Supporting Information
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Supporting Information

Synthesis of 6- and 7-membered chloromethyl-substituted heterocycles via palladium-catalyzed amino and oxychlorination

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Table of Contents

I. General Information .................................................................................................................. 2
II. Preparation of substrates ....................................................................................................... 3
III. Characterization of compounds ........................................................................................... 6
IV. $^1$H and $^{13}$C NMR spectra ................................................................................................. 13
I. General Information

All reagents were purchased from chemical suppliers and used without further purification. Reactions were performed using freshly distilled solvents under an argon atmosphere. DCM was dried on calcium hydride. Dry DMF, toluene, diethylether and acetonitrile were purchased from chemical suppliers. Analytical thin layer chromatography was performed on commercial silica gel plates 60F254. Flash column chromatography was performed on silica gel 60 (40–63 µm). NMR spectra were recorded on a 250 or 500 MHz spectrometer as specified. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.00 ppm) or the CHCl₃ residual peak (δ 7.26) or the MeOH residual peak (δ 3.31) or the C₆H₆ residual peak (δ 7.16) for ¹H NMR. Chemical shifts of ¹³C NMR are reported relative to CDCl₃ (δ 77.16) or C₆D₆ (δ 128.06) or CD₃OD (δ 49.00). Coupling constant (J) are reported in Hertz unit (Hz). Multiplicities are described with standard following abbreviations: s = singlet, br = broad, d = doublet, t = triplet, q = quadruplet, m = multiplet. Low resolution mass spectra (LRMS) were recorded with an ion trap mass analyzer under electrospray ionization (ESI) in positive or negative ionization mode detection or atmospheric pressure chemical ionization (APCI). High resolution mass spectra (HRMS) were recorded with a TOF mass analyzer under electrospray ionization (ESI) in positive or negative ionization mode detection, atmospheric pressure chemical ionization or atmospheric pressure photoionization (APPI). Melting points were measured on a Köfler bench. IR spectra were recorded on a FT-IR spectrophotometer, and the wavelengths reported in cm⁻¹.
II. Preparation of substrates

Substrates were synthesized according to general schemes depicted below:

- Preparation of N-allylbenzylamine:

The N-allylbenzylamine was synthesized using a reported procedure. In a round bottom flask was placed at 0°C, 4.0 equiv. of MgSO₄ in dry DCM (C = 0.2 mol/L) under argon, then 1.0 equiv. of benzaldehyde was added, followed by 1.1 equiv. of allylamine. The suspension was stirred at room temperature for 24h, then the reaction mixture was filtrated and the solvent was removed under vaccum. The crude imine was used directly without purification in the next step. The oily residue was dissolved in MeOH (C = 1 mol/L) and 2.0 equiv. of sodium borohydride were added by small portions at 0°C. The solution was stirred at room temperature for 2h, then the solvent was evaporated and the reaction was quenched carefully with a saturated aqueous solution of ammonium chloride. The aqueous phase was extracted.

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1 Manick, A.-D.; Duret, G.; Tran, D. N.; Berhal, F.; Prestat, G. Org. Chem. Front. 2014, 1, 1058
with DCM (3 times) and the combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The resulting N-allylbenzylamine showed clean NMR spectra and was used without further purification.

- General procedure for the tosylation reaction:
The nitrogen tosylation was done using a reported procedure.³ In a round bottom flask, 2.4 equiv. of Na₂CO₃ was dissolved in 70°C water (C = 0.66 mol/L). Then 1.0 equiv. of the desired anthranilic acid was added followed by 1.4 equiv. of tosyl chloride. The suspension was stirred at 70°C for 40 mn then at 85°C for 5 mn. The reaction mixture was then directly filtrated and the solid washed with 85°C water. The filtrate was cooled to room temperature and then acidified to pH = 1 using an aqueous 6M HCl solution. The precipitated solid was collected by suction and dried over vacuum. The resulting tosyl anthranilic acids were used without further purification.

- General procedure for peptidic coupling of anthranilic and salicylic acid derivatives:
In a round bottom flask, 1.0 equiv. of allyl benzylamine was placed in DCM (C = 0.067 mol/L) under argon. Then 1.2 equiv. of the desired tosyl/boc anthranilic acid or salicylic acid were added, followed successively by 1.2 equiv. of EDC.HCl and 1.2 equiv. of HOBt. The clear solution was stirred at room temperature or reflux until starting material was totally consumed (monitored by TLC). The reaction mixture was then quenched with water. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/Et₂O as eluent (9:1 to 1:1).

- General procedure for peptidic coupling for amino acid derivatives:
In a round bottom flask, 1.0 equiv. of the desired amino acid and 1.2 equiv. of allylbenzylamine were placed in DMF (C = 0.44 mol/L) under argon. Then 1.5 equiv. of HATU and 1.5 equiv. of HOAt were added. After 20 mn, 2.0 equiv. of DiPEA was added. The solution was stirred at room temperature until starting material was totally consumed (monitored by TLC). The reaction mixture was then quenched with water. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with

MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using cyclohexane/AcOEt as eluent (9:1 to 6:4).

- Preparation of N-allyl-2-amino-N-benzylacetamide:
In a round bottom flask, 1.0 equiv. of tert-butyl (2-(allyl(benzyl)amino)-2-oxoethyl)carbamate was placed in DCM (C = 0,34 mol/L) under argon. Then 40.0 equiv. of TFA were added. The solution was stirred at room temperature until starting material was totally consumed (monitored by TLC). The solvent was removed under vacuum. The reaction mixture was washed with an aqueous NaOH 1M solution. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The product was used without further purification.

- Preparation of 2-acetamido-N-allyl-N-benzylacetamide:
In a round bottom flask, 1.0 equiv. of N-allyl-2-amino-N-benzylacetamide was placed in pyridine (C = 0,13 mol/L) under argon. Then 2.0 equiv. of acetic anhydride was added. The solution was stirred at room temperature until starting material was totally consumed (monitored by TLC). The reaction mixture was then quenched with an aqueous HCl 1M solution. The aqueous layer was extracted with AcOEt (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using AcOEt/MeOH as eluent (100% to 9:1).

- Preparation of N-allyl-N-benzyl-2-nitroaniline:
In a vial, 1.0 equiv. of fluoronitrobenzene and 2.5 equiv. of allylbenzylamine were placed in toluene (C = 2,7 mol/L). The mixture was irradiated at 80°C (power input : 100W) for 1h30. The reaction mixture was then quenched with a saturated aqueous NH₄Cl solution. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using cyclohexane/AcOEt as eluent (98:2 to 96:4).

- Preparation of N-allyl-N-benzylbenzene-1,2-diamine:
In a round bottom flask under argon, 3.2 equiv. of NaBH₄ was added to a solution of 0.2 equiv. of Cu(acac)₂ in EtOH (C = 0,056 mol/L). The reaction mixture was stirred at room
temperature for 30mn. Then 1.0 equiv. of N-allyl-N-benzyl-2-nitroaniline in EtOH was added dropwise. The mixture was stirred at room temperature for 3h and then filtrated under Celite®. The filtrate was diluted with DCM and washed with a saturated aqueous NH₄Cl solution. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using cyclohexane/AcOEt as eluent (100% to 9:1).

- Preparation of N-(2-(allyl(benzyl)amino)phenyl)-4-methylbenzenesulfonamide:

In a round bottom flask under argon, 1.0 equiv. of N-allyl-N-benzylbenzene-1,2-diamine and 1.3 equiv. of tosyl chloride were placed in DCM (C = 0.1 mol/L), followed by 1.3 equiv. of pyridine. After stirring at room temperature for 18h, the reaction mixture was quenched with a saturated aqueous NH₄Cl solution. The aqueous layer was extracted with DCM (3 times). The combined organic phases were then dried with MgSO₄, filtrated and the solvent was removed under vacuum. The crude residue was purified by silica gel flash chromatography using pentane/Et₂O as eluent (100% to 7:3).

### III. Characterization of compounds

**Tosylglycine (15a):**

White solid, m = 4.39 g, 72% Yield, (known compound)¹ ¹H NMR (MeOD, 500 MHz, ppm): δ 7.74 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 3.67 (s, 2H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 172.0, 144.7, 138.7, 130.6, 128.1, 44.8, 21.4. MS (ESI): m/z = 230.0 [M+H⁺]. IR (ν = cm⁻¹): 3213, 2987, 1620, 1453, 1382, 1326, 1163. Mp: 148°C.

**Tosyl-L-alanine (15b):**

White solid, m = 1.42 g, 52% Yield, (known compound)² ¹H NMR (MeOD, 500 MHz, ppm): δ 7.70 (dt, J = 2.0, 8.0 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 3.93 (q, J = 7.0 Hz, 1H), 2.42 (s, 3H), 1.27 (d, J = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 174.1, 144.7, 139.2, 130.6, 128.1, 52.8, 21.4, 19.1. IR (ν = cm⁻¹): 3266, 3200, 2987, 1620, 1453, 1382, 1326, 1163.

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¹ Li, G.-L.; Zhao, G. Org. Lett. 2006, 8, 633.
Tosyl-L-phenylalanine (15c):
White solid, m = 4.79 g, 75% Yield, (known compound6), \(^1\)H NMR (MeOD, 500 MHz, ppm): \(\delta\) 7.54 (d, \(J = 8.5\) Hz, 2H), 7.23 (d, \(J = 8.5\) Hz, 2H), 7.21-7.15 (m, 3H), 7.15-7.08 (m, 2H), 4.01 (dd, \(J = 5.5, 8.5\) Hz, 1H), 3.03 (dd, \(J = 6.0, 14.0\) Hz, 1H), 2.84 (dd, \(J = 8.5, 13.5\) Hz, 1H), 2.38 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 174.3, 144.4, 139.1, 137.8, 130.5, 130.4, 129.4, 128.0, 127.7, 58.8, 39.9, 21.4. IR (\(\nu = \text{cm}^{-1}\)): 3317, 2988, 2909, 1712, 1690, 1344, 1331, 1271, 1168, 1157, 1089, 934, 821, 704. Mp: 144°C. [\(\alpha\)]\(^{20}\)_D = -3.7 (c 0.95, MeOH).

Tosyl-L-alloisoleucine (15d):
White solid, m = 4.22 g, 78% Yield, (known compound7) \(^1\)H NMR (MeOD, 500 MHz, ppm): \(\delta\) 7.72 (dt, \(J = 2.0, 8.5\) Hz, 2H), 7.33 (d, \(J = 8.5\) Hz, 2H), 3.66 (d, \(J = 5.5\) Hz, 1H), 2.41 (s, 3H), 1.79-1.68 (m, 1H), 1.55-1.42 (m, 1H), 1.23-1.11 (m, 1H), 0.91 (d, \(J = 6.5\) Hz, 3H), 0.86 (t, \(J = 7.5\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 174.2, 144.6, 139.2, 130.5, 128.3, 61.7, 39.2, 25.9, 21.4, 15.9, 11.5. IR (\(\nu = \text{cm}^{-1}\)): 3277, 2970, 2935, 2883, 1708, 1333, 1284, 1235, 1161, 1092, 802, 662. [\(\alpha\)]\(^{20}\)_D = +25 (c 2.2, MeOH). Mp: 136°C.

N-allyl-N-benzyl-2-((4-methylphenyl)sulfonyl)acetamide (1a):
White solid, m = 595 mg, 84% Yield, (known compound8) \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 7.76 (d, \(J = 8.0\) Hz, 1.2H), 7.69 (d, \(J = 8.5\) Hz, 0.8H), 7.36-7.24 (m, 5H), 7.13-6.95 (m, 2H), 5.73-5.65 (m, 1H), 5.65-5.54 (m, 1H), 5.21-5.12 (m, 1H), 5.06-4.97 (m, 1H), 4.50 (s, 1H), 4.32 (s, 1H), 3.93 (d, \(J = 6.0\) Hz, 1H), 3.81 (d, \(J = 4.0\) Hz, 1.3H), 3.79 (d, \(J = 4.5\) Hz, 0.7H), 3.68-3.63 (m, 1H), 2.43 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 167.4, 167.2, 143.7, 143.6, 136.4, 136.3, 136.1, 135.3, 132.0, 131.4, 129.8, 129.2, 128.8, 128.3, 128.1, 127.9, 127.5, 127.4, 126.4, 118.5, 117.7, 49.2, 48.7, 48.2, 43.9, 43.7, 21.7. MS (ESI): m/z = 359.0 [M+H\(^+\)]. HRMS (ESI): m/z

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calcd for C_{19}H_{23}O_{3}N_{2}S [M+H^{+}] 359.1424, found 359.1414. IR (ν = cm\(^{-1}\)) : 3217, 2924, 1652, 1419, 1333, 1159, 705, 679. Mp: 101-106°C.

tert-Butyl (2-(allyl(benzyl)amino)-2-oxoethyl)carbamate (Ib): 

Colorless foam, m = 315 mg; 91% Yield, (known compound\(^9\)) \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): δ 7.41-7.14 (m, 5H), 5.82-5.67 (m, 1H), 5.66-5.46 (brs, 1H), 5.28-5.09 (m, 2H), 4.62 (s, 1.2H), 4.46 (s, 0.8H), 4.10-3.98 (m, 2.7H), 3.79 (d, J = 5.0 Hz, 1.3H), 1.47 (s, 5.8H), 1.45 (s, 3.2H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): δ 168.9, 168.8, 155.9, 155.8, 136.9, 135.8, 132.4, 131.8, 129.1, 128.8, 128.3, 127.9, 127.7, 126.6, 118.2, 117.7, 79.7, 49.3, 48.8, 48.4, 48.3, 42.5, 42.3, 28.5. MS (ESI): m/z = 305.2 [M+H\(^{+}\)]. HRMS (ESI): m/z calcd for C\(_{17}\)H\(_{25}\)O\(_3\)N\(_2\) [M+H\(^{+}\)] 305.1860, found 305.1857. IR (ν = cm\(^{-1}\)) : 3419, 3233, 3064, 2978, 2927, 1713, 1654, 1496, 1466, 1454, 1392, 1366, 1251, 1221, 1169, 1055, 1029, 950, 870, 735, 700, 627.

2-acetamido-N-allyl-N-benzylacetamide (Ic):

Pale yellow foam, m = 67 mg, 83% Yield, \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): δ 7.33-7.02 (m, 5H), 6.67-6.44 (brs, 1H), 5.75-5.57 (m, 1H), 5.23-5.00 (m, 2H), 4.55 (s, 1.2H), 4.40 (s, 0.8H), 4.05 (s, 2H), 3.96 (d, J = 6.0 Hz, 0.8H), 3.74 (d, J = 4.5 Hz, 1.2H), 1.98 (s, 1.8H), 1.96 (s, 1.1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): δ 170.2, 168.6, 168.5, 136.7, 135.5, 132.2, 131.7, 129.2, 128.9, 128.3, 128.1, 127.8, 126.5, 118.4, 117.8, 49.3, 48.9, 48.4, 48.3, 41.6, 41.5, 23.2. MS (ESI): m/z = 247.4 [M+H\(^{+}\)]. HRMS (ESI): m/z calcd for C\(_{14}\)H\(_{15}\)O\(_2\)N\(_2\) [M+H\(^{+}\)] 247.1441, found 247.1441. IR (ν = cm\(^{-1}\)) : 3314, 3075, 2923, 1743, 1643, 1547, 1496, 1472, 1452, 1371, 1224, 1178, 1080, 1029, 927, 819, 738, 700, 627.

205.4 [M+H⁺]. HRMS (ESI): m/z calcd for C₁₂H₁₇ON₂ [M+H⁺] 205.1335, found 205.1328. IR (ν = cm⁻¹): 3297, 3018, 2920, 2851, 2336, 1746, 1650, 1496, 1453, 1360, 1277, 1168, 1079, 1029, 927, 747, 702, 663.

(S)-N-allyl-N-benzyl-2-((4-methylphenyl)sulfonamido)propanamide (1e):

Yellow oil, m = 115 mg, 55% Yield, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.75-7.67 (m, 2H), 7.32-7.22 (m, 5H), 7.07-6.91 (m, 2H), 5.94 (d, J = 8.5 Hz, 1H), 5.54-5.43 (m, 1H), 5.10 (dd, J = 1.5, 10.5 Hz, 1H), 5.00-4.92 (m, 1H), 4.60 (d, J = 15.0 Hz, 0.6H), 4.40-4.15 (m, 2.4H), 3.91 (dd, J = 6.0, 15.5 Hz, 0.4H), 3.75-3.66 (m, 1.6H), 2.44 (s, 1.1H), 2.42 (s, 1.9H), 1.37 (d, J = 6.5 Hz, 1.8H), 1.31 (d, J = 6.5 Hz, 1.2H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 172.2, 171.9, 143.4, 137.5, 137.4, 136.6, 135.5, 132.0, 131.8, 129.8, 129.7, 129.1, 128.8, 128.1, 128.0, 127.7, 127.3, 127.2, 126.8, 118.1, 118.0, 49.8, 49.1, 49.1, 48.7, 48.5, 48.0, 21.6, 21.1, 21.0. MS (ESI): m/z = 373.6 [M+H⁺]. HRMS (ESI): m/z calcd for C₂₉H₂₅O₃N₃S [M+H⁺] 373.1580, found 373.1576. IR (ν = cm⁻¹): 3209, 2986, 1637, 1412, 1339, 1163, 1093, 815, 699, 662. [α]²⁰D = +18 (c 1.1, CHCl₃).

(S)-N-allyl-N-benzyl-2-((4-methylphenyl)sulfonamido)-3-phenylpropanamide (1f):

Colorless oil, m = 162 mg, 77% Yield, ¹H NMR (CDCl₃, 500 MHz, ppm): δ 7.63 (d, J = 8.5 Hz, 1.2H), 7.58 (d, J = 8.5 Hz, 0.8H), 7.30-7.24 (m, 3H), 7.21-7.13 (m, 5H), 7.10-6.84 (m, 4H), 5.73 (d, J = 9.5 Hz, 0.6H), 5.70 (d, J = 9.0 Hz, 0.4H), 5.60-5.49 (m, 0.4H), 5.29-5.20 (m, 0.6H), 5.14-4.88 (m, 2H), 4.56 (d, J = 15.0 Hz, 0.6H), 4.44-4.34 (m, 1.1H), 4.24-4.10 (m, 1.4H), 3.94 (dd, J = 5.5, 14.5 Hz, 0.4H), 3.69 (dd, J = 6.5, 15.0 Hz, 0.4H), 3.48-3.38 (m, 1.2H), 3.04-2.81 (m, 2H), 2.41 (s, 1.2H), 2.39 (s, 1.8H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 171.1, 171.0, 143.4, 143.4, 137.7, 137.6, 136.5, 135.9, 135.8, 132.1, 132.0, 129.7, 129.7, 129.0, 128.7, 128.6, 127.9, 127.7, 127.3, 127.2, 127.0, 118.5, 118.4, 54.4, 54.3, 49.8, 48.8, 48.7, 48.5, 41.0, 40.8, 21.7. MS (ESI): m/z = 449.7 [M+H⁺]. HRMS (ESI): m/z calcd for C₂₉H₂₉O₃N₃S [M+H⁺] 449.1893, found 449.1904. IR (ν = cm⁻¹): 3193, 3029, 2924, 1632, 1454, 1416, 1337, 1159, 1092, 929, 700. [α]²⁰D = +5 (c 2.0, CHCl₃).

(2S,3R)-N-allyl-N-benzyl-3-methyl-2-((4-methylphenyl)sulfonamido)pentanamide (1g):
Colorless oil, m = 234 mg, 81% Yield, \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 7.75-7.68 (m, 2H), 7.35-7.20 (m, 5H), 7.07-6.88 (m, 2H), 5.86 (d, \(J = 9.0\) Hz, 0.4H), 5.84 (d, \(J = 9.0\) Hz, 0.6H), 5.45-5.33 (m, 1H), 5.13 (dd, \(J = 1.5, 10.5\) Hz, 0.6H), 5.07 (dd, \(J = 1.5, 10.0\) Hz, 0.4H), 4.96 (dd, \(J = 1.0, 17.0\) Hz, 0.6H), 4.88 (dd, \(J = 1.5, 17.0\) Hz, 0.4H), 4.63 (d, \(J = 15.0\) Hz, 0.6H), 4.36 (d, \(J = 16.5\) Hz, 0.4H), 4.30 (d, \(J = 16.0\) Hz, 0.4H), 4.19 (d, \(J = 15.0\) Hz, 0.6H), 4.07 (dd, \(J = 3.5, 9.0\) Hz, 0.4H), 3.98 (dd, \(J = 3.5, 9.0\) Hz, 0.6H), 3.86 (dd, \(J = 6.0, 15.0\) Hz, 0.4H), 3.74-7.58 (m, 1.6H), 2.45 (s, 1.2H), 2.43 (s, 1.8H), 1.69-1.56 (m, 1H), 1.55-1.39 (m, 1H), 1.20-1.09 (m, 1H), 1.04 (d, \(J = 6.5\) Hz, 1.8H), 1.00 (d, \(J = 7.0\) Hz, 1.2H), 0.91-0.81 (m, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 171.0, 170.7, 143.4, 137.2, 137.1, 136.6, 135.5, 132.0, 131.9, 129.7, 129.6, 128.9, 128.7, 128.2, 128.1, 127.6, 127.5, 127.0, 118.6, 117.9, 58.2, 57.9, 49.8, 48.9, 48.2, 47.6, 38.4, 38.1, 22.9, 22.8, 21.6, 16.3, 11.6. MS (ESI): m/z = 415.3 [M+H\(^+\)]. HRMS (ESI): m/z calcd for C\(_{23}\)H\(_{31}\)O\(_3\)N\(_2\)S [M+H\(^+\)] 415.2050, found 415.2055. IR (\(\nu = \text{cm}^{-1}\)): 3224, 2967, 2934, 2877, 1635, 1409, 1163, 1094, 814, 701, 665. [\(\alpha\)]\(^{20}\)\(_D\) = +66 (c 4.2, CHCl\(_3\)).

\(N\)-allyl-\(N\)-benzyl-2-nitroaniline (16):

Yellow-orange oil, m = 910 mg, 83 % Yield, \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 7.71 (dd, \(J = 2.0, 8.5\) Hz, 1H), 7.39-7.34 (m, 1H), 7.33-7.26 (m, 4H), 7.25-7.20 (m, 1H), 7.12 (dd, \(J = 1.5, 8.5\) Hz, 1H), 7.00-6.94 (m, 1H), 5.90-5.76 (m, 1H), 5.21-5.10 (m, 2H), 4.32 (s, 2H), 3.68 (dt, \(J = 1.5, 6.5\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 144.6, 143.9, 137.5, 133.8, 132.7, 128.6, 128.2, 127.4, 125.8, 123.2, 121.3, 118.7, 56.2, 56.1. MS (ESI): m/z = 269.2 [M+H\(^+\)]. HRMS (ESI): m/z calcd for C\(_{16}\)H\(_{17}\)O\(_2\)N\(_2\) [M+H\(^+\)] 269.1285, found 269.1280. IR (\(\nu = \text{cm}^{-1}\)): 3027, 2912, 2850, 1602, 1517, 1494, 1488, 1455, 1347, 1294, 1273, 1221, 926, 853.

\(N\)-allyl-\(N\)-benzylbenzene-1,2-diamine (17):

Orange oil, m = 91 mg, 66% Yield, \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 7.28-7.16 (m, 5H), 6.93 (d, \(J = 7.5\) Hz, 1H), 6.88 (t, \(J = 8.0\) Hz, 1H), 6.69 (d, \(J = 8.0\) Hz, 1H), 6.65 (t, \(J = 7.5\) Hz, 1H), 5.84-5.74 (m, 1H), 5.16-5.04 (m, 2H), 4.07 (s, 2H), 4.06-3.95 (brs, 2H), 3.49 (d, \(J = 6.5\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 142.5, 138.6, 137.3, 135.0, 128.9, 128.2, 127.0, 124.9, 123.0, 118.1, 117.6, 115.3, 56.7, 54.9. MS (ESI): m/z = 239.2 [M+H\(^+\)]. HRMS (ESI): m/z calcd for C\(_{16}\)H\(_{19}\)N\(_2\) [M+H\(^+\)]
239.1543, found 239.1541. IR (ν = cm$^{-1}$): 3436, 3348, 3063, 3026, 2926, 2816, 1639, 1607, 1498, 1455, 1417, 1364, 1295, 1268, 1199, 1136, 1104, 1077, 1028, 993, 919, 851, 822.
\(N\)-(2-(allyl(benzyl)amino)phenyl)-4-methylbenzenesulfonamide (3):

Colorless oil, \(m = 322\) mg, 98\% Yield, \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 8.21-8.06 (brs, 1H), 7.66 (d, \(J = 8.0\) Hz, 2H), 7.55 (dd, \(J = 1.5, 8.5\) Hz, 1H), 7.32-7.21 (m, 3H), 7.15 (d, \(J = 8.5\) Hz, 2H), 7.11 (dd, \(J = 1.5, 7.5\) Hz, 2H), 7.08-7.01 (m, 2H), 6.99-6.92 (m, 1H), 5.68-5.56 (m, 1H), 5.08-4.99 (m, 2H), 3.82 (s, 2H), 3.29 (d, \(J = 6.5\) Hz, 2H), 2.32 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 143.8, 139.4, 137.1, 136.7, 134.2, 133.9, 129.6, 129.0, 128.5, 127.5, 127.2, 126.1, 124.3, 123.5, 118.7, 117.5, 58.5, 57.0, 21.5. MS (ESI): \(m/z = 393.2\) [M+H\(^+\)]. HRMS (ESI): \(m/z\) calcd for \(C_{23}H_{24}O_2N_2S\) [M+H\(^+\)] 393.1631, found 393.1636. IR (\(\nu = \text{cm}^{-1}\)): 3247, 2921, 2847, 1492, 1455, 1381, 1335, 1289, 1216, 1164, 1091, 1031, 1010, 921, 813.
IV. $^1$H and $^{13}$C NMR spectra
NOESY: