Supporting Information

Catalytic *N*-Sulfonyliminium Ion-Mediated Cyclizations to α -Vinyl-Substituted Isoquinolines and β -Carbolines and Applications in Metathesis

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General information. Unless otherwise noted, materials were purchased from commercial suppliers and used without purification. Toluene, dichloromethane and acetonitrile were freshly distilled from calcium hydride. Tetrahydrofuran and diethylether were freshly distilled from sodium with benzophenone as indicator. Triethylamine was stored over potassium hydroxide pellets and used as such. All air and moisture sensitive reactions were carried out under an inert atmosphere of dry nitrogen. Column chromatography was performed using silica gel (70-230 mesh, 60Å). R_f values were obtained by using thin layer chromatography (TLC) on silica gel-coated plastic sheets (silica gel 60 F₂₅₄) with the indicated solvents. Infrared spectra were recorded on a FTIR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ and obtained on a 400 or 500 MHz machine. Spectra are reported in units of ppm on the δ scale, relative to chloroform (7.26 ppm for ¹H-NMR and 77.0 ppm for ¹³C-NMR). Mass spectra were measured using a four-sector mass spectrometer. Melting points are uncorrected. 4-Pentenoyl chloride, phenethyl amine, (*R*)-(+)- β -methylphenethylamine, 3-chlorophenethylamine, 3-methoxyphenethylamine, 4-methoxyphenethylamine, 3,4-dimethoxyphenethylamine, L-dopa, tryptamine, L-tryptophan, veratrylamine and 5-chloroindole-3-carboxaldehyde are commercially available and were used without purification. 4-Pentenoyl chloride, phenethyl amine, (*R*)-(+)- β -methylphenethylamine, 3-chlorophenethylamine, 3-methoxyphenethylamine, 4-methoxyphenethylamine, 3,4-dimethoxyphenethylamine, L-dopa, tryptamine, L-tryptophan, veratrylamine and 5-chloroindole-3-carboxaldehyde are commercially available and were used without purification. Benzyl propadienyl ether was prepared following the procedure described by Brandsma et al.¹ (*S*)- α -carboxylic acid-3,4-dimethoxyphenethylamine methyl ester was synthesized using a literature procedure.² 3-Butenoyl chloride (vinylacetic acid chloride) was always freshly prepared before use.³ The ionic liquids [TMAH][Al₂Cl₇] and [BMIm][N(Tf)₂] were a kind gift of N.V. Organon (Oss, The Netherlands).

General procedure for the preparation of the non-commercial arylethylamines. A solution of the corresponding arylaldehyde (~0.2 M) in nitromethane or nitroethane and ammonium acetate (0.85 equiv) was refluxed for 2 h, concentrated and in most cases crystallized from diethyl ether/pentane. The purified solid or the crude oil was diluted with some THF and slowly added to an ice-cold solution of LiAlH₄ (4 equiv, ~0.5 M) in THF. After the addition, the solution was refluxed for 3 h and allowed to cool to room temperature. H₂O (1.3 g/g LiAlH₄) was slowly added under vigorous stirring, followed by 15% aqueous NaOH (1.3 g/g LiAlH₄), followed again by H₂O (3.25 g/g LiAlH₄). After stirring vigorously for 10 minutes the white precipitate was collected on a filter. The white solid was washed with diethyl ether (3 $\times$) and the combined filtrates dried and concentrated to yield the amine. The amines were immediately used in the following step.

3-Methylphenethylamine. *m*-Tolualdehyde (2.0 mL, 16.96 mmol) was condensed with nitromethane followed by LiAlH₄ reduction according to the general procedure. Yield over 2 steps 2.2 g (16.3 mmol, 96%).

***rac*- α -Methyl-3-methoxyphenethylamine.** 3-Methoxybenzaldehyde (5.0 mL, 41.1 mmol) was condensed with nitroethane followed by LiAlH₄ reduction according to the general procedure. Yield over 2 steps 5.0 g (30.4 mmol, 74%).

***rac*- α -Methyl-3,4-dimethoxyphenethylamine.** 3,4-Dimethoxybenzaldehyde (8.3 g, 50.0 mmol) was condensed with nitroethane, followed by LiAlH₄ reduction according to the general procedure. Yield over 2 steps 9.4 g (48 mmol, 96%).

2-Furan-2-yl-ethylamine. Furfural (0.95 mL, 11.14 mmol) was condensed with nitromethane and reduced by LiAlH₄ according to the general procedure. The crude amine was immediately protected as a sulfonamide.

***rac*- α -Methylphenethylamine.** Benzaldehyde (2.0 mL, 19.7 mmol) was condensed with nitroethane followed by LiAlH₄ reduction according to the general procedure. Yield over 2 steps 1.86 g (13.7 mmol, 70%).

1 L. Brandsma, H. D. Verkruijsse, *Synthesis of acetylenes, allenes and cumulenes, a laboratory manual in Studies in Organic Chemistry* vol. 8, Elsevier, Amsterdam, **1981**, p. 94.

2 Schrecker, A. W.; Hartwell, J. L. *J. Am. Chem. Soc.* **1957**, 79, 3827.

3 Marson, C. M.; Grabowska, U.; Fallah, A. *J. Org. Chem.* **1994**, 59, 291.

General procedure for the preparation of the sulfonamides. To a stirred solution of the amine (~0.5 M) in dichloromethane at 0 °C was added the arylsulfonyl chloride (1.05 equiv), followed by Et₃N (3 equiv). After stirring for 6 hours at room temperature, H₂O was added and the product extracted into ether. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated. The crude sulfonamide was purified by trituration with diethyl ether or by flash column chromatography.

N-Tosyl-3-methoxyphenethylamine (12). 3-Methoxyphenethylamine (3.6 g, 34.3 mmol) was treated with tosyl chloride analogous to the general procedure. No purification was necessary. Yield 94% (32.4 mmol). *R_f* 0.44 (pentane/ethyl acetate 1:1). Mp. 51.5-57.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.29-7.16 (m, 3H), 6.77-6.60 (m, 3H), 4.39 (br s, NH), 3.77 (s, 3H), 3.21 (t, *J* = 6.7 Hz, 2H), 2.73 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 159.8, 143.4, 139.2, 136.9, 129.7, 129.6, 127.1, 121.0, 114.4, 112.1, 55.1, 44.1, 35.7, 21.5. HRMS (FAB) calculated for C₁₆H₁₉O₃NS (MH⁺): 306.1164, found 306.1163.

N-Tosylphenethylamine (13). Phenethylamine (4.40 mL, 35.0 mmol) was treated with tosyl chloride according to the general procedure. No purification was necessary. Yield 91% (31.6 mmol). *R_f* 0.44 (pentane/ethyl acetate 2:1). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.30-7.22 (m, 5H), 7.09-7.07 (m, 2H), 4.45 (br s, NH), 3.21 (t, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 143.4, 137.7, 129.7, 128.8, 128.7, 127.1, 126.8, 44.2, 35.8, 21.5.

N-4-Nitrobenzenesulfonyl-3-methylphenethylamine (14). Crude 3-Methylphenethylamine (0.66 g, 4.9 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. Column chromatography (pentane/diethyl ether 1:1) afforded a solid, which was trituated with pentane/diethyl ether to afford the pure sulfonamide. Yield 0.913 g (1.85 mmol, 58%). *R_f* 0.25 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1216, 1473, 3020, 3155 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.30 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 4.51 (br s, NH), 3.30 (q, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 145.9, 138.6, 137.0, 129.5, 128.8, 128.2, 127.8, 125.6, 124.3, 44.3, 35.7, 21.3; HRMS (FAB) calculated for C₁₅H₁₇O₄N₂S (MH⁺): 321.0909, found 321.0903.

N-4-Nitrobenzenesulfonyl-3-chlorophenethylamine (15). 3-chlorophenethylamine (2 mL, 14.38 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. Trituration of the crude product with diethyl ether afforded the product as an off-white solid. Yield 3.89 g (11.41 mmol, 79%). Mp. 96.5-97.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 5.2 Hz, 2H), 7.02 (s, 1H), 6.99-6.97 (m, 2H), 4.56 (t, *J* = 6.0 Hz, NH), 3.32 (q, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.7 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 149.8, 145.5, 139.1, 134.4, 129.9, 128.6, 128.0, 127.0, 126.8, 124.2, 43.9, 35.4; HRMS (FAB) calculated for C₁₄H₁₄O₄N₂SCl (MH⁺): 341.0363, found 341.0365.

N-4-Nitrobenzenesulfonyl-4-methoxyphenethylamine (16). 4-methoxyphenethylamine (2 mL, 13.66 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. Trituration of the crude product with diethyl ether afforded the product as an off-white solid. Yield 4.00 g (11.89 mmol, 87%). Mp. 105.9-106.8 °C; IR (CHCl₃) ν 1166, 1249, 1349, 1533, 2937 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.55 (t, *J* = 5.8 Hz, NH), 3.77 (s, 3H), 3.26 (q, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 6.7 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 158.4, 149.7, 145.6, 129.5, 128.8, 128.0, 124.1, 114.0, 55.1, 44.4, 34.7; HRMS (FAB) calculated for C₁₅H₁₇N₂O₅S (MH⁺): 337.0858, found 337.0855.

rac-N-4-Nitrobenzenesulfonyl-α-methyl-3-methoxyphenethylamine (17). Crude *rac*-α-methyl-3-methoxyphenethylamine (2.0 g, 12.1 mmol) was reacted with 4-nitrobenzenesulfonyl chloride analogous to the general procedure. Column chromatography (pentane/diethyl ether 1:1-1:2) afforded the sulfonamide as a yellow solid. Yield 2.98 g (8.5 mmol, 70%). *R_f* 0.14 (pentane/diethyl ether 1:1);

Mp: 75.4-80.2 °C; IR (CHCl₃) ν 1165, 1350, 1530, 3294 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 9.3 Hz, 1H), 6.59 (d, *J* = 7.3 Hz, 1H), 6.40 (s, 1H), 4.93 (br s, NH), 3.69 (s, 3H), 3.56-3.52 (m, 1H), 2.75 (dd, *J* = 4.9, 13.9 Hz, 1H), 2.54 (dd, *J* = 9.0, 13.9 Hz, 1H), 1.31 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 159.6, 149.5, 145.9, 138.5, 129.5, 127.8, 123.9, 121.5, 114.8, 111.7, 54.9, 52.0, 43.2, 22.8.

***N*-4-Nitrobenzenesulfonyl-3,4-dimethoxyphenethylamine (18a).** 3,4-Dimethoxyphenethylamine (2.0 mL, 11.85 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. No additional purification necessary. Yield 4.158 g (11.35 mmol, 96%). IR (CHCl₃) ν 1166, 1262, 1349, 1517, 1534, 2938 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.58 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 6.7 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 149.9, 149.2, 148.1, 145.8, 129.5, 128.2, 124.3, 120.7, 111.8, 111.4, 55.9, 55.8, 44.5, 35.4; HRMS (FAB) calculated for C₁₆H₁₉N₂O₆S (MH⁺): 367.0964, found 367.0954.

***N*-2,4-Dinitrobenzenesulfonyl-3,4-dimethoxyphenethylamine (18b).** 3,4-Dimethoxyphenethylamine (2.0 mL, 11.85 mmol) was treated with 2,4-dinitrobenzenesulfonyl chloride according to the general procedure. Trituration of the crude product with ethyl acetate/diethyl ether afforded the product as a yellow solid. Yield 2.69 g (6.54 mmol, 55%). IR (CHCl₃) ν 1169, 1262, 1348, 1517, 1542, 2938 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.58 (s, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 6.63-6.60 (m, 2H), 6.53 (s, 1H), 5.38 (br s, NH), 3.78 (s, 3H), 3.77 (s, 3H), 3.53-3.50 (m, 2H), 2.77 (t, *J* = 6.6 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 148.8, 148.1, 139.4, 131.9, 129.6, 126.9, 120.9, 120.6, 111.9, 111.2, 55.8, 45.8, 35.7. HRMS (FAB) calculated for C₁₆H₁₈N₂O₈S (MH⁺): 412.0815, found 412.0821.

***rac*-*N*-4-Nitrobenzenesulfonyl- α -methyl-3,4-dimethoxyphenethylamine (19).** Crude *rac*- α -Methyl-3,4-dimethoxyphenethylamine (9.38 g, 48 mmol) was reacted with 4-nitrobenzenesulfonyl chloride analogous to the general procedure. Crystallization from dichloromethane/ethyl acetate/diethyl ether afforded the product as a yellow solid. Yield 9.9 g (27 mmol, 55%). Mp: 74.0-81.1 °C; IR (CHCl₃) ν 1163, 1351, 1532, 3059 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.43 (s, 1H), 4.86 (d, *J* = 7.3 Hz, NH), 3.81 (s, 3H), 3.74 (s, 3H), 3.53-3.50 (m, 1H), 2.71 (dd, *J* = 5.2, 13.9 Hz, 1H), 2.49 (dd, *J* = 8.6, 13.9 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃) δ 149.5, 148.7, 148.0, 146.2, 129.3, 127.8, 123.8, 121.1, 112.1, 110.9, 55.7, 52.2, 42.9, 22.5.

(*S*)-*N*-4-Nitrobenzenesulfonyl- α -carboxylic acid-3,4-dimethoxyphenethylamine methyl ester (20). (*S*)- α -carboxylic acid-3,4-dimethoxyphenethylamine methyl ester (5.89 g, 21.4 mmol) was protected with 4-nitrobenzenesulfonyl chloride according to the general procedure. Crystallization from EtOAc/diethyl ether afforded the product as a yellowish solid. Yield 6.25 g (14.7 mmol, 69%). Mp: 194.0-194.9 °C; [α]_D -14.9 (*c* 1, CHCl₃); IR (CHCl₃) ν 1168, 1351, 1535, 1746, 2953, 3361 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 6.55 (s, 1H), 5.26 (d, *J* = 9.2 Hz, NH), 4.28-4.22 (m, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.62 (s, 3H), 3.07 (dd, *J* = 4.9, 14.0 Hz, 1H), 2.93 (dd, *J* = 7.1, 14 Hz, 1H), ¹³C NMR (500 MHz, CDCl₃) δ 171.1, 149.9, 148.9, 148.5, 145.6, 128.1, 127.0, 124.0, 121.4, 112.3, 111.1, 57.1, 55.8, 52.7, 38.9; HRMS (FAB) calculated for C₁₈H₂₁O₈N₂S (MH⁺): 425.1019, found 425.0998.

***N*-(2-Furan-2-yl-ethyl)-*N*-4-nitrobenzenesulfonamide (21).** The crude amine 2-furan-2-ylethylamine was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. The product was obtained by trituration of the crude solid with pentane/diethyl ether. Yield 1.78 g (6.00 mmol, 54% over 3 steps). IR (CHCl₃) ν 1166, 1350, 1534, 3384 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 3.7 Hz, 1H), 6.26 (d, *J* = 1.7 Hz, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 4.82 (br s, NH), 3.32 (q, *J* = 6.3 Hz, 2H), 2.83 (t, *J* = 6.4 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 179.0, 151.3, 145.9, 142.0, 128.2, 124.4, 110.4, 107.3, 41.8, 28.3; HRMS (FAB) calculated for C₁₂H₁₃N₂O₅S (MH⁺): 297.0545, found 297.0541.

***N*-Tosyltryptamine (22).**⁴ Tryptamine (8.0 g, 50.0 mmol) was treated with tosyl chloride according to the general procedure. The light brown solid product needed no further purification. Yield 98% (48.8 mmol). R_f 0.8 (pentane/ethyl acetate 1:2). ^1H NMR (400 MHz, CDCl_3) δ 8.02 (br s, NH), 7.65-6.99 (m, 9H), 4.33 (br s, NH), 3.28 (q, J = 6.6 Hz, 2H), 2.94 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 143.3, 136.7, 136.4, 129.6, 127.0, 126.8, 122.6, 122.2, 119.5, 118.4, 111.3, 43.0, 25.5,

***(S)*-N-Tosyltryptophan methyl ester (23).**⁴ (*S*)-Tryptophan methyl ester.HCl (6.38 g, 25.0 mmol) was treated with tosyl chloride according to the general procedure. The crude product was purified by crystallization from ethyl acetate/pentane. Yield 86% (21.5 mmol). R_f 0.46 (pentane/ethyl acetate 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (br s, NH), 7.62-7.04 (m, 9H), 5.07 (br s, NH), 4.24 (t, J = 5.6 Hz, 1H), 3.43 (s, 3H), 3.23 (d, J = 5.5 Hz, 2H), 2.38 (s, 3H).

General procedure for the preparation of the *N,O*-acetals. To a solution of the sulfonamide (~0.2 M) in acetonitrile was added Et_3N (1.5 equiv), $\text{Pd}(\text{OAc})_2$ (5 mol%), dppp (5 mol%) and benzyl propadienyl ether (1.1 equiv). After stirring for 6 h at room temperature the solution was concentrated and purified by column chromatography with silica gel with some Et_3N in the eluent.

⁴ Shono, T.; Matsumura, Y.; Tsubata, K.; Uchida, K. Kanazawa, T.; Tsuda, K. *J. Org. Chem.* **1984**, *49*, 3711.

***N*-(1-Benzyloxyallyl)-*N*-tosyl-3-methoxyphenethylamine (24).** Amide **12** (1.00 g, 3.27 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 8:1-2:1) afforded the product as a solidifying oil. Yield 1.35 g (2.98 mmol, 91%). Mp. 68.9-75.4 °C. R_f 0.42 (pentane/diethyl ether 1:1). IR (CH_2Cl_2) ν 1160, 1339, 1599, 2838, 2941, 3033 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.37-7.17 (m, 8H), 6.76-6.70 (m, 3H), 5.71 (d, $J = 1.7$ Hz, 1H), 5.53-5.46 (m, 2H), 5.27 (dd, $J = 1.2, 8.8$ Hz, 1H), 4.74 (d, $J = 11.9$ Hz, 1H), 4.58 (d, $J = 11.9$ Hz, 1H), 3.77 (s, 3H), 3.42-3.38 (m, 1H), 3.29-3.23 (m, 1H), 2.96 (t, $J = 8.5$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 159.7, 143.4, 140.6, 137.7, 137.5, 133.8, 129.7, 129.5, 128.3, 127.7, 127.0, 121.1, 119.1, 114.5, 111.7, 86.3, 69.4, 55.1, 45.2, 37.4, 21.5; HRMS (FAB) calculated for $\text{C}_{26}\text{H}_{29}\text{NO}_3\text{S}$ (MH^+): 452.1896, found 452.1919.

***N*-(1-Benzyloxyallyl)-*N*-tosylphenethylamine (25).** Amide **13** (1.10 g, 4.0 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 8:1-1:1) afforded the acetal. Yield 89% (3.56 mmol). R_f 0.59 (pentane/ethyl acetate 2:1). IR (CH_2Cl_2) ν 1162, 1340, 3031 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 8.3 Hz, 2H), 7.36-7.14 (m, 12H), 5.70 (d, J = 2.0 Hz, 1H), 5.52-5.45 (m, 2H), 5.28-5.25 (dd, J = 8.3, 2.2 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 3.39-3.35 (m, 1H), 3.28-3.21 (m, 1H), 2.98 (t, J = 8.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (400 MHz, CDCl_3) δ 143.3, 139.0, 137.4, 133.7, 130.0, 128.7, 128.4, 128.2, 127.5, 127.0, 126.3, 118.9, 86.3, 69.3, 45.3, 37.3, 21.4. HRMS (FAB) calculated for $\text{C}_{25}\text{H}_{28}\text{NO}_3\text{S}$ (MH^+): 422.1790, found 422.1793.

***N*-(1-Benzyloxyallyl)-*N*-4-nitrobenzenesulfonyl-3-methylphenethylamine (26).** Amide **14** (0.502 g, 1.56 mmol) was reacted with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 4:1) afforded the product as a colorless oil. Yield 0.36 g (0.772 mmol, 98%). R_f 0.41 (pentane/diethyl ether 2:1). IR (CHCl₃) ν 1168, 1350, 1534, 3150 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, J = 9.0 Hz, 2H), 8.0 (d, J = 9.0 Hz, 2H), 7.40-7.29 (m, 5H), 7.19 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.98 (br s, 2H), 5.72 (s, 1H), 5.61-5.51 (m, 2H), 5.38 (d, J = 10.0 Hz, 1H), 3.45-3.39 (m, 1H), 3.35-3.30 (m, 1H), 3.01-2.96 (m, 2H), 2.33 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 149.9, 146.3, 138.3, 136.9, 133.0, 129.6, 129.5, 128.3, 128.0, 127.6, 127.4, 127.3, 125.8, 125.6, 124.3, 124.2, 119.9, 86.5, 69.7, 45.8, 37.3, 21.3; HRMS (FAB) calculated for C₂₅H₂₇N₂O₅S (MH⁺): 467.1641, found 467.1645.

***N*-(1-Benzyloxyallyl)-*N*-4-nitrobenzenesulfonyl-3-chlorophenethyl amine (27).** Amide **15** (0.499 g, 1.47 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 4:1-2:1) afforded the product as a colorless oil. Yield 0.716 g (1.47 mmol, 100%). R_f 0.49 (pentane/diethyl ether 1:1). ^1H NMR (500 MHz, CDCl_3) δ 8.30 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.39-7.28 (m, 5H), 7.24-7.22 (m, 2H), 7.14 (s, 1H), 7.06-7.05 (m, 1H), 5.72 (s, 1H), 5.56-5.54 (m, 2H), 5.39-5.37 (m, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 11.7$ Hz, 1H), 3.48-3.40 (m, 1H), 3.34-3.29 (m, 1H), 3.02-2.99 (m, 2H); ^{13}C NMR (500 MHz, CDCl_3) δ 150.0, 146.1, 140.4, 136.8, 134.4, 132.9, 129.9, 128.9, 128.5, 128.3, 128.0, 127.7, 127.0, 126.9, 124.3, 120.1, 86.7, 69.7, 45.4, 37.0; HRMS (FAB) calculated for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5\text{SCl}$ (MH^+): 487.1094, found 487.1069; HRMS (FAB) calculated for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_5\text{SCl}$ (MNa^+): 509.0914, found 509.0954.

***N*-(1-Benzyloxyallyl)-*N*-(4-methoxyphenyl)benzenesulfonamide (28).** Amide **16** (0.503 g, 1.49 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 4:1-2:1) afforded the product as a colorless oil. Yield 0.693 g (1.44 mmol, 96%). R_f 0.44 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1168, 1351, 1536, 3050 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, J = 8.8 Hz, 2H), 8.00 (d, J = 8.8 Hz, 2H), 7.39-7.29 (m, 5H), 7.09 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.71 (s, 1H), 5.59-5.50 (m, 2H), 5.37 (d, J = 10.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 11.7 Hz, 1H), 3.80 (s, 3H), 3.41-3.38 (m, 1H), 3.32-3.27 (m, 1H), 2.98-2.93 (m, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 158.4, 149.9, 146.3, 137.0, 133.0, 130.4, 129.7, 128.5, 128.3, 128.0, 127.7, 124.3, 119.9, 114.0, 86.8, 69.7, 55.2, 45.9, 36.4; HRMS (FAB) calculated for C₂₅H₂₇N₂O₆S (MH⁺): 483.1590, found 483.1599.

***rac*-N-(1-Benzyloxyallyl)-N-4-nitrobenzenesulfonyl- α -methyl-3-methoxy phenethylamine (29).**

Amide **17** (1.02 g, 2.85 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 4:1-1:1) afforded the product as a colorless oil. Yield 0.92 g (1.85 mmol, 65%). R_f 0.53 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1165, 1350, 1534, 2981, 3155 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both diastereoisomers δ 8.31 (d, J = 9.0 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.41-7.27 (m, 5H), 7.19 (t, J = 7.9 Hz, 1H), 6.78-6.65 (m, 3H), 5.79-5.75 (m, 1/2H), 5.69-5.63 (m, 1/2H), 5.60-5.51 (m, 2H), 5.43 (d, J = 10.5 Hz, 1/2H), 5.32 (d, J = 10.5 Hz, 1/2H), 4.71-4.56 (m, 2H), 3.92-3.88 (m, 1/2H), 3.85-3.80 (m, 1/2H), 3.79 (s, 1 1/2H), 3.75 (s, 1 1/2H), 3.16-3.09 (m, 1H), 3.06-3.01 (m, 1/2H), 2.94-2.90 (m, 1/2H), 1.34 (d, J = 6.8 Hz, 1 1/2H), 1.19 (d, J = 6.8 Hz, 1 1/2H); ¹³C NMR (500 MHz, CDCl₃) δ 159.7, 149.7, 148.2, 148.0, 140.7, 140.2, 137.1, 136.9, 134.0, 133.7, 129.4, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.6, 124.2, 121.7, 121.5, 119.7, 119.6, 115.1, 115.0, 111.9, 111.8, 87.2, 69.8, 69.6, 55.4, 55.1, 44.4, 42.9, 20.0, 18.7; HRMS (FAB) calculated for C₂₆H₂₉N₂O₆S (MH⁺): 497.1746, found 497.1725.

***N*-(1-Benzyloxyallyl)-*N*-4-nitrobenzenesulfonyl-3,4-dimethoxy phenethyl amine (30a).** Amide **18a** (4.16 g, 11.4 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 2:1-0:1) afforded the *N,O*-acetal as a slightly yellow colored oil. Yield 5.46 g (10.7 mmol, 94%). R_f 0.24 (pentane/diethyl ether 1:1). The product was immediately subjected to cyclization.

***N*-(1-Benzyloxyallyl)-*N*-2,4-dinitrobenzenesulfonyl-3,4-dimethoxy phenethylamine (30b).**

Amide **18b** (2.69 g, 6.54 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 1:1-0:1) afforded the product. Yield 1.54 g (2.77 mmol, 42%). R_f 0.30 (pentane/diethyl ether 1:2). IR (CHCl₃) ν 1028, 1169, 1263, 1350, 1542, 1556, 2938 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 8.31 (d, J = 8.7 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 7.38-7.28 (m, 5H), 6.75 (d, J = 7.8 Hz, 1H), 6.69-6.66 (m, 2H), 5.87-5.79 (m, 1H), 5.74 (br s, 1H), 5.65 (d, J = 17.1 Hz, 1H), 5.45 (d, J = 10.4 Hz, 1H), 4.73-4.56 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.55-3.42 (m, 2H), 2.94 (t, J = 8.2 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 149.5, 149.0, 147.9, 140.8, 138.8, 136.8, 133.1, 132.4, 130.8, 128.6, 128.5, 128.0, 127.7, 127.0, 126.0, 120.7, 120.3, 119.6, 112.1, 111.3, 87.2, 70.0, 55.9, 46.3, 36.8; HRMS (FAB) calculated for C₂₆H₂₈N₃O₉S (MH⁺): 558.1546, found 558.1556.

***rac*-N-(1-Benzyloxyallyl)-N-4-nitrobenzenesulfonyl- α -methyl-3,4-dimethoxy phenethylamine (31).** Amide **19** (1.02 g, 2.63 mmol) was converted into the *N,O*-acetal following the general procedure. Column chromatography (pentane/diethyl ether 4:1-2:1) afforded the product as a yellow oil. Yield 0.81 g (1.54 mmol, 58%). R_f 0.37 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1163, 1350, 1466, 1516, 1608, 2938 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both diastereoisomers δ 8.27 (d, J = 9.0 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.05-8.02 (m, 2H), 7.37-7.26 (m, 5H), 6.78-6.72 (m, 2H), 6.67 (d, J = 6.1 Hz, 1H), 5.77-5.74 (m, 1/2H), 5.66-5.63 (m, 1/2H), 5.60-5.50 (m, 2H), 5.41 (d, J = 10.5 Hz, 1/2H), 5.31 (d, J = 10.5 Hz, 1/2H), 4.69-4.57 (m, 2H), 3.84-3.74 (dm, 1H), 3.84 (s, 3H), 3.82 and 3.74 (s, 3H), 3.13-3.11 (m, 1H), 3.09-2.97 (m, 1/2H), 2.91-2.90 (m, 1/2H), 1.34 (d, J = 6.8 Hz, 1 1/2H), 1.21 (d, J = 7.0 Hz, 1 1/2H); ¹³C NMR (500 MHz, CDCl₃) δ 149.4, 148.6, 147.9, 147.7, 147.5, 147.4, 137.0, 136.7, 133.9, 133.4, 131.5, 131.0, 128.2, 128.1, 127.7, 127.6, 127.4, 127.3, 127.2, 126.6, 124.0, 123.9, 121.0, 119.3, 119.1, 112.3, 112.2, 111.0, 110.9, 87.1, 86.9, 69.5, 65.5, 64.8, 55.6, 55.5, 55.4, 43.8, 42.2, 19.6, 18.4; HRMS (FAB) calculated for C₂₇H₃₁N₂O₇S (MH⁺): 527.1852, found 527.1858.

(S)-N-(1-Benzyloxyallyl)-N-4-nitrobenzenesulfonyl- α -carboxylic

acid-3,4-

dimethoxyphenethylamine methyl ester (32). Amide **20** (1.99 g, 4.72 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 1:1-1:2) afforded the product as a stiff yellow oil. Yield 1.98 g (3.47 mmol, 74%). IR (CHCl₃) ν 1028, 1164, 1351, 1535, 1748, 2953 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both

diastereoisomers δ 8.26-8.22 (m, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.35-7.22 (m, 5H), 6.84-6.83 (m, 1H), 6.78-6.71 (m, 2H), 5.68-5.65 (m, $\frac{1}{2}$ H), 5.61-5.50 (m, $2\frac{1}{2}$ H), 5.36-5.30 (m, 1H), 4.69 (d, J = 11.7 Hz, 1H), 4.50-4.38 (m, 2H), 3.82 (s, $1\frac{1}{2}$ H), 3.80 (s, $1\frac{1}{2}$ H), 2.78 (s, $1\frac{1}{2}$ H), 3.72 (s, $1\frac{1}{2}$ H), 3.64 (s, $1\frac{1}{2}$ H), 3.55 (s, $1\frac{1}{2}$ H), 3.22-3.18 (m, 1H), 2.95-2.91 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 170.6, 170.1, 149.6, 149.5, 148.4, 148.3, 147.5, 146.5, 146.2, 136.7, 136.5, 133.2, 133.1, 130.4, 129.9, 128.8, 128.6, 128.2, 128.1, 127.7, 127.6, 127.4, 127.2, 126.5, 123.7, 123.6, 121.3, 119.6, 112.6, 110.8, 110.7, 86.5, 86.3, 69.8, 59.8, 59.1, 55.5, 55.4, 55.3, 52.0, 38.5, 37.1; HRMS (FAB) calculated for C₂₈H₃₁N₂O₉S (MH⁺): 571.1750, found 571.1755.

***N*-(1-Benzyloxyallyl)-*N*-(2-furan-2-yl-ethyl)-*N*-4-nitrobenzenesulfonamide (33).** Amide **21** (0.500 g, 1.69 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 4:1-1:1) afforded the acetal as an oil. Yield 0.637 g (1.44 mmol, 85%). R_f 0.43 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1169, 1351, 1534, 2931 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.8 Hz, 2H), 7.36-7.29 (m, 6H), 6.27 (m, 1H), 6.02 (d, J = 3.1 Hz, 1H), 5.71 (d, J = 3.6 Hz, 1H), 5.61-5.52 (m, 2H), 5.35 (d, J = 9.5 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 11.9 Hz, 1H), 3.59-3.51 (m, 1H), 3.44-3.38 (m, 1H), 3.06 (t, J = 8.0 Hz, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 152.0, 149.8, 145.8, 141.3, 136.8, 132.6, 128.3, 128.2, 127.8, 127.5, 124.1, 119.9, 110.1, 106.2, 86.7, 69.5, 42.5, 29.4; HRMS (FAB) calculated for C₂₂H₂₃N₂O₆S (MH⁺): 443.1277, found 443.1273.

***N*-(1-Benzyloxyallyl)-*N*-tosyltryptamine (34).** *N*-Tosyltryptamine **22** (1.26 g, 4.0 mmol) was converted into the *N,O*-acetal following the general procedure. Column chromatography (pentane/ethyl acetate 8:1-2:1) afforded the product as a slightly yellow oil. Yield 74% (2.97 mmol). R_f 0.54 (pentane/ethyl acetate 2:1). IR (CH_2Cl_2) ν 1162, 1339, 2360, 2930, 3064, 3469 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.96 (br s, NH), 7.74 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 1H), 7.39-7.10 (m, 7H), 6.99 (d, $J = 2.2$ Hz, 1H), 5.73 (d, $J = 1.7$ Hz, 1H), 5.78-5.67 (m, 1H), 5.47 (dd, $J = 2.9, 8.3$ Hz, 1H), 5.27 (dd, $J = 2.0, 8.1$ Hz, 1H), 4.78 (d, $J = 12.2$ Hz, 1H), 4.61 (d, $J = 12.2$ Hz, 1H), 3.75-3.70 (m, 1H), 3.58-3.52 (m, 1H), 3.45-3.38 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 143.2, 137.3, 136.0, 133.6, 129.6, 129.5, 128.2, 128.1, 127.5, 127.4, 127.0, 126.7, 121.9, 121.6, 119.0, 118.8, 118.5, 112.4, 111.1, 86.2, 69.1, 44.3, 27.0, 21.1; HRMS (FAB) calculated for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ (MH^+): 461.1899, found 461.1871.

INDEX	FREQUENCY	PPM	HEIGHT
1	18000.458	143.232	21.1
2	17267.559	137.381	17.5
3	17257.050	137.297	26.8
4	17099.158	136.041	20.5
5	16792.435	133.600	-29.5
6	16389.085	129.602	-4.4
7	16273.006	129.468	-62.9
8	16111.819	128.186	-4.9
9	16101.802	128.122	-95.7
10	16020.676	127.460	-101.7
11	16037.722	127.637	-48.2
12	15964.556	127.014	22.6
13	15924.048	126.692	-64.4
14	15757.822	121.948	-22.0
15	15283.095	121.592	-28.0
16	14954.912	118.980	-31.2
17	14937.934	118.846	21.4
18	14894.582	118.517	-26.2
19	14331.996	112.434	25.2
20	13947.433	111.129	-25.5
21	20806.934	86.219	-28.3
22	9709.886	77.252	8.8
23	9677.818	76.997	9.6
24	9645.749	76.742	9.2
25	8688.790	69.128	24.4
26	2575.488	44.313	25.2
27	5392.767	27.093	17.9
28	2654.342	21.118	-25.8

***N*-(1-Benzyloxyallyl)-*N*-tosyltryptophan methyl ester (35).** (*S*)-*N*-Tosyltryptophan methyl ester **23** (1.49 g, 4.0 mmol) was treated with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 8:1-1:1) afforded the product as a slightly yellow oil, solidifying upon standing. Yield 64% (2.57 mmol). R_f 0.40 (pentane/diethyl ether 1:1). IR (CH₂Cl₂) ν 1159, 1339, 1745, 2952, 3064, 3468 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both diastereoisomers δ 8.02 (br s, NH), 7.82 and 7.79 (d, J = 8.3 Hz, 2H), 7.64 and 7.58 (d, J = 8.1 Hz, 1H), 7.35-6.92 (m, 10H), 5.81-5.75 (m, 0.5H), 5.58-5.55 (m, 1.5H), 5.44 (dd, J = 2.0, 2.7 Hz, 1H), 5.25 (d, J = 10.7 Hz, 0.5H), 5.01 (t, J = 8.8 Hz, 0.5H), 4.57-4.43 (m, 0.5H), 3.91 and 3.82 (dd, J = 4.1, 10.3 Hz, 1H), 3.63 and 3.46 (s, 3H), 3.26 and 3.10 (dd, J = 4.9, 9.5 Hz, 1H), 2.44 and 2.42 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 171.0, 143.5, 142.7, 138.8, 138.1, 137.7, 137.3, 135.9, 134.3, 133.7, 129.5, 129.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 127.3, 124.1, 123.8, 121.8, 121.7, 119.3, 119.1, 119.0, 118.9, 112.3, 112.1, 111.0, 86.6, 86.3, 70.0, 69.9, 57.7, 57.6, 52.1, 51.8, 29.1, 27.4, 21.5, 21.4; HRMS (FAB) calculated for C₂₉H₃₁N₂O₅S (MH⁺): 519.1954, found 519.1947.

General procedure for cyclizations with catalytic Sn(OTf)₂. To an icecold solution of the *N,O*-acetal (~ 0.05 M) in dichloromethane was added Sn(OTf)₂ (2 mol%). The mixture was stirred for 1-2 h at 0 °C and quenched with a few drops of Et₃N. The solution was concentrated in vacuo and purified by column chromatography as indicated.

General procedure for cyclizations with trifluoroacetic acid. To an icecold solution of the *N,O*-acetal (~ 0.05 M) in dichloromethane was added TFA (3 equiv). The mixture was stirred for 1-2 h at 0 °C and quenched with Et₃N (5 equiv). The solution was concentrated in vacuo and purified by column chromatography as indicated.

6-Methoxy-2-tosyl-1-vinyl-1,2,3,4-tetrahydroisoquinoline (36). According to the general procedure, precursor **24** (50 mg, 0.11 mmol) was cyclized using Sn(OTf)₂. Column chromatography (pentane/ethyl acetate 8:1-2:1) afforded the product as a slightly yellow oil. Yield 87% (0.097 mmol). *R_f* 0.51 (toluene/diethyl ether 3:1). IR (CHCl₃) ν 1160, 1341, 1612, 1713, 2932, 3062 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.73-6.71 (m, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 5.92-5.84 (m, 1H), 5.48 (d, *J* = 5.5 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 5.00 (d, *J* = 17.0 Hz, 1H), 3.83-3.79 (m, 1H), 3.74 (s, 3H), 3.35-3.28 (m, 1H), 2.73-2.69 (m, 1H), 2.60-2.56 (m, 1H), 2.36 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 158.3, 142.9, 137.7, 137.6, 134.7, 129.3, 128.8, 127.1, 125.8, 117.2, 113.3, 112.4, 57.6, 55.1, 39.1, 27.9, 21.3; HRMS (FAB) calculated for C₁₉H₂₂NO₃S (MH⁺): 344.1320, found 344.1324.

6-Methoxy-3-methyl-2-(4-nitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydro isoquinoline (38). Precursor **29** (228 mg, 0.458 mmol) was subjected to catalytic $\text{Sn}(\text{OTf})_2$ according to the general procedure. Column chromatography (pentane/diethyl ether 4:1-2:1) afforded the product as an oil. Yield 141 mg (0.363 mmol, 79%). R_f 0.51 (pentane/diethyl ether 1:2). IR (CHCl_3) ν 1167, 1353, 1533, 1610, 2930 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) major *cis*-isomer: δ 8.18 (d, $J = 8.8$ Hz, 2H), 7.88 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 6.66 (d, $J = 8.3$ Hz, 1H), 6.55 (s, 1H), 6.01-5.96 (m, 1H), 5.47 (d, $J = 5.6$ Hz, 1H), 5.21 (d, $J = 10.0$ Hz, 1H), 5.17 (d, $J = 17.1$ Hz, 1H), 4.16-4.12 (m, 1H), 3.74 (s, 3H), 2.78 (dd, $J = 6.3, 15.6$ Hz, 1H), 2.60 (dd, $J = 6.6, 15.6$ Hz, 1H), 1.37 (d, $J = 6.6$ Hz, 3H); minor *trans*-isomer: δ 8.18 (d, $J = 8.5$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 1H), 6.78 (d, $J = 8.3$ Hz, 1H), 6.68-6.64 (m, 1H), 5.71-5.64 (m, 1H), 5.47 (d, $J = 6.1$ Hz, 1H), 5.22-5.11 (m, $1\frac{1}{2}\text{H}$), 5.04 (d, $J = 10.0$ Hz, $\frac{1}{2}\text{H}$), 4.41-4.38 (m, 1H), 3.79 (s, 3H), 3.05 (dd, $J = 4.6, 15.4$ Hz, 1H), 2.62-2.57 (m, 1H), 1.18 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (500 MHz, CDCl_3) major *cis*-isomer: δ 158.9, 149.5, 145.8, 138.3, 133.8, 128.3, 125.6, 123.8, 117.4, 113.9, 111.7, 58.7, 55.1, 49.7, 34.9, 23.1; minor *trans*-isomer: δ 159.0, 148.3, 145.8, 138.2, 134.1, 128.3, 126.5, 123.9, 116.8, 114.3, 112.4, 60.4, 55.2, 50.6, 36.1, 21.0; HRMS (FAB) calculated for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_5\text{S}$ (MH^+): 389.1171, found 389.1178; Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_5\text{S}$: C, 58.75; H, 5.19; N, 7.21; found C, 58.16; H, 4.64; N, 6.39.

6,7-Dimethoxy-2-(4-nitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydroisoquinoline (39a). Precursor **30a** (5.45 g, 10.6 mmol) was cyclized with $\text{Sn}(\text{OTf})_2$ according to the general procedure. The crude product was triturated with diethyl ether to afford the product as a yellow colored solid. Yield 3.95 g (9.8 mmol, 92%). IR (CHCl_3) ν 1121, 1165, 1247, 1351, 1532, 2938 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.8$ Hz, 2H), 7.95 (d, $J = 8.8$ Hz, 2H), 6.51 (s, 1H), 6.46 (s, 1H), 5.89-5.80 (m, 1H), 5.48 (d, $J = 6.0$ Hz, 1H), 5.19 (d, $J = 10$ Hz, 1H), 5.07 (d, $J = 17.0$ Hz, 1H), 3.95-3.91 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.38-3.30 (m, 1H), 2.69-2.65 (m, 1H), 2.59-2.54 (m, 1H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.6, 148.2, 147.5, 146.6, 136.4, 128.1, 124.9, 124.6, 123.9, 118.2, 111.1, 110.1, 58.0, 55.8, 55.7, 39.3, 27.1; HRMS (FAB) calculated for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_6\text{S}$ (MH^+): 405.1120, found 405.1114.

6,7-Dimethoxy-2-(2,4-dinitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydro isoquinoline (39b).

Precursor **30b** (1.54 g, 2.76 mmol) was treated with $\text{Sn}(\text{OTf})_2$ according to the general procedure. The crude product was triturated with diethyl ether to afford the product as a yellow colored solid. Yield 0.918 g (2.04 mmol, 74%). R_f 0.16 (pentane/diethyl ether 1:1). IR (CHCl_3) ν 1121, 1167, 1248, 1351, 1519, 1556, 2939 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 8.42 (d, $J = 9.9$ Hz, 1H), 8.23 (d, $J = 9.1$ Hz, 1H), 6.55 (s, 1H), 6.54 (s, 1H), 5.98-5.89 (m, 1H), 5.48 (d, $J = 5.7$ Hz, 1H), 5.20 (d, $J = 10.2$ Hz, 1H), 5.03 (d, $J = 17.0$ Hz, 1H), 4.04-4.00 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.53-3.45 (m, 1H), 2.92-2.84 (m, 1H), 2.70-2.65 (m, 1H); ^{13}C NMR (400 MHz, CDCl_3) δ 149.5, 148.5, 148.0, 147.7, 139.7, 136.6, 132.3, 126.0, 125.1, 124.5, 119.8, 118.7, 115.2, 111.4, 110.3, 58.5, 56.0, 55.9, 40.2, 27.9; HRMS (FAB) calculated for $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_8\text{S}$ (MH^+): 450.0971, found 450.0980.

***rac*-6,7-Dimethoxy-3-methyl-2-(4-nitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydro isoquinoline (40).**

Precursor **31** (177 mg, 0.34 mmol) was subjected to catalytic $\text{Sn}(\text{OTf})_2$ according to the general procedure. Column chromatography (pentane/diethyl ether 1:1) afforded the product as an oil. Yield 123 mg (0.29 mmol, 88%). R_f 0.28 (pentane/diethyl ether 1:2). IR (CHCl_3) ν 855, 994, 1166, 1351, 1533, 1610, 2938 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) both diastereoisomers: δ 8.27 (d, $J = 9.0$ Hz, 1H), 8.22 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.8$ Hz, 1H), 8.02 (d, $J = 8.8$ Hz, 1H), 6.62 and 6.58 (s, 1H), 6.56 and 6.52 (s, 1H), 5.99-5.92 and 5.69-5.63 (m, 1H), 5.48-5.46 (m, 1H), 5.29 (d, $J = 17.1$ Hz, $\frac{1}{2}\text{H}$), 5.25 (d, $J = 10.0$ Hz, $\frac{1}{2}\text{H}$), 5.17 (d, $J = 16.8$ Hz, $\frac{1}{2}\text{H}$), 5.08 (d, $J = 10.0$ Hz, $\frac{1}{2}\text{H}$), 4.34-4.32 and 4.25-4.23 (m, 1H), 3.86 and 3.85 (s, 3H), 3.82 (s, 3H), 2.94 (dd, $J = 4.6, 15.4$ Hz, $\frac{1}{2}\text{H}$), 2.77 (dd, $J = 6.3, 15.6$ Hz, $\frac{1}{2}\text{H}$), 2.56-2.49 (m, 1H), 1.30 (d, $J = 6.8$ Hz, $1\frac{1}{2}\text{H}$), 1.25 (d, $J = 6.6$ Hz, $1\frac{1}{2}\text{H}$); ^{13}C NMR (500 MHz, CDCl_3) both diastereoisomers: δ 149.6, 149.5, 148.4, 148.3, 147.8, 147.5, 146.2, 138.2, 137.8, 128.4, 128.3, 127.4, 126.8, 125.9, 124.9, 124.8, 123.9, 123.8, 117.9, 117.3, 111.7, 110.2, 60.5, 58.3, 55.9, 55.8, 50.5, 49.0, 35.4, 34.0, 22.2, 20.7; HRMS (FAB) calculated for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_6\text{S}$ (MH^+): 419.1277, found 419.1282.

6,7-Dimethoxy-2-(4-nitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydro isoquinoline-3-(S)-carboxylic acid methyl ester (41). Precursor **32** (0.234 g, 0.41 mmol) was cyclized using TFA according to the general procedure. Column chromatography (pentane/diethyl ether 1:1-1:2) afforded the product as a mixture of diastereoisomers. Yield 0.143 g (0.31 mmol, 76%). IR (CHCl₃) ν 856, 1121, 1166, 1256, 1350, 1465, 1532, 1747, 2957 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both diastereoisomers: δ 8.29 and 8.25 (d, J = 7.8 Hz, 2H), 8.05 and 8.02 (d, J = 7.8 Hz, 2H), 6.61 and 6.56 (s, 1H), 6.55 and 6.54 (s, 1H), 5.90-5.83 and 5.60-5.53 (m, 1H), 5.42-5.40 (m, 1H), 5.20-5.10 and 5.03-5.01 (m, 2H), 4.92 and 4.75-4.72 (m, 1H), 3.82 (s, 3H), 3.81 and 3.79 (s, 3H), 3.67 and 3.58 (s, 3H), 3.17-3.10 and 3.02-2.98 (m, 2H); ¹³C NMR (500 MHz, CDCl₃) major *cis*-isomer: δ 171.2, 149.8, 148.5, 147.8, 145.4, 136.8, 128.8, 125.0, 123.7, 123.6, 117.8, 111.1, 109.9, 58.8, 55.8, 55.7, 54.9, 52.4, 30.0; minor *trans*-isomer: 170.9, 149.7, 148.3, 148.1, 146.7, 137.9, 128.7, 126.4, 123.7, 122.7, 117.0, 110.9, 109.9, 60.6, 56.3, 31.7; HRMS (FAB) calculated for C₂₁H₂₃N₂O₈S (MH⁺): 463.1175, found 463.1176.

2-Tosyl-1-vinyl-2,3,4,9-tetrahydro-1H- β -carboline (42). Precursor **34** (150 mg, 0.33 mmol) was cyclized with $\text{Sn}(\text{OTf})_2$ according to the general procedure. The reaction was quenched with saturated NaHCO_3 solution (7 mL), the layers separated and the product extracted with diethyl ether (2×10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuo. Column chromatography (pentane/ethyl acetate 8:1-2:1) afforded the product as a slightly yellow, solidifying oil. Yield 65% (0.212 mmol). R_f 0.57 (pentane/ethyl acetate 2:1). Mp. 176-177 °C. IR (CH_2Cl_2) ν 1161, 1341, 2369, 2949, 2989, 3081, 3457 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.74 (br s, NH), 7.62 (d, $J = 8.3$ Hz, 2H), 7.40-7.06 (m, 6H), 6.01-5.93 (m, 1H), 5.61 (d, $J = 6.1$ Hz, 1H), 5.24 (dd, $J = 12.2, 17.1$ Hz, 2H), 4.05 (m, 1H), 3.31 (m, 1H), 2.60 (t, $J = 4.4$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 143.3, 136.0, 135.2, 130.0, 129.5, 126.9, 122.1, 119.5, 118.4, 118.2, 110.9, 108.9, 54.9, 39.8, 21.4, 20.7; HRMS (FAB) calculated for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ (MH^+): 353.1324, found 353.1300.

Note: Due to the size of the paper on which the spectrum was drawn, two signals are not visible: The Ts CH_3 and one CH_2 on the right side.

2-Tosyl-1-vinyl-2,3,4,9-tetrahydro-1H- β -carboline-3-carboxylic acid methyl ester (43). *N*-(1-Benzoyloxyallyl)-*N*-tosyltryptophan methyl ester **35** (100 mg, 0.211 mmol) was treated with $\text{Sn}(\text{OTf})_2$ according to the general procedure. The reaction was quenched with saturated NaHCO_3 solution (15 mL), the layers separated and the product extracted with diethyl ether (4×15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated in vacuo. Column chromatography (pentane/diethyl ether 2:1-1:4) afforded the product as a slightly yellow, solidifying oil. Yield 80% (0.169 mmol). R_f 0.40 (pentane/diethyl ether 1:1). Mp. 187-190 °C. IR (CH_2Cl_2) ν 1168, 1350, 1748, 2337, 2946, 2970, 3027, 3460 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) both diastereoisomers δ 8.02 (br s, NH), 7.77-7.74 (m, 2H), 7.49-7.46 (m, 1H), 7.31-7.09 (m, 5H), 6.23-6.16 and 5.76-5.73 (m, 1H), 5.63 and 5.58 (d, $J = 7.6$ Hz, 1H), 5.37-5.27 (m, 2H), 5.24 and 5.02 (t, $J = 5.4$ Hz, 1H), 3.67 and 3.53 (s, 3H), 3.46-3.43 and 3.42-3.37 (m, 1H), 3.20-3.16 and 2.89-2.84 (m, 1H), 2.38 and 2.36 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3) both diastereoisomers δ 171.1, 171.0, 143.5, 143.4, 137.9, 137.3, 136.6, 136.5, 136.4, 136.1, 130.5, 129.5, 129.1, 128.9, 127.5, 127.2, 126.6, 126.5, 122.2, 122.1, 119.5, 118.4, 118.3, 118.1, 111.0, 110.9, 106.9, 106.1, 57.4, 56.1, 55.5, 53.5, 52.4, 52.1, 24.1, 22.7, 21.4, 21.3; HRMS (FAB) calculated for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_4\text{S}$ (MH^+): 411.1379, found 411.1386.

***rac*-N-4-Nitrobenzenesulfonyl- α -methylphenethylamine.** Crude ***rac*- α -Methylphenethylamine** (1.86 g, 13.7 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. Column chromatography (pentane/diethyl ether 1:1, R_f 0.16) afforded the product as an off-white solid. Yield after recrystallization 2.28 g (7.12 mmol, 52%). Mp: 106.5 – 107.6 °C; IR (CHCl₃) ν 855, 1090, 1165, 1350, 1532, 3282 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.18-7.14 (m, 3H), 6.98-6.96 (m, 2H), 4.53 (s, NH), 3.62-3.54 (m, 1H), 2.77 (dd, J = 5.5, 13.8 Hz, 1H), 2.60 (dd, J = 8.1, 13.8 Hz, 1H), 1.25 (d, J = 6.5 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃) δ 149.6, 146.2, 137.0, 129.1, 128.5, 127.9, 126.7, 124.1, 52.0, 43.3, 22.3; HRMS (FAB) calculated for C₁₅H₁₇N₂O₄S (MH⁺): 321.0909, found 321.0912.

***rac*-N-(1-Benzyloxyallyl)-N-4-nitrobenzenesulfonyl- α -methylphenethyl amine (44).** *rac*-N-4-Nitrobenzenesulfonyl- α -methylphenethylamine (1.0 g, 3.12 mmol) was reacted with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane diethyl ether 4:1) afforded the product as a colorless oil. Yield 1.06 g (2.28 mmol, 73%). R_f 0.47 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1165, 1351, 1532, 2919, 3022 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) both diastereoisomers δ 8.31-8.27 (m, 2H), 8.05 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.40-7.11 (m, 10H), 5.65-5.62 (m, $\frac{1}{2}$ H), 5.58-5.57 (m, $\frac{1}{2}$ H), 5.55-5.49 (m, 2H), 5.42 (d, J = 10.5 Hz, $\frac{1}{2}$ H), 5.31 (d, J = 10.3 Hz, $\frac{1}{2}$ H), 4.67-4.56 (m, 2H), 3.92-3.79 (dm, 1H), 3.17-3.14 (m, 1H), 3.09-3.04 (m, $\frac{1}{2}$ H), 2.96-2.94 (m, $\frac{1}{2}$ H), 1.31 (d, J = 6.8 Hz, 1 $\frac{1}{2}$ H), 1.18 (d, J = 7.1 Hz, 1 $\frac{1}{2}$ H); ¹³C NMR (500 MHz, CDCl₃) δ 149.7, 148.2, 148.1, 139.1, 138.6, 137.1, 136.9, 133.9, 133.6, 129.4, 129.2, 128.5, 128.4, 128.0, 127.9, 127.7, 127.6, 126.6, 126.5, 124.2, 119.7, 119.6, 87.2, 69.9, 69.5, 55.5, 44.3, 42.9, 19.8, 18.6; HRMS (FAB) calculated for C₂₅H₂₇N₂O₅S (MH⁺): 467.1641, found 467.1665.

Acetic acid 3-[(4-nitrobenzenesulfonyl)-(2-*m*-tolylethyl)amino]-allyl ester (45). *N,O*-acetal **26** (92 mg, 0.20 mmol) was dissolved in Ac₂O (5 mL). HOAc (200 μ L, 3.5 mmol, 18 equiv) was added and the solution was heated at 120 $^{\circ}$ C for 16 h. Evaporation of the solvent and purification by column chromatography (pentane/diethyl ether 2:1) afforded the enamide. Yield 80 mg (0.19 mmol, 97%). *R*_f 0.34 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1167, 1247, 1345, 1538, 1750, 2960 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.38 (s, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03-6.99 (m, 2H), 5.15-5.11 (m, 1H), 4.62 (d, *J* = 7.3 Hz, 2H), 3.59 (t, *J* = 8.1 Hz, 2H), 2.90 (t, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 2.09 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 170.7, 150.1, 144.3, 138.4, 137.2, 130.8, 129.4, 128.6, 128.5, 128.2, 128.1, 127.6, 125.6, 124.5, 105.0, 63.3, 47.3, 33.4, 21.2, 21.0; HRMS (FAB) calculated for C₂₀H₂₃N₂O₆S (MH⁺): 419.1277, found 419.1278.

Acetic acid 3-[[2-(4-methoxyphenyl)ethyl]-[4-nitrobenzenesulfonyl] amino]allyl ester (46).

N,O-acetal **28** (100 mg, 0.207 mmol) was dissolved in Ac₂O (5 mL). HOAc (200 μL, 3.5 mmol, 17 equiv) was added and the solution was heated at 120 °C for 16 h. Evaporation of the solvent and purification by column chromatography (pentane/diethyl ether 2:1) afforded the enamide.

Yield 84 mg (0.193 mmol, 94%). *R*_f 0.22 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1168, 1247,

1350, 1514, 1534, 1657, 1732, 2957 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 14.2 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 5.12-5.08 (m, 1H), 4.60 (d, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.55 (t, *J* = 7.9 Hz, 2H), 2.87 (t, *J* = 7.8 Hz, 2H), 2.08 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 170.8, 158.5, 150.1, 144.3, 130.8, 129.6, 129.3, 128.1, 124.5, 114.1, 105.1, 63.3, 55.2, 47.5, 32.6, 21.0; HRMS (FAB) calculated for C₂₀H₂₃N₂O₇S (MH⁺): 435.1226, found 435.1228.

Acetic acid 3-[(1-methyl-2-phenylethyl)-(4-nitrobenzenesulfonyl)amino]allyl ester (47). *N,O*-acetal **44** (0.40 g, 0.86 mmol) was dissolved in Ac₂O (10 mL). HOAc (1 mL, 17 mmol, 20 equiv) was added and the solution was heated at 130 °C for 16 h. Evaporation of the solvent and purification by column chromatography (pentane/diethyl ether 2:1) afforded the enamide. Yield 0.32 g (0.76 mmol, 89%). *R_f* 0.43 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1169, 1231, 1350, 1534, 1736, 2995 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.20 (t, *J* = 3.2 Hz, 3H), 7.07-7.04 (m, 2H), 6.45 (d, *J* = 14.3 Hz, 1H), 5.63-5.56 (m, 1H), 4.59 (d, *J* = 7.0 Hz, 2H), 4.52-4.45 (m, 1H), 2.98-2.92 (m, 1H), 2.82-2.76 (m, 1H), 2.08 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 170.5, 149.7, 145.1, 137.5, 128.9, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 126.5, 124.0, 113.8, 63.4, 56.8, 40.2, 20.8, 18.4; HRMS (FAB) calculated for C₂₀H₂₃N₂O₆S (MH⁺): 419.1277, found 419.1278.

General procedure for the cleavage of the nitrobenzenesulfonyl group. To an icecold solution of the tetrahydroisoquinoline or tetrahydrocarboline (0.1 M) in MeCN was added potassium thiophenolate (1.5 equiv, prepared by adding KO^tBu (1 equiv) to an icecold solution of thiophenol (1 equiv) in diethyl ether after which the product salt could be obtained by collecting it on a filter, washing it repeatedly with diethyl ether followed by drying. The solution became cloudy and was stirred at room temperature for 8 hours after which additional thiophenolate was added (0.5 equiv), followed by stirring it for another 24 h. The reaction time can be shortened to a few hours by heating the mixture at 50 °C and by adding some additional thiophenol and K₂CO₃ during the reaction. H₂O was added and the product extracted with EtOAc (3 ×). The organic layers were washed with brine, dried over Na₂SO₄ and concentrated. The free amine was purified using column chromatography as indicated.

6-Methoxy-3-methyl-1-vinyl-1,2,3,4-tetrahydroisoquinoline. Isoquinoline **38** (123 mg, 0.32 mmol) was deprotected according to the general procedure. Column chromatography (CH₂Cl₂/MeOH/25% NH₃ 95:5:½) afforded solely the *cis* product. Yield 45 mg (0.22 mmol, 69%). IR (CHCl₃) ν 1239, 1502, 1611, 2960 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) *cis* diastereoisomer δ 7.06 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 1H), 5.88-5.83 (m, 1H), 5.39 (d, *J* = 17.1 Hz, 1H), 5.30 (d, *J* = 9.8 Hz, 1H), 4.50 (d, *J* = 9.5 Hz, 1H), 3.80 (s, 3H), 3.14-3.11 (m, 1H), 2.76-2.65 (m, 2H), 2.10 (br s, NH), 1.29 (d, *J* = 6.10 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) *cis* diastereoisomer δ 158.0, 140.4, 136.2, 128.8, 127.8, 117.7, 113.5, 111.8, 61.8, 55.2, 48.9, 38.1, 22.3; HRMS (FAB) calculated for C₁₃H₁₈NO (MH⁺): 204.1388, found 204.1375.

6,7-Dimethoxy-1-vinyl-1,2,3,4-tetrahydroisoquinoline (53). **39a** (3.90 g, 9.6 mmol) was deprotected according to the general procedure. Column chromatography (diethyl ether-CH₂Cl₂/MeOH/25% NH₃ 95:5:½) afforded the product as a solidifying oil. Yield 1.58 g (7.2 mmol, 75%). *R_f* 0.41 (CH₂Cl₂/MeOH/25% NH₃ 90:10:½). Mp. 71.6-74.5 °C. IR (CHCl₃) ν 1033, 1109, 1256, 1465, 1513, 1611, 2835, 2938 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.48 (s, 1H), 6.46 (s, 1H), 5.87-5.79 (m, 1H), 5.17-5.13 (m, 2H), 4.31 (d, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.15-3.09 (m, 1H, NH), 2.95-2.88 (m, 1H), 2.75-2.68 (m, 1H), 2.61-2.55 (m, 1H); ¹³C NMR (400 MHz, CDCl₃) δ 147.5, 146.9, 139.9, 127.8, 126.5, 117.4, 111.5, 110.0, 59.5, 55.7, 55.6, 41.1, 28.6; HRMS (FAB) calculated for C₁₃H₁₈NO₂ (MH⁺): 220.1338, found 220.1329; Anal. calcd. for C₁₃H₁₇NO₂: C, 71.21; H, 7.81; N, 6.39; found C, 71.18; H, 7.75; N, 6.28.

6,7-Dimethoxy-2-methyl-1-vinyl-1,2,3,4-tetrahydroisoquinoline (54). A solution of **53** (0.5 g, 2.28 mmol) and formaldehyde (37% solution, 0.25 mL, 2.74 mmol, 1.2 equiv) in formic acid (1 mL, 5.7 mmol, 2.5 equiv) was refluxed for 16 hours until the evolution of CO₂ ceased. The mixture was concentrated and two times co-evaporated with ethyl acetate. Column chromatography (CH₂Cl₂/MeOH/25% NH₃ 98:2:½-90:10:½) afforded the product as an oil. Yield 0.354 g (1.52 mmol, 67%). R_f 0.58 (CH₂Cl₂/MeOH/25% NH₃ 90:10:½).

IR (CHCl₃) ν 1256, 1514, 2937 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.60 (s, 1H), 6.59 (s, 1H), 5.78-5.69 (m, 1H), 5.35-5.27 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.66 (d, *J* = 8.4 Hz, 1H), 3.07-2.95 (m, 2H), 2.71-2.66 (m, 1H), 2.56-2.51 (m, 1H), 2.43 (s, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 147.4, 146.9, 139.7, 126.1, 118.2, 110.9, 110.5, 69.3, 55.7, 55.6, 51.1, 43.8, 28.5; HRMS (FAB) calculated for C₁₄H₂₀NO₂ (MH⁺): 234.1494, found 234.1490.

2-Ethoxycarbonylmethyl-6,7-dimethoxy-2-methyl-1-vinyl-1,2,3,4-tetrahydroisoquinolinium bromide.⁵

According to the literature procedure, **54** (0.334 g, 1.43 mmol) was dissolved in bromoethyl acetate (167 μ L, 1.50 mmol, 1.05 equiv) and stirred for 2 hours at room temperature. The mixture was triturated with diethyl ether (3×10 mL) and ethyl acetate (2×10 mL). It could not be crystallized from THF/EtOH, but solidified upon standing in the refrigerator. Pure product was obtained by recrystallization from ethyl acetate/EtOH (10:1). Yield 0.522 g (1.30 mmol, 91%). ¹H NMR (500 MHz, CDCl₃) δ 6.57 (br s, 1H), 6.38 (br s, 1H), 6.04 (br s, 1H), 5.95-5.84 (br m, 2H), 5.67 (br s, 1H), 4.91-4.88

(br m, 1H), 4.51-4.47 (br m, 1H), 4.27 (br s, 1H), 4.10-4.07 (br m, 2H), 3.84 (br s, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 3.38 (br s, 3H), 3.10-3.05 (m, 1H), 2.92-2.87 (m, 1H), 1.11 (br m, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 164.6, 149.4, 148.5, 129.3, 129.1, 120.3, 120.2, 110.7, 110.5, 72.9, 62.6, 57.8, 55.8, 54.1, 46.8, 23.4, 13.6; HRMS (FAB) calculated for C₁₈H₂₆NO₄ (M⁺): 320.1862, found 320.1856.

9,10-Dimethoxy-3-methyl-2,3,4,5-tetrahydro-1H-benzo[d]azonine-4-carboxylic acid ethyl ester (55).⁵

A solution of **2-Ethoxycarbonylmethyl-6,7-dimethoxy-2-methyl-1-vinyl-1,2,3,4-tetrahydroisoquinolinium bromide** (0.258 g, 0.645 mmol) in THF (10 mL) was treated with DBU (116 μ L, 0.773 mmol, 1.2 equiv) as described in the literature. After 1 hour at room temperature the mixture was concentrated in vacuo and purified using column chromatography (pentane/ethyl acetate 1:1-0:1). Yield 143.4 mg (0.449 mmol, 70%), (*E*)/(*Z*) 96:4. ¹H NMR (500 MHz, CDCl₃) only *E*-isomer: δ 6.78 (s, 1H), 6.64 (s, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 5.53-5.47 (m, 1H), 4.17-4.07 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H),

3.55 (d, *J* = 5.1 Hz, 1H), 2.84-2.80 (m, 2H), 2.73-2.63 (m, 2H), 2.69 (s, 3H), 2.37-2.32 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 172.8, 146.8, 146.6, 134.2, 133.4, 131.6, 130.2, 113.3, 110.2, 66.7, 60.1, 56.0, 55.9, 55.5, 44.8, 37.6, 35.8, 14.4; HRMS (FAB) calculated for C₁₈H₂₆NO₄ (MH⁺): 320.1862, found 320.1848.

⁵ Bailey, T. S.; Bremner, J. B.; Carver, J. A. *Tetrahedron Lett.* **1993**, 34, 3331.

2-Allyl-6,7-dimethoxy-1-vinyl-1,2,3,4-tetrahydroisoquinoline (56). A solution of 6,7-dimethoxy-1-vinyl-1,2,3,4-tetrahydroisoquinoline **53** (100 mg, 0.456 mmol), allyl bromide (43 μ L, 0.50 mmol, 1.1 equiv) and K_2CO_3 (0.125 g, 0.912 mmol, 2 equiv) in MeCN (10 mL) was refluxed for 48 hours. H_2O (20 mL) was added and the product extracted with EtOAc (3×15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. Column chromatography (pentane/ethyl acetate 1:1-1:2) was used to separate the mono- and dialkylated product. Yield of dialkylated product 16 mg (0.053 mmol, 12%), yield of monoalkylated product 61 mg (0.235 mmol, 52%). R_f (di) 0.64, R_f (mono) 0.28 (EtOAc). IR ($CHCl_3$) ν 925, 994, 1120, 1225, 1465, 1515, 2836, 2938 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 5.96-5.86 (m, 1H), 5.84-5.75 (m, 1H), 5.30-5.14 (m, 4H), 3.96 (d, $J = 8.4$ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.45 (dd, $J = 5.4, 13.9$ Hz, 1H), 3.11-2.99 (m, 2H), 2.86-2.78 (m, 1H), 2.75-2.68 (m, 1H), 2.56-2.50 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.4, 146.8, 139.4, 135.4, 127.8, 126.5, 117.9, 117.4, 111.0, 110.9, 66.1, 57.4, 55.7, 55.6, 46.1, 28.1; HRMS (FAB) calculated for $C_{16}H_{22}NO_2$ (MH^+): 260.1651, found 260.1649.

2-Butenyl-6,7-dimethoxy-1-vinyl-1,2,3,4-tetrahydroisoquinoline (57). Amine **53** (100 mg, 0.456 mmol) was alkylated with 4-bromobutene in the same way as for **56**. Column chromatography (pentane/ethyl acetate 1:1-0:1) afforded the product as an oil. Yield 74 mg (0.27 mmol, 60%). R_f 0.47 (EtOAc). IR (CHCl₃) ν 1100, 1375, 1469, 3150 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.58 (s, 2H), 5.86-5.79 (m, 2H), 5.25 (dd, J = 10.1, 17.1 Hz, 2H), 5.04 (dd, J = 10.1, 17.1 Hz, 2H), 3.99 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.11-3.08 (m, 1H), 2.86-2.76 (m, 3H), 2.63-2.54 (m, 2H), 2.33-2.25 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 146.9, 139.7, 118.2, 115.0, 111.0, 110.9, 99.9, 66.0, 55.7, 55.6, 53.5, 46.9, 46.4, 32.3, 27.5; HRMS (FAB) calculated for C₁₇H₂₄NO₂ (MH⁺): 274.1807, found 274.1803.

1-(6,7-Dimethoxy-1-vinyl-3,4-dihydro-1H-isoquinolin-2-yl)-propenone (58). To an icecold solution of **53** (100 mg, 0.456 mmol) and 2,6-lutidine (47 μ L, 0.405 mmol, 1.05 equiv) in dichloromethane (10 mL) was added acryloyl chloride (37 μ L, 0.456 mmol, 1.0 equiv). After stirring for 1 hour at 0 $^{\circ}$ C, the crude mixture was concentrated in vacuo. Column chromatography (pentane/ethyl acetate 1:1-0:1) afforded the product as a colorless oil. Yield 124 mg (0.454 mmol, 100%). R_f 0.35 (EtOAc). ^1H NMR (400 MHz, CDCl_3) both conformers: δ 6.62-6.56 (m, 3H), 6.28 (d, J = 16.8 Hz, 1H), 6.05 (br s, $\frac{1}{2}$ H), 5.97-5.91 (m, 1H), 5.66 (d, J = 10.3 Hz, 1H), 5.34 (br s, $\frac{1}{2}$ H), 5.17-4.97 (m, 2H), 4.50 (br d, J = 11.6 Hz, $\frac{1}{2}$ H), 3.89 (br d, J = 11.9 Hz, $\frac{1}{2}$ H), 3.80 (s, 3H), 3.88 (s, 3H), 3.49-3.40 (m, $\frac{1}{2}$ H), 3.10-3.00 (m, $\frac{1}{2}$ H), 2.87-2.79 (m, 1H), 2.69-2.61 (m, 1H); ^{13}C NMR (400 MHz, CDCl_3) both conformers: δ 148.0, 147.7, 137.0, 128.0, 127.6, 126.3, 125.8, 116.7, 115.9, 111.2, 111.0, 110.7, 109.9, 58.0, 55.8, 55.7, 54.2, 40.1, 36.8, 28.6, 27.6; HRMS (FAB) calculated for $\text{C}_{16}\text{H}_{20}\text{NO}_3$ (MH^+): 274.1443, found 274.1454.

1-(6,7-Dimethoxy-1-vinyl-3,4-dihydro-1H-isoquinolin-2-yl)-but-3-en-1-one (59). In the same way as for **58**, 6,7-dimethoxy-1-vinyl-1,2,3,4-tetrahydroisoquinoline **53** (160 mg, 0.729 mmol) was treated with freshly prepared 3-butenoyl chloride. Column chromatography (pentane/ethyl acetate 1:1-1:3) afforded the product as a colorless oil. Yield 190 mg (0.66 mmol, 91%). R_f 0.62 (CH₂Cl₂/MeOH/25% NH₃ 90:10:½). IR (CHCl₃) ν 1126, 1253, 1442, 1517, 1630, 2937 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) both conformers: δ 6.63 (s, 3H), 6.60 (s, 3H), 6.07-5.91 (m, 2H), 5.27-5.10 (m, 4H), 5.02 (d, J = 17.0 Hz, 0.7H), 4.59 (dd, J = 3.2, 11.2 Hz, 0.3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.86-3.79 (m, 1H), 3.51-3.44 (m, 0.7H), 3.27-3.18 (m, 2H), 3.09-3.02 (m, 0.3H), 2.92-2.82 (m, 1H), 2.74-2.67 (m, 1H); ¹³C NMR (400 MHz, CDCl₃) both conformers: δ 170.0, 169.3, 147.9, 147.6, 137.2, 137.1, 131.7, 131.5, 127.2, 126.5, 125.9, 125.7, 117.9, 117.7, 116.8, 116.1, 111.5, 111.0, 110.9, 110.1, 58.3, 56.0, 55.9, 54.1, 40.3, 39.1, 38.7, 36.5, 28.7, 27.9; HRMS (FAB) calculated for C₁₇H₂₂NO₃ (MH⁺): 288.1600, found 288.1597.

1-(6,7-Dimethoxy-1-vinyl-3,4-dihydro-1H-isoquinolin-2-yl)-pent-4-en-1-one (60). Similar to **58**, Amine **53** (75 mg, 0.34 mmol) was treated with 4-pentenoyl chloride. Column chromatography (pentane/ethyl acetate 1:1-0:1) afforded the product as a colorless oil. Yield 90 mg (0.30 mmol, 88%). R_f 0.76 ($\text{CH}_2\text{Cl}_2/\text{MeOH}/25\% \text{NH}_3$ 90:10:1/2). IR (CHCl_3) ν 1126, 1253, 1440, 1518, 1629, 2938 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) both conformers: δ 6.58 (s, 1H), 6.57 (s, 1H), 6.03 (d, $J = 4.9$ Hz, $\frac{1}{2}\text{H}$), 5.94-5.81 (m, $1\frac{1}{2}\text{H}$), 5.25-4.92 (m, $4\frac{1}{2}\text{H}$), 4.60-4.50 (m, $\frac{1}{2}\text{H}$), 3.81 (s, 3H), 3.79 (s, 3H), 3.81-3.76 (m, 1H), 3.46-3.41 (m, $\frac{1}{2}\text{H}$), 3.05-2.96 (m, $\frac{1}{2}\text{H}$), 2.83-2.79 (m, 1H), 2.71-2.62 (m, 1H), 2.51-2.38 (m, 4H); ^{13}C NMR (400 MHz, CDCl_3) both conformers: δ 171.0, 170.4, 148.0, 147.7, 147.4, 137.4, 137.3, 137.2, 137.0, 127.0, 126.5, 125.8, 125.6, 116.4, 115.8, 115.0, 114.9, 111.3, 110.9, 110.7, 110.0, 58.0, 55.8, 55.7, 53.9, 39.9, 36.2, 32.6, 32.4, 29.0, 28.5, 27.7; HRMS (FAB) calculated for $\text{C}_{18}\text{H}_{24}\text{NO}_3$ (MH^+): 302.1756, found 302.1762.

9,10-Dimethoxy-3,6,7,11b-tetrahydropyrido[2,1-a]isoquinolin-4-one (62). A solution of **59** (95 mg, 0.33 mmol) in dichloromethane (20 mL) was degassed using argon and refluxed for 30 min. 2nd Generation Grubbs catalyst (14 mg, 0.016 mmol, 5 mol%) was added and the solution was refluxed for 1 hour. The mixture was concentrated and purified by column chromatography (pentane/ethyl acetate 2:1-0:1) to yield the product as a yellowish, solidifying oil. Yield 55.2 mg (0.213 mmol, 65%). R_f 0.12 (pentane/ethyl acetate). Mp. 29.5-29.6 °C. IR (CHCl₃) ν 1014, 1118, 1224, 1256, 1466, 1515, 1632, 2938 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.72 (s, 1H), 6.64 (s, 1H), 6.20 (dd, J = 2.4, 10.3 Hz, 1H), 5.90 (dd, J = 2.4, 10.3 Hz, 1H), 5.25 (br s, 1H), 4.80-4.78 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.06-2.92 (m, 4H), 2.69-2.66 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 166.3, 147.9, 147.5, 128.2, 127.0, 123.7, 122.9, 111.7, 107.9, 56.6, 56.0, 55.8, 40.5, 31.8, 27.8; HRMS (FAB) calculated for C₁₅H₁₈NO₃ (MH⁺): 260.1287, found 260.1293; Anal. calcd. for C₁₅H₁₇NO₃: C, 69.48; H, 6.61; N, 5.40; found C, 66.19; H, 6.21; N, 4.93.

10,11-Dimethoxy-3,7,8,12b-tetrahydro-4H-azepino[2,1-a]isoquinolin-5-one (63). A solution of **60** (76.5 mg, 0.254 mmol) in dichloromethane (10 mL) was degassed using argon and refluxed for 30 min. 2nd Generation Grubbs catalyst (25 mg, 0.0296 mmol, 10 mol%) was added and the solution was refluxed for 2 hours. The mixture was concentrated and purified by column chromatography (pentane/ethyl acetate 1:1-0:1) to yield the product as a yellowish oil. Yield 68 mg (0.249 mmol, 98%). R_f 0.13 (EtOAc). IR (CHCl₃) ν 1121, 1229, 1254, 1435, 1464, 1518, 1633, 2938 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.65 (s, 1H), 6.63 (s, 1H), 5.78-5.69 (m, 3H), 4.06-4.02 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.52-3.47 (m, 1H), 3.40-3.37 (m, 1H), 2.76-2.74 (m, 2H), 2.54-2.50 (m, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 173.6, 147.9, 147.8, 133.0, 131.5, 128.0, 127.3, 110.9, 109.4, 56.0, 55.8, 52.4, 38.3, 33.4, 28.5, 25.4; HRMS (FAB) calculated for C₁₆H₂₀NO₃ (MH⁺): 274.1443, found 274.1443.

2-(5-Chloro-1*H*-indol-3-yl)ethylamine. 2-Carboxaldehyde-5-chloroindole (**64**, 2.01 g, 11.1 mmol) was condensed with nitromethane, followed by LiAlH₄ reduction according to the general procedure. Yield over 2 steps 2.15 g (11.1 mmol, 100%). The amine was used immediately in the next step.

***N*-[2-(5-Chloro-1*H*-indol-3-yl)ethyl]-4-nitrobenzenesulfonamide (**65**).** Crude 2-(5-chloro-1*H*-indol-3-yl)ethylamine (2.14 g, 11.06 mmol) was treated with 4-nitrobenzenesulfonyl chloride according to the general procedure. Column chromatography (pentane/ethyl acetate 2:1–0.1) afforded the product as a brownish yellow oil. Yield 3.153 g (8.30 mmol, 75%). *R_f* 0.63 (ethyl acetate). IR (CHCl₃) ν 1166, 1350, 1533, 3475 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.31 (s, NH), 8.08 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.23 (s, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 4.97 (t, *J* = 5.6 Hz, NH), 3.33 (q, *J* = 6.1 Hz, 2H), 2.89 (t, *J* = 6.4 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 149.5, 144.9, 134.6, 127.7, 127.6, 125.1, 124.3, 123.9, 122.5, 117.7, 112.4, 110.7, 42.8, 25.1; HRMS (FAB) calculated for C₁₆H₁₅N₃O₄SCl (MH⁺): 380.0472, found 380.0479.

***N*-(1-Benzyloxyallyl)-*N*-[2-(5-chloro-1*H*-indol-3-yl)ethyl]-4-nitrobenzene sulfonamide.**

Amide **65** (2.99 g, 7.87 mmol) was reacted with benzyl propadienyl ether according to the general procedure. Column chromatography (pentane/diethyl ether 2:1-1:3) afforded the product as an oil. Yield 3.40 g (6.50 mmol, 83%). R_f 0.49 (pentane/ethyl acetate 1:1). ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, J = 8.8 Hz, 2H), 8.12 (br s, NH), 7.97 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 1.8 Hz, 1H), 7.38-7.30 (m, 5H), 7.23 (d, J = 8.6 Hz, 1H), 7.12 (dd, J = 2.0, 8.6 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H), 5.75 (d, J = 2.7 Hz, 1H), 5.60-5.55 (m, 2H), 5.40-5.37 (m, 1H), 4.73 (d, J = 13.1 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 3.51-3.43 (m, 1H), 3.39-3.32 (m, 1H), 3.15-3.11 (m, 2H); ^{13}C NMR (400 MHz, CDCl_3) δ 145.8, 140.6, 136.8, 134.4, 132.9, 128.4, 128.3, 128.1, 127.9, 127.8, 127.5, 126.8, 125.0, 124.1, 124.0, 122.2, 119.9, 118.1, 112.2, 112.1, 86.6, 69.6, 44.5, 26.8.

6-Chloro-2-(4-nitrobenzenesulfonyl)-1-vinyl-2,3,4,9-tetrahydro-1H- β -carboline (66). The previous acetal (3.19 g, 6.06 mmol) was cyclized using $\text{Sn}(\text{OTf})_2$, according to the general procedure. The crude reaction mixture was diluted with EtOAc and washed with H_2O (30 mL), brine (30 mL), dried over Na_2SO_4 and concentrated. Column chromatography (pentane/ethyl acetate 2:1) afforded the product as a yellow solid. Yield 2.37 g (5.7 mmol, 94%). R_f 0.26 (pentane/ethyl acetate 2:1). Mp. 225.6-226.0 °C. IR (CHCl_3) ν 1030, 1248, 1708, 3387 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 + acetone- d_6) δ 9.52 (br s, NH), 7.98 (d, J = 9.0 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 2.0 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.79 (dd, J = 2.0, 8.5 Hz, 1H), 5.73-5.67 (m, 1H), 5.46 (d, J = 5.9 Hz, 1H), 5.01 (d, J = 10.0 Hz, 1H), 4.95 (d, J = 17.1 Hz, 1H), 3.93-3.89 (m, 1H), 3.17-3.11 (m, 1H), 2.39-2.35 (m, 2H); ^{13}C NMR (500 MHz, CDCl_3 + acetone- d_6) δ 149.3, 146.2, 134.2, 134.0, 131.2, 127.6, 127.0, 124.3, 123.6, 121.6, 118.2, 117.0, 111.7, 107.1, 54.7, 39.4, 20.1; HRMS (FAB) calculated for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_4\text{SCl}$ (MH^+): 418.0628, found 418.0628; Anal. calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_3\text{O}_4\text{SCl}$: C, 54.61; H, 3.86; N, 10.06; found C, 54.74; H, 3.92; N, 9.94.

1-[6-Chloro-2-(4-nitrobenzenesulfonyl)-1-vinyl-1,2,3,4-tetrahydro- β -carbolin-9-yl]-propenone (67). To an icecold solution of the olefin **66** (0.1 g, 0.24 mmol) in THF (10 mL) was added a 0.5 M solution of KHMDS (0.72 mL, 0.36 mmol, 1.5 equiv). After stirring for 1.5 hours at room temperature, acryloyl chloride (80 μ L, 0.96 mmol, 4 equiv) was added at once. After 1 hour H₂O (20 mL) was added and the product extracted with EtOAc (2 $\times$ 20 mL). The combined organic layers were washed with H₂O (20 mL), brine (20 mL), dried over Na₂SO₄ and concentrated. Column chromatography (pentane/ethyl acetate 3:1-1:1) afforded the product. Yield 46 mg (0.097 mmol, 41%). *R*_f 0.14 (pentane/ethyl acetate 2:1). IR (CHCl₃) ν 1167, 1350, 1533, 1691; ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.33 (s, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.95 (dd, *J* = 10.3, 16.9 Hz, 1H), 6.65 (d, *J* = 16.8 Hz, 1H), 6.36 (d, *J* = 4.6 Hz, 1H), 6.15 (d, *J* = 10.5 Hz, 1H), 6.02-5.93 (m, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 4.87 (d, *J* = 17.1 Hz, 1H), 4.20 (m, 1H), 3.47-3.40 (m, 1H), 2.69-2.62 (m, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 164.6, 149.8, 146.5, 134.3, 133.4, 132.9, 131.9, 130.3, 130.1, 129.1, 128.0, 124.8, 124.2, 119.0, 118.5, 116.0, 115.4, 54.6, 38.2, 20.5; HRMS (FAB) calculated for C₂₂H₁₉N₃O₅SCl (MH⁺): 472.0734, found 472.0746.

3-[6-Chloro-2-(4-nitrobenzenesulfonyl)-2,3,4,9-tetrahydro-1H-β-carbolin-1-yl] acrylic acid methyl ester (68). To a degassed solution of the olefin **66** (50 mg, 0.12 mmol) in dry toluene (7 mL) was added methyl acrylate (54 μL, 0.6 mmol, 5 equiv.) and Hoveyda-Grubbs cat. (1.5 mg, 2 mol%). The mixture was heated at 60 °C for 24 hours and concentrated in vacuo. Column chromatography (pentane/ethyl acetate 3:1-1:1) afforded the product as an oil. Yield 33 mg (0.069 mmol, 58%). R_f 0.13 (pentane/ethyl acetate 2:1). ^1H NMR (500 MHz, CDCl_3) δ 8.27 (d, J = 8.8 Hz, 2H), 8.12 (s, NH), 7.99 (d, J = 8.8 Hz, 2H), 7.36 (s, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 8.8 Hz, 1H), 6.90 (dd, J = 6.1, 15.6 Hz, 1H), 5.98 (d, J = 15.6 Hz, 1H), 5.81 (d, J = 6.1 Hz, 1H), 4.20-4.16 (m, 1H), 3.76 (s, 3H), 3.34-3.28 (m, 1H), 2.67-2.59 (m, 2H); ^{13}C NMR (500 MHz, CDCl_3) δ 165.8, 150.1, 146.2, 142.4, 134.5, 129.2, 128.1, 127.4, 126.0, 124.4, 124.1, 123.4, 118.2, 112.2, 53.5, 52.1, 40.4, 20.6.

6-Chloro-1-vinyl-2,3,4,9-tetrahydro-1H- β -carboline (69). Sulfonamide **66** (0.40 g, 0.955 mmol) was deprotected according to the general procedure, but instead of room temperature the mixture was kept at 50 °C. Column chromatography (CH₂Cl₂/MeOH/25% NH₃ 90:10: ½) afforded the product as an off-white solid. Yield 177 mg (0.76 mmol, 80%). *R_f* 0.12 (CH₂Cl₂/MeOH/25% NH₃ 90:10:½). IR (CHCl₃) ν 1064, 1294, 1441, 2205, 2360, 2918, 3466 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (br s, NH), 7.45 (d, *J* = 1.9 Hz, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.08 (dd, *J* = 2.0, 8.6 Hz, 1H), 6.00-5.92 (m, 1H), 5.37 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 3.36-3.31 (m, 1H), 3.11-3.05 (m, 1H), 2.80-2.65 (m, 2H), 1.91 (br s, NH); ¹³C NMR (400 MHz, CDCl₃) δ 137.9, 134.9, 133.9, 128.6, 124.9, 121.6, 118.2, 117.6, 111.5, 108.8, 56.4, 42.0, 22.0; HRMS (FAB) calculated for C₁₃H₁₄N₂Cl (MH⁺): 233.0846, found 233.0835; Anal. calcd. for C₁₃H₁₃N₂Cl: C, 67.10; H, 5.63; N, 12.04; found C, 67.02; H, 5.54; N, 12.15.

6-Chloro-2-*tert*-butyloxycarbonyl-1-vinyl-2,3,4,9-tetrahydro-1*H*- β -carboline (70). To a solution of 6-chloro-1-vinyl-2,3,4,9-tetrahydro-1*H*- β -carboline **69** (0.218 g, 0.937 mmol) in dichloromethane (20 mL) was added Boc₂O (0.205 g, 0.937 mmol, 1 equiv). The solution was refluxed for 6 h, then H₂O (50 mL) was added, followed by layer separation. The aqueous layer was extracted with EtOAc (30 mL) and the combined organic layers were washed with 1% aqueous HCl (30 mL), saturated aqueous NaHCO₃ (30 mL), brine (30 mL) and concentrated in vacuo. Column chromatography (pentane/ethyl acetate 4:1-2:1) afforded the product as an off-white solid. Yield 0.312 g (0.937 mmol, 100%). *R*_f 0.42 (pentane/ethyl acetate 2:1). IR (CHCl₃) ν 1167, 1413, 1679, 2981, 3466 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (s, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.13 (dd, *J* = 2.0, 8.8 Hz, 1H), 6.04-5.97 (m, 1H), 5.90-5.50 (br m, 1H), 5.27 (d, *J* = 10.0 Hz, 1H), 5.18 (br d, *J* = 15.6 Hz, 1H), 4.60-4.20 (br m, 1H), 3.13 (br s, 1H), 2.85-2.79 (m, 1H), 2.72-2.67 (m, 1H), 1.54 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 154.7, 135.0, 134.5, 133.1, 129.0, 128.0, 127.5, 125.2, 122.0, 117.8, 117.5, 111.8, 80.31, 29.7, 28.5, 21.3; HRMS (FAB) calculated for C₁₈H₂₂N₂O₂Cl (MH⁺): 333.1370, found 333.1388.

6-Chloro-1-(2-methoxycarbonylvinyl)-1,3,4,9-tetrahydro- β -carboline-2-carboxylic acid *tert*-butyl ester (71). To a degassed solution of **70** (0.365 g, 1.1 mmol) in toluene (20 mL) was added methyl acrylate (1.0 mL, 11 mmol, 10 equiv) and Hoveyda-Grubbs 2nd generation catalyst (15 mg, 0.022 mmol, 2 mol%). The solution was heated at 60 °C for 48 hours. After concentration in vacuo, column chromatography (pentane/diethyl ether 2:1-1:1) afforded the product as a colorless oil. Yield 0.353 g (0.902 mmol, 82%). R_f 0.13 (pentane/diethyl ether 1:1). IR (CHCl₃) ν 1166, 1284, 1414, 1678, 2981, 3327, 3463 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.27 and 8.72 (br s, NH), 7.42 (s, 1H), 7.20 (br d, J = 8.1 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 6.99 (br d, J = 12.8 Hz, 1H), 6.00-5.73 (m, 2H), 4.45 and 4.32 (br s, 1H), 3.75 and 3.67 (br s, 3H), 3.09-3.01 (m, 1H), 2.84-2.76 (m, 1H), 2.66-2.63 (m, 1H), 1.56 and 1.47 (br s, 9H). HRMS (FAB) calculated for C₂₀H₂₄N₂O₄Cl (MH⁺): 391.1425, found 391.1420.

6-Chloro-1-(2-methoxycarbonylethyl)-1,3,4,9-tetrahydro- β -carboline-2-carboxylic acid *tert*-butyl ester (72). The olefin **71** (0.29 g, 0.742 mmol) was dissolved in dry methanol (15 mL) together with a catalytic amount of PtO_2 . The stirred solution was exposed to 1 atm H_2 pressure for 1 hour. Filtration of the suspension over Hyflo and concentration in vacuo afforded the product as a yellowish foam. Yield 0.29 g (0.74 mmol, 99%). R_f 0.55 (pentane/ethyl acetate 1:1). IR (CHCl_3) ν 1167, 1232, 1367, 1417, 1671, 1725, 2932, 2980, 3327, 3463 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.17 and 8.77 (br s, NH), 7.44 (s, 1H), 7.22 (d, $J = 8.5$ Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 5.41 and 5.30 (br s, 1H), 4.50 and 4.31 (br s, 1H), 3.76 and 3.65 (br s, 3H), 3.18-3.08 (m, 1H), 2.83-2.79 (m, 1H), 2.65 (d, $J = 15.4$ Hz, 1H), 2.51-2.46 (m, 1H), 2.25-2.19 (m, 1H), 2.13-2.05 (m, 1H), 1.55 and 1.51 (br s, 9H); ^{13}C NMR (500 MHz, CDCl_3) both conformers: δ 173.9, 155.4, 154.6, 135.6, 135.2, 134.4, 127.8, 124.8, 121.7, 117.5, 111.9, 108.5, 107.9, 80.2, 51.6, 50.7, 50.2, 38.6, 37.3, 30.6, 29.6, 29.4, 28.3, 21.2, 20.9; HRMS (FAB) calculated for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_4\text{Cl}$ (MH^+): 393.1581, found 393.1578.

10-Chloro-6-oxo-1,2,3a,4,5,6-hexahydroindolo[3,2,1-*de*][1,5]naphthyridine-3-carboxylic acid *tert*-butyl ester (73). To an icecold solution of the ester **72** (0.213g, 0.542 mmol) in dry toluene (10 mL) was added NaHMDS (1 M in toluene, 1.88 mL, 1.88 mmol) and stirring was continued for 2 hours at room temperature. The solution was cooled to 0 °C and icecold saturated aqueous NaHCO₃ (15 mL) was added. The product was extracted with CH₂Cl₂ (2 × 15 mL) after layer separation. The organic layers were washed with brine (15 mL), dried over Na₂SO₄ and concentrated. Column chromatography (pentane/ethyl acetate 3:1-1:1) afforded the product as a colorless oil. Yield 76 mg (0.211 mmol, 39%). *R_f* 0.49 (pentane/ethyl acetate 1:1).

IR (CHCl₃) ν 1216, 1402, 1692, 3020 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.31 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 4.98 (d, *J* = 9.5 Hz, 1H), 4.48 (d, *J* = 12.4 Hz, 1H), 2.96-2.88 and 2.73-2.68 (m, 5H), 2.58-2.54 (m, 1H), 1.94-1.90 (m, 1H), 1.56 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 167.8, 154.8, 135.3, 133.3, 130.3, 129.8, 124.7, 118.1, 117.2, 114.1, 80.8, 49.3, 40.5, 33.2, 28.5, 27.8, 21.7.

Vincantril (74).⁶ To an icecold solution of the carbamate **73** (50 mg, 0.139 mmol) in CH_2Cl_2 (4 mL) was added TFA (0.32 mL, 4.15 mmol, 30 equiv). The solution was stirred at room temperature for 6 hours and then icecold saturated aqueous NaHCO_3 (10 mL) was added. The product was extracted with CH_2Cl_2 (3×10 mL) after layer separation. The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated. Column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}/25\% \text{NH}_3$ 95:5:1/2) afforded vincantril as a slightly greenish solid. Yield 32 mg (0.123 mmol, 88%). R_f 0.37 ($\text{CH}_2\text{Cl}_2/\text{MeOH}/25\% \text{NH}_3$ 90:10:1/2). Mp. 171.5-172.6 °C (lit.⁷ 161-163 °C). IR (CHCl_3) ν 1382, 1448, 1602, 1706, 2360, 2928, 3606, 3691 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, $J = 8.5$ Hz, 1H), 7.39 (s, 1H), 7.28 (d, $J = 3.9$ Hz, 1H), 4.02-3.99 (m, 1H), 3.55-3.51 (m, 1H), 2.89-2.60 (m, 4H), 2.34-2.29 (m, 1H), 1.87-1.78 (m, 1H), 1.69 (br s, NH); ^{13}C NMR (500 MHz, CDCl_3) δ 168.0, 137.5, 132.9, 131.2, 129.5, 124.4, 118.0, 117.0, 112.3, 50.6, 43.7, 33.1, 29.0, 21.5; HRMS (FAB) calculated for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{OCl}$ (MH^+): 261.0795, found 261.0805; Anal. calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OCl}$: C, 64.49; H, 5.03; N, 10.74; found C, 64.56; H, 4.95; N, 10.66.

⁶ Koletar, G. I.; Najer, H.; Lefevre, J. P. G.; Dupont, R.; Giudicelli, P. R. L.; Morel, C. C. H. *US4190657*; *Chem. Abstr.* **1978**, 88:50831j.

⁷ According to the Combined Chemical Dictionary on CD-ROM, Chapman & Hall/CRC, London, 2001, compound number NCV30-I.