), 128.4 (ArCH), 133.4 (=Cq), 139.6 (q). IR (neat): 3340, 2829, 1625. Anal. Calcd for C₁₀H₁₂BrN: C, 53.12; H, 5.43; N, 6.19; Br, 35.34. Found: C, 53.17; H, 5.43; N, 6.22; Br, 35.49 .

***N*-Allylbenzylamine**⁵

Obtained from excess allylamine (5eq) and benzyl bromide in 73% yield according to method B.

bp: 105-107 / 19 Torr.

¹HNMR (300 MHz): 1.51 (1H, bs, NH), 3.28 (2H, dt, *J* = 6.0, 1.5 Hz), 3.80 (2H, s), 5.01-5.24 (2H, m), 5.85-6.01 (1H, m), 7.20-7.36 (5H, m). ¹³CNMR (75.4 MHz): 51.78 (CH₂), 53.27 (CH₂), 116.01 (=CH₂), 126.94 (ArCH), 128.18 (ArCH), 128.40 (ArCH), 136.78 (=CH), 140.26 (q). IR (neat): 3313, 3062, 3026, 2916, 1643, 1494, 1454, 1107, 918, 736, 698.

***N*-Benzyl-2-(1-cyclohexenyl)ethylamine**⁶

Obtained from 2-(1-cyclohexenyl)ethylamine and benzyl bromide. Purified by flash chromatography on silica gel (*t*-BuOMe /NEt₃ 100:1).

¹HNMR (300 MHz): 1.42-1.66 (5H, m+NH), 1.83 (2H, bs), 1.98 (2H, bs), 2.16 (2H, bt, *J* = 6.0 Hz), 2.68 (2H, t, *J* = 6.0 Hz), 3.79 (2H, s), 5.45 (1H, bs), 7.2-7.36 (5H,

⁴Mori, M.; Chiba, K.; Okita, M.; Kayo, I.; Ban, Y. *Tetrahedron*, **1985**, *41*, 375-385.

⁵Barluenga, J.; Canteli, R.-M.; Florez, J. *J. Org. Chem.*, **1994**, *59*, 602-606.

⁶Guy, A.; Barbetti, J.F. *Synthetic Commun.* **1992**, *22*, 853-857.

m). ^{13}C NMR (75.4 MHz): 22.44 (CH_2), 22.91 (CH_2), 25.21 (CH_2), 28.05 (CH_2), 38.24(CH_2), 46.87(CH_2), 53.87 (CH_2), 122.72 (=CH), 126.81 (ArCH), 128.07 (ArCH), 128.35 (ArCH), 135.39 (q), 140.49 (q). IR (neat): 3325, 3060, 3026, 2923, 1494, 1452, 1118, 732, 698. Anal Calcd. for $\text{C}_{15}\text{H}_{21}\text{N}$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.63; H, 9.97; N, 6.57.

***N*-Benzyl-3-butenylamine**

Obtained from 4-bromobutene and benzylamine according to a published procedure⁷ (method C) in 76% yield.

***N*-Benzyl-2-chloroallylamine**

From benzylamine and 2,3-dichloropropene in 59% yield according to method C. Purified by flash chromatography (hexane/ AcOEt 9:1).

^1H NMR (200MHz): 1.75 (1H, bs), 3.47 (2H, s), 3.78 (2H, s, NCH_2Ar), 5.40 (2H, s), 7.20-7.40 (5H, m). ^{13}C NMR (50.3 MHz): 51.6 (CH_2), 54.7 (CH_2), 113.6 (=CH₂), 127.1 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 139.8 (=Cq), 140.9 (q). IR (neat): 3350, 3040, 2829, 1630.

***N*-Benzyl-3-bromo-3-butenylamine**

Obtained (method A) from benzylamine and 2,4-dibromobutene in 48 % yield. ^1H NMR (200 MHz): 2.63 (2H, t), 2.85 (2H, t), 3.81 (2H, s), 5.47 (1H, bs), 5.65 (1H, bs), 7.35 (5H, m).

***N*-Benzyl-(2-cyclohexenyl)methylamine**

Obtained from 2-cyclohexenecarboxylic acid and benzylamine in two steps.

***N*-Benzyl-2-cyclohexenecarboxamide**

⁷ Brands, K.M.J.; Meekel, A.A.P.; Pandit, U.K. *Tetrahedron* **1991**, *47*, 2005-2026.

Oxalyl chloride (4.1 ml, 47 mmol) was dropwise added, at room temperature under Argon atmosphere, to a solution of 2-cyclohexenecarboxylic acid⁸ (2 g, 15.9 mmol) in dry benzene (25 ml). The mixture was stirred at room temperature for 2 hours. Removal of the solvent and the excess of oxalyl chloride gave the crude acid chloride, that was dissolved in dichloromethane (25 ml) and cooled at 0 °C. (*i*-Pr)₂NEt (2.77 ml, 15.9 mmol) and Benzylamine (1.73 ml, 15.9 mmol) were dropwise added to the solution under Argon atmosphere. The stirring was maintained at 0 °C for 2 hours and at room temperature for 12 hours. The reaction mixture was poured into saturated aqueous sodium carbonate solution and extracted with dichloromethane. The organic layer was washed with aqueous 2N HCl, dried and evaporated. Flash chromatography of the resulting oil (Hexane/AcOEt 25%) gave the amide (2.6 g, 76%).

¹H-NMR (200 MHz): 1.52-1.76 (2H, m), 1.84-1.96 (2H, m), 1.97-2.10 (2H, m), 3.01 (1H, bb, 1-H), 4.43 (2H, AB system, NCH₂Ar), 5.70 (1H, dm, *J* = 10 Hz), 5.93 (1H, dm, *J* = 10 Hz), 6.10 (1H, bb, NH), 7.20-7.40 (5H, m). ¹³C-RMN (50.3 MHz): 20.4 (CH₂), 24.9 (CH₂), 26.5 (CH₂), 43.0 (CH), 43.5 (NCH₂Ar), 124.5 (=CH), 127.4 (=CH), 127.6 (ArCH), 128.7 (ArCH), 131.9 (ArCH), 138.5 (ArC_q), 174.5 (CO). IR (neat): 1544 and 1606 (C=C), 1639 (CO amide), 3278 (bb, NH). Anal. Calcd. for C₁₄H₁₇NO: C, 78.29; H, 7.96; N, 6.51. Found: C, 78.02; H, 8.05; N, 6.46.

N-Benzyl-(2-cyclohexenyl)methylamine:

A solution of *N*-Benzyl-2-cyclohexenecarboxamide (1.94 g, 9 mmol) in anhydrous ether (10 ml) was dropwise added during a 30 min period to a suspension of LiAlH₄ (683 mg, 18 mmol) in anhydrous ether (80 ml) cooled at 0 °C under Argon. After stirring the mixture at room temperature for 18 hours, water was dropwise added until gas evolution finished. The solution was separated and the solid residue was boiled with ether (100 ml) for 3 hours. The organic solution was combined with the previous

⁸ Walton, J.C. *J. Chem. Soc. Perkin Trans. II* **1986**, 1641-1646.

one and the mixture was washed with aqueous 2N HCl. The organic layer was separated and solid sodium carbonate was added to the aqueous phase to reach pH 12. Extraction with dichloromethane, drying and evaporation afforded the amine (1.38 g, 76%) as an oil, which was used without further purification in the next reaction.

¹H-NMR (50.3 MHz): 1.20-1.90 (5H, m), 1.94-2.06 (2H, m), 2.30 (1H, bb, 1-H), 2.56 and 2.59 (2H, AB system, $J = 6.8$ and 3.4 Hz, NCH₂), 3.81 (2H, s, NCH₂Ar), 5.61 (1H, dm, $J = 10.2$ Hz, 2-H), 5.75 (1H, dm, $J = 10.2$ Hz, 3-H), 7.20-7.40 (5H, m, Ar-H).

***N*-Benzyl-2-bromoaniline**⁹

2-Bromoaniline (9.5 g, 55.2 mmol), benzaldehyde (6.5 mL, ca 67 mmol) and 0.12 mL of acetic acid are dissolved in benzene (85 mL) and heated in a Dean-Stark apparatus for 30 hours distilling of the water produced by the imine formation. The volatiles are evaporated at vacuum and the residue containing the crude imine essentially pure is dissolved in MeOH (70 mL) and cooled with an ice-water bath. NaBH₄ (3.78 g, 0.1 mol) is added in portions to the stirred mixture during 15 min and after removing the cooling bath, the mixture is left at room temperature during 14 hours. A control of the reaction (TLC) indicated that some imine was still present so a second portion of NaBH₄ (0.54 g, 14 mmol) is added and the mixture stirred 24 hours at room temperature. The solvents are evaporated and the residue is poured into ice-water (80 mL) and extracted with dichloromethane. The crude was purified by flash chromatography (hexane / *t*-BuOMe 20:1) affording the secondary amine (10.29 g, 39.26 mmol, 71%).

¹H-NMR (200 MHz): 4.41 (1H, s), 4.44 (1H, s), 4.79 (1H, bs), 6.56-6.65 (2H, m), 7.11-7.50 (7H, m). **¹³C-NMR** (50.29MHz): 47.96 (CH₂), 109.64 (q), 111.59 (ArCH), 117.92 (ArCH), 127.20 (ArCH), 127.30 (ArCH), 128.45 (ArCH), 128.68

⁹ Couture, A.; Deniau, E.; Grandclaoudon, P. *J. Chem. Soc., Chem. Commun.* **1994**, 1329-1330.

(ArCH), 132.34 (ArCH), 138.66 (q), 144.76 (q). IR (neat): 3431 3086, 3031, 1598, 1509, 1320, 1019.

Synthesis of tertiary amines

Method D: The halide (45 mmol) was added dropwise at room temperature under argon to a mixture of the secondary amine (35 mmol) and anh. K_2CO_3 (70 mmol) in dry acetonitrile (65 ml). The reaction mixture was stirred at room temperature (unless otherwise stated) for 18 hours. The solvent was removed, and the crude residue was taken up in Et_2O and washed with water. Drying and evaporation of the organic extracts gave an oil, which was purified by flash chromatography.

Method E. A solution of 2,3-dibromopropene (30 mmol) and Et_3N (30 mmol) in Et_2O (10 mL) is added dropwise under argon over the secondary amine (30 mmol). The reaction mixture is stirred at room temperature for 12 h. The resulting precipitate is separated by filtration and the solids washed with Et_2O . The combined ethereal phases are washed with brine (3x10 mL), dried and evaporated to furnish crude amine which is purified by flash chromatography.

N-Allyl-*N*-benzyl-2-bromoallylamine (1a)

Obtained from *N*-benzyl-2-bromoallylamine and allyl bromide in 51% yield using method D (using NEt_3 instead of K_2CO_3) after purification by flash chromatography (hexane/ AcOEt 95:5).

1H NMR (200 MHz): 3.12 (2H, dm, $J = 6.2$ Hz), 3.28 (2H, s), 3.64 (2H, s), 5.12-5.29 (2H, m), 5.34 (1H, s), 5.59 (1H, q, $J = 1.2$ Hz), 5.76-5.99 (1H, m), 7.20-7.38 (5H, m). ^{13}C NMR (50 MHz): 56.0 (CH_2), 57.3 (CH_2), 61.4 (CH_2), 117.7 ($=CH_2$), 118.1 ($=CH_2$), 127.0 (ArCH), 128.2 (ArCH), 128.7 (ArCH), 132.1 (q), 135.2 ($=CH$), 139.0 (q). IR(neat): 3062, 3026, 2808, 1627, 1494, 1454, 1369, 1255, 1122, 921, 889, 738,

698. Anal Calcd. for $C_{13}H_{16}NBr$: C, 58.66; H, 6.06; N, 5.26; Br, 30.02. Found: C, 58.63; H, 6.05; N, 5.23; Br, 29.91.

***N*-Benzyl-*N*-(2-bromo-2-propenyl)-3-methyl-2-butenylamine (1b).**

Obtained from *N*-benzyl-2-bromoallylamine and prenyl bromide in 82% yield using method D at 70°C. Flash chromatography on hexanes/EtOAc 95:5. 1H NMR (200 MHz): 1.59 (3H, bs), 1.73 (3H, bs), 3.07 (2H, d, $J = 6.8$ Hz), 3.25 (2H, bs), 3.62 (2H, s), 5.27 (1H, bt, $J = 6.8$ Hz), 5.58 (1H, bs), 5.94 (1H, bs), 7.35 (5H, m). ^{13}C NMR (50.3 MHz): 17.9 (CH₃), 25.8 (CH₃), 50.7 (CH₂), 57.4 (CH₂), 61.5 (CH₂), 117.7 (=CH₂), 121.2 (=CH), 126.9 (ArCH), 128.1 (ArCH), 128.7 (ArCH), 132.4 (q), 135.3 (q), 139.2 (q). IR (neat): 2915, 2804, 1629, 1450 cm^{-1} . Anal. Calcd for $C_{15}H_{20}BrN$: C, 61.23; H, 6.85; Br, 27.15; N, 4.76. Found: C, 61.04; H, 6.92; N, 4.64.

***N*-Allyl-*N*-benzyl-2-chloroallylamine (1c)**

Obtained from *N*-Allyl-benzylamine and 2,3-dichloropropene in 50% yield (Method D) after flash chromatography on silicagel eluting with Hexane/EtOAc 99:1.

1H NMR (200 MHz): 3.14 (2H, d, $J = 6.2$ Hz), 3.23 (2H, s), 3.66 (2H, s), 5.13-5.28 (2H, m), 5.34 (1H, s), 5.48 (1H, q, $J = 1.2$ Hz), 5.78-5.99 (1H, m), 7.2-7.36 (5H, m). ^{13}C NMR (75.43 MHz): 56.13 (CH₂), 57.42 (CH₂), 59.54 (CH₂), 113.79 (=CH₂), 117.70 (=CH₂), 126.97 (ArCH), 128.27 (ArCH), 128.67 (ArCH), 135.31 (=CH), 138.99 (q), 140.19 (q). IR(neat): 3062, 3026, 2921, 2806, 1641, 1633, 1494, 1454, 1369, 1255, 1122, 921, 889, 738, 698. Anal Calcd. for $C_{13}H_{16}NCl$: C, 70.42; H, 7.27; N, 6.32; Cl, 15.99. Found: C, 70.40; H, 7.26; N, 6.38; Cl, 15.80.

***N*-Benzyl-*N*-(2-bromo-2-propenyl)-2-cyclohexenylamine (2a)**

Obtained according to Method D from *N*-Benzyl-2-cyclohexenylamine and 2,3-dibromopropene in 72% yield after flash chromatography on Hexane/EtOAc 99:1.

¹H-NMR (200 MHz): 1.35-2.03 (6H, m), 3.24 and 3.38 (2H, AB system, $J = 15.6$ Hz, NCH₂Ar), 3.32-3.44 (1H, m), 3.59 and 3.78 (2H, AB system, $J = 14.3$ Hz, NCH₂), 5.53 (1H, d, $J = 1$ Hz), 5.67 (1H, d, $J = 10.4$ Hz), 5.84 (1H, dm, $J = 10.4$ Hz), 5.99 (1H, bb), 7.20-7.45 (5H, m). **¹³C-RMN** (75.4 MHz) : 21.72 (CH₂), 23.7 (CH₂), 25.3 (CH₂), 53.90 (NCH₂Ar), 54.90 (NCH), 58.11 (NCH₂), 117.17 (=CH₂), 126.77 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 130.05 (=CH), 130.54 (=CH), 133.67 (=CBr), 140.03 (q). **IR** (neat): 3022, 2929, 1635, 1627, 1452, 1145, 1124, 738, 698. Anal. Calcd. for C₁₆H₂₀BrN: C, 62.75; H, 6.58; N, 4.57. Found: C, 62.73; H, 6.54; N, 4.62.

***N*-Benzyl-*N*-(2-bromo-2-cyclohexenyl)-2-propenylamine (3)**

Obtained from 2,3-dibromocyclohexene¹⁰ and *N*-allylbenzylamine according to method D in 96% yield after flash chromatography on Hexane/EtOAc 96:4.

¹H-RMN (200MHz): 1.50-2.20 (6H, m), 3.03 and 3.39 (2H, AB system, $J = 14$ Hz, NCH₂), 3.51 and 4.01 (2H, AB system, $J = 14$ Hz, NCH₂Ar), 3.52-3.64 (1H, m, CH), 5.14 (1H, d, $J = 10.2$ Hz), 5.29 (1H, d, $J = 17.2$ Hz), 5.84-6.06 (1H, m) 6.36 (1H, bb), 7.20-7.55 (5H, m). **¹³C-RMN** (50.3 MHz): 20.86 (CH₂), 24.19 (CH₂), 27.84 (CH₂), 52.53 (CH₂), 53.48 (CH₂), 58.99 (CH), 116.42 (=CH₂), 126.63 (ArCH), 127.5 (=CBr), 128.04 (ArCH), 128.59 (ArCH), 133.77 (=CH), 137.35 (=CH), 140.2 (q). **IR** (neat): 3060, 3024, 2933, 2833, 1639, 1492, 1452, 1153, 1126, 991, 918, 736, 698. Anal. Calcd. for C₁₆H₂₀NBr: C, 62.75; H, 6.58; N, 4.57. Found: C, 62.77; H, 6.59; N, 4.68.

***N*-Benzyl-*N*-(2-chloro-2-propenyl)(cyclohex-1-enyl)methylamine (4)**

1-cyclohexenylmetanol² (1.95 g, 17.4 mmol) is dissolved in dry dichloromethane (20 mL) under argon, cooled with an ice-water bath and successively treated with dry

¹⁰ Stevens, C.L.; Valicenti, J.A. *J. Am. Chem. Soc.* **1965**, *87*, 838-842. Sonnenberg, J.; Winstein, S. *J. Org. Chem.* **1962**, *27*, 748-751.

NEt₃ (3.8 mL, 28 mmol), DMAP (43 mg, 0.36 mmol) and methanesulfonylchloride (1.95 mL, 25 mmol). The mixture is allowed to warm at room temperature overnight. The reaction was poured into a cold aqueous solution saturated with NaHCO₃ the phases separated and the aqueous one extracted with CH₂Cl₂. Drying and evaporation afforded an oil which was dissolved in anhydrous acetone and treated with dry LiBr (3.04 g, 35 mmol) at room temperature for 24 hours. The volatiles were evaporated and the residue dissolved in MeCN (15 mL). To this solution was added *N*-Benzyl-2-chloroallylamine (2.18 g, 12 mmol) and solid K₂CO₃ (2.76 g, 20 mmol). The mixture was stirred at room temperature for 40 hours, filtered, and the filtrate evaporated to give an oil, which was purified by flash chromatography (hexane/AcOEt 20:1) to give 2.78 g (10.1 mmol, 84%) of the amine.

¹H NMR (200 MHz): 1.51-1.72 (4H, m), 2.0-2.14 (4H, m); 2.96 (2H, s), 3.18 (2H, s), 3.61 (2H, s), 5.36 (1H, s), 5.51 (1H, m), 5.67 (1H, m), 7.25-7.46 (5H, m). ¹³C NMR (50.3 MHz): 22.61(CH₂), 22.77 (CH₂), 25.23 (CH₂), 26.87 (CH₂), 57.52(CH₂), 59.62 (CH₂), 61.00 (CH₂), 113.55 (=CH₂), 124.93 (=CH), 126.75 (ArCH), 128.11 (ArCH), 128.57 (ArCH), 135.71 (q), 139.46 (q), 140.57 (q). IR(neat): 3060, 3026, 2923, 2833, 1633, 1494, 1452, 1367, 1251, 1170, 1116, 975, 887, 736, 696. Anal Calcd. for C₁₇H₂₂NCl: C, 74.03; H, 8.04; N, 5.08; Found: C, 74.13; H, 7.94; N, 5.17.

***N*-Benzyl-*N*-(2-bromo-2-propenyl)-2-cyclooctenylamine (5)**

Obtained from *N*-Benzyl-2-cyclooctenylamine and 2,3-dibromopropene in 90% yield after flash chromatography (hexane/AcOEt 99:1).

¹H-NMR (200 MHz): 0.80-2.10 (10H, m), 3.27 and 3.43 (2H, AB system, *J* = 15.6 Hz, NCH₂), 3.57 and 3.84 (2H, AB system, *J* = 14.1 Hz, NCH₂Ar), 3.66 (1H, bb), 5.56 (1H, s), 5.55-5.86 (2H, m), 5.99 (1H, bb), 7.20-7.50 (5H, m). ¹³C-RMN (50.3 MHz): 25.0 (CH₂), 26.3 (CH₂), 26.5 (CH₂), 29.3 (CH₂), 33.6 (CH₂), 54.8 (CH₂), 56.2 (C-1), 58.9 (CH₂), 117.4 (=CH₂), 126.8 (ArCH), 128.2 and 128.6 (ArCH),

129.4 (=CH), 131.1 (=CH), 133.5 (q), 140.0 (q). IR (neat) cm^{-1} : 3060, 2923, 1627, 1492, 1452, 1139, 1072, 892, 738, 698.

***N*-Benzyl-*N*-(2-propenyl)-2-bromoaniline¹¹ (6).**

Obtained from *N*-Benzyl-2-bromoaniline and allyl bromide (3eq) according to general method D at 80°C. The yield was 94% after flash chromatography (hexane/AcOEt 80:20).

¹HNMR (200 MHz): 3.64 (2H, d, $J= 6.2$ Hz), 4.25 (2H, s), 5.08-5.22 (2H, m), 5.83 (1H, ddd, $J=10.4, 6.4, 6.2$), 6.89 (1H, td, $J= 8.0, 1.6$ Hz), 7.10 (1H, dd, $J= 8.2, 1.6$ Hz), 7.1-7.4 m (6H, m), 7.58 (1H, dd, $J= 8.0, 1.4$ Hz). ¹³CNMR (50.3 MHz): 55.29 (CH₂), 56.35 (CH₂), 117.76 (=CH₂), 121.37 (q), 124.28 (ArCH), 124.54 (ArCH), 126.91 (ArCH), 127.51 (ArCH), 128.13 (ArCH), 128.49 (ArCH), 133.78 (ArCH), 134.54 (=CH), 138.22 (q), 148.94 (q). IR (neat): 3060, 2837, 2813, 1583, 1473, 12113, 1027, 758, 730. Anal. Calcd for C₁₆H₁₆BrN: C, 63.59; H, 5.34; Br, 26.44; N, 4.63. Found: C, 63.52; H, 5.36; Br, 26.47, N, 4.64.

***N*-Allyl-*N*-benzyl-3-bromo-3-butenylamine (7).** Obtained from *N*-allylbenzylamine and 2,4-dibromo-1-butene according to method D at 70°C for 24 h. Flash chromatography on hexanes/EtOAc 95:5. ¹HNMR (200 MHz): 2.60 (2H, m), 2.73 (2H, m), 3.10 (2H, d, $J=4.2$ Hz), 3.61 (2H, s), 5.18 (2H, m), 5.41 (1H, bs), 5.57 (1H, bs), 5.88 (1H, m), 7.30 (5H, m). ¹³CNMR (50.3 MHz): 39.2 (CH₂), 51.6 (CH₂), 56.7 (CH₂), 58.0 (CH₂), 117.3 (=CH₂), 117.4 (=CH₂), 126.8 (ArCH), 128.1 (ArCH), 128.8 (ArCH), 132.5 (q), 135.6 (=CH), 139.2 (q). IR (neat): 3250, 2890, 1625 cm^{-1} . Anal.

¹¹ Tidwell, J.H.; Senn, D.R.; Buchwald, S.L. *J. Am. Chem. Soc.* **1991**, *113*, 4685-4686

Calcd for C₁₄H₁₈BrN: C, 60.01; H, 6.47; Br, 28.51; N, 4.99. Found: C, 60.22; H, 6.35; N, 4.72.

***N*-Benzyl-*N*-(3-bromo-3-butenyl)-2-cyclohexenylamine (8)**

Prepared from *N*-benzyl-2-cyclohexenylamine and 2,4-dibromo-1-butene according to method D in 80% yield.

¹HNMR (300 MHz): 1.42-1.55 (2H, m), 1.78-1.90 (2H, m), 1.94-2.03 (2H, m), 2.50 (2H, dd, *J* = 7.4, 6.6 Hz), 2.64-2.83 (2H, m), 3.34 (1H, bs), 3.54-3.80 (2H, AB_{sys}, δ_A=3.58, δ_B= 3.75, *J*_{AB} = 14.3 Hz); 5.38 (1H,bs), 5.51 (1H, bs), 5.67 (1H, bd, *J* = 10.3 Hz), 5.78-5.84 (1H, m), 7.20-7.40 (5H, m). ¹³CNMR (75.4 MHz): 21.79 (CH₂), 23.88 (CH₂), 25.24 (CH₂), 41.42 (CH₂), 48.92 (CH₂), 54.75 (CH₂), 56.55 (CH), 117.26 (=CH₂), 126.54 (CH), 128.01 (CH), 128.29 (CH), 129.93 (CH), 130.54(CH), 132.68 (q), 140.84 (q). IR (CCl₄): 3083, 3064, 3024, 2933, 2836, 1629, 1494, 1451, 1160, 1027, 887, 698. Anal Calcd. for C₁₇H₂₂NBr: C, 63.75; H, 6.92; N, 4.37. Found: C, 63.76; H, 6.92; N, 4.32.

***N*-Allyl-*N*-benzyl-2-bromobenzylamine (9)**

Prepared from *N*-allylbenzylamine and 2-bromobenzylbromide according to method D in 96% yield after flash chromatography on Hexane/EtOAc 99:1

¹HNMR (200 MHz): 3.11 (2H, d, *J* = 6.6 Hz), 3.63 (2H, s), 3.69 (2H, s), 5.11-5.30 (2H, m), 5.82-6.05 (1H, m), 7.05-7.75 (9H, m). ¹³CNMR (50.3 MHz): 56.56 (CH₂), 57.17 (CH₂), 57.94 (CH₂), 117.48 (=CH₂), 124.22 (q), 126.84 (ArCH), 127.23 (ArCH), 128.11 (ArCH), 128.20 (ArCH), 128.65 (ArCH), 130.35 (ArCH), 132.54 (ArCH), 135.71 (=CH), 138.89 (q), 139.44 (q). IR (neat): 3062, 3028, 2918, 2798, 1643, 1566, 1494, 1438, 1374, 1124, 1026, 919, 750, 698. Anal Calcd. for C₁₇H₁₈NBr: C, 64.57; H, 5.74; N, 4.43; Br, 25.27 Found: C, 64.48; H, 5.63; N, 4.43; Br, 25.50.

***N*-Benzyl-*N*-(2-bromo-2-propenyl)-3-butenylamine (10)**

Prepared from *N*-Benzyl-3-butenylamine and 2,3-dibromopropene according to method E. The product was obtained in 61% yield after flash chromatography (Hexane/EtOAc 99:1).

¹H NMR (200 MHz): 2.22 (2H, t), 2.56 (2H, t), 3.25 (2H, bs), 3.65 (2H, s, CH₂-Ar), 4.95 (2H, m), 5.55 (1H, bs), 5.75 (1H, ddd, *J* 17.1, 10.0, and 6.8), 5.91 (1H, bs), 7.30 (5H, m). ¹³C NMR (50.3 MHz): 31.6 (CH₂), 52.7 (CH₂), 57.7 (CH₂), 62.0 (CH₂), 115.6 (=CH₂), 118.0 (=CH₂), 127.0 (ArCH), 128.2 (ArCH), 128.6 (ArCH), 132.2 (=CH), 136.6 (q), 139.0 (q). IR (film): 3082, 3060, 3020, 1637, 1494, 1452. Anal. Calcd. for C₁₄H₁₈BrN: C, 60.01; H, 6.47; N, 5.00; Br, 28.52. Found: C, 60.20; H, 6.44; N, 5.02; Br, 28.49.

***N*-Benzyl-*N*-(2-cyclohexenyl)methyl-2-bromo-2-propenylamine (11)**

Obtained from *N*-Benzyl-(2-cyclohexenyl)methylamine and 2,3-dibromopropene in 84% yield after flash chromatography (Hexane/AcOEt 95:5).

¹H-NMR (200 MHz): 1.20-2.10 (6H, m), 2.38 (3H, bb), 3.23 and 3.34 (2H, AB system, *J* = 15.1 Hz, NCH₂), 3.58 and 3.73 (2H, AB system, *J* = 13.8 Hz, NCH₂Ar), 5.60 (1H, s), 5.71 (2H, bb), 5.93 (1H, d, *J* = 0.8 Hz), 7.20-7.50 (5H, m). ¹³C-RMN (50.3 MHz): 21.1 (CH₂), 25.5 (CH₂), 27.3 (CH₂), 33.5 (CH), 58.3 (CH₂); 59.1 (CH₂), 62.6 (CH₂), 118.3 (=CH₂), 126.9 (ArCH), 127.8 (ArCH), 128.1 (ArCH), 128.8 (=CH), 130.0 (=CH), 132.4 (q), 139.2 (q). IR (neat) cm⁻¹: 3060, 3024, 2927, 2796, 1629, 1494, 1450, 1369, 1251, 1124, 892, 738, 698. Anal. Calcd. for C₁₇H₂₂BrN: C, 63.75; H, 6.92; N, 4.37. Found: C, 63.64; H, 7.04; N, 4.44.

***N*-Benzyl-*N*-(2-bromo-2-propenyl)-2-(1-cyclohexenyl)ethylamine (12)**

Prepared from *N*-Benzyl-2-(1-cyclohexenyl)ethylamine and 2,3-dibromopropene according to method E at room temperature for 72 h in 93 % yield after flash chromatography on Hexane/EtOAc 90:10.

¹H NMR (300 MHz): 1.48-1.64 (4H, m), 1.86 (2H, bs), 1.95 (2H, bs), 2.12 (2H, bt, *J* = 7.2 Hz), 2.57 (2H, dd, *J* = 6.8, 7.2 Hz), 3.28 (2H, s), 3.65 (2H, s); 5.39 (1H, bs), 5.57

(1H, s), 5.87 (1H, s), 7.2-7.40 (5H, m). ¹³CNMR (75.4 MHz): 22.41 (CH₂), 22.94 (CH₂), 25.26 (CH₂), 28.37 (CH₂), 35.43 (CH₂), 51.88 (CH₂), 57.69 (CH₂), 61.98 (CH₂), 117.82 (=CH₂), 122.19 (=CH), 126.87 (ArCH), 128.15 (ArCH), 128.68 (ArCH), 132.37(q), 135.81 (q), 139.30 (q). IR (neat): 3083, 3060, 3026, 2923, 1627, 1494, 1452, 1116, 892, 736, 698. Anal Calcd. for C₁₈H₂₄NBr: C, 64.67; H, 7.24; N, 4.19, Br, 23.90. Found: C, 64.70; H, 7.31; N, 4.25, Br, 23.96.

Synthesis of amides

N-(2-bromo-2-propenyl)-*N*-2-cyclohexenylacetamide (2d)

Acetic anhydride (1 ml, 10.95 mmol) was dropwise added to a mixture of amine 5 (1.57 g, 7.3 mmol) and Et₃N (3 ml, 21.9 mmol) cooled at 0 °C. The resulting mixture was stirred at 0 °C for 1 hour and at room temperature for 2 hours. After pouring into ice-water (10 ml) and stirring for 30', the mixture was basified with solid sodium carbonate and extracted with methylene chloride. The organic layer was washed with water, dried and evaporated. Flash chromatography of the residue (Hexane/AcOEt 15%) afforded amide 7 (1.73g, 92%).

¹H-NMR (200 MHz): 1.30-2.00 (6H, m), 2.06 (2H, s, CH₃ rotamer), 2.16 (1H, s, CH₃ rotamer), 3.80-4.20 (2H, m, NCH₂), 4.40 (0.33H, bb, 1-H rotamer), 5.20 (0.66H, m, 1-H rotamer), 5.30-6.00 (4H, m). ¹³C-RMN (CDCl₃): 21.1 and 21.3 (C-5), 21.8 (CH₃), 24.3 and 24.5 (C-4), 27.6 and 28.7 (C-6), 50.1 and 52.4 (NCH₂), 51.0 and 55.8 (C-1), 115.4 and 116.2 (=CH₂), 127.0 (C-3), 129.5 and 130.1 (=CBr), 132.4 and 132.6 (C-2), 170.4 and 171.4 (NCO). IR (neat): 3050, 3020, 1654, 1649, 1420. Anal. Calcd. for C₁₁H₁₆BrNO: C, 51.18; H, 6.25; N, 5.43. Found: C, 51.24; H, 6.25; N, 5.47.

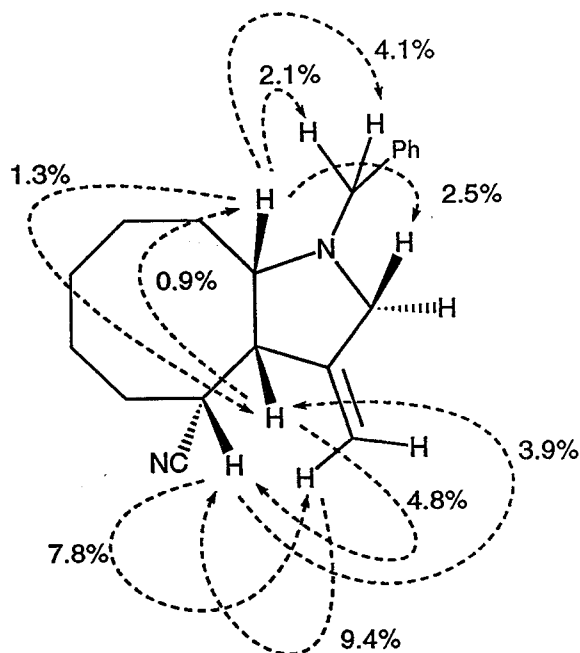
***N*-Allyl-*N*-2-bromo-2-propenylacetamide 1d**

In an analogous procedure, the reaction of *N*-allyl-2-bromoallylamine, acetic anhydride and NEt₃ afforded the amide in 63% yield after flash chromatography (hexane/ AcOEt 80:20).

¹H-NMR (300 MHz): 2.09 (3H, bs), 3.84-3.91 (2H, m), 3.99-3.91 (1H, m), 4.02 (1H, bs), 4.20 (1H, bs), 5.02-5.24 (2H, m), 5.56 (1H, m), 5.61-5.80 (2H, m). ¹³C-RMN (75MHz): 21.2 and 21.3 (CH₃), 47.3 and 50.0 (CH₂), 52.1 and 55.0 (CH₂), 117.0 and 117.5 (=CH₂), 117.8 and 118.1 (CH₂), 128.1 and 128.6 (=CBr), 132.1 and 132.6 (=CH), 170.4 and 171.4 (N-CO). IR (neat): 2981, 1654, 1649, 1429.

Structure Determination on compound 19

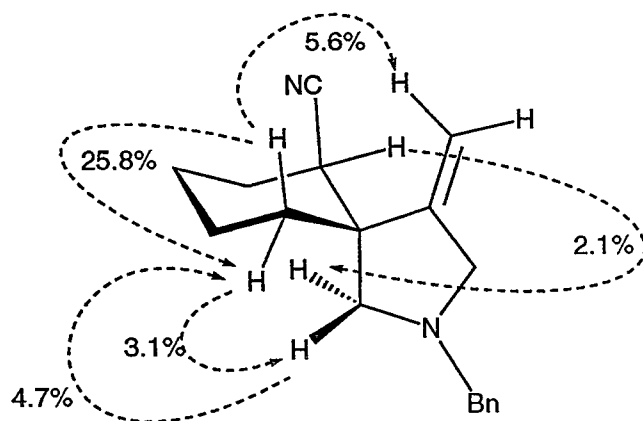
Selected NOE enhancements



Full assignment for ^1H and ^{13}C peaks was obtained by COSY and HETCOR experiments.

Structure determination on spirocompound 18

Selected NOE enhancements

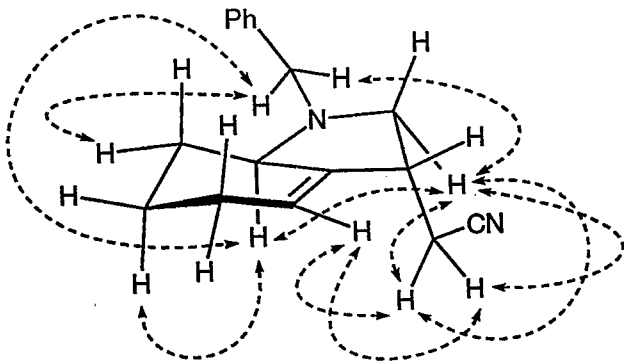


Full assignment for ^1H and ^{13}C NMR peaks was obtained by COSY and HETCOR experiments.

MMX calculations on **18** showed that the depicted conformation with an axial cyano group was slightly energetically favoured (0.22 Kcal/ mol) over the conformation with an equatorial cyano.

STRUCTURE DETERMINATION FOR 17c

ROESY correlations



Full assignment for ^1H and ^{13}C peaks was obtained by COSY and HETCOR experiments.