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Supporting Information for

Anodic Benzylic C(sp³)-H Amination: A Unified Access to Pyrrolidines and Piperidines

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1. General Remarks

All solvents and reagents employed were purchased from Aldrich, Acros, TCI and Fluorochem. Column chromatography was performed on silica gel (PanReac AppliChem, Silica Gel 60, 0.063-0.2 mm). NMR spectroscopy was performed on a Bruker Avance 300 MHz, 400 MHz or 500 MHz, respectively. The chemical shifts are given in ppm normalized to the shift of residual chloroform in the deuterated chloroform (δ_H = 7.26 ppm and δ_C = 77.16 ppm). The multiplicities are stated as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS measurements were performed on a Kratos MS 50. IR spectroscopy was performed using a Bruker Alpha instrument in the solid state. Melting points were determined employing a Büchi B-540 instrument.

Cyclic voltammetry studies were carried out in a three-electrode cell using a Parstat 2273 potentiostat (Princeton Applied Research). As working electrode a glassy carbon disk (diameter: 3 mm) and as counter electrode a platinum wire were used. The working electrode was polished using alumina (0.05 μ m) prior to each experiment. As reference served a Ag/AgNO₃ electrode (silver wire in 0.1 M Bu₄NClO₄/CH₃CN; 0.01 M AgNO₃).^[1] The reference electrode was separated from the cell with a Vycor frit. 1,1,1,3,3,3-Hexafluoroisopropanol (99%, Fluorochem) was used as received. As supporting electrolyte served Bu₄NBF₄ (99%, Aldrich). The electrolyte was purged with Argon (5 min) prior to each experiment.

2. General protocol (GP 1) for the synthesis of the substrates for 5membered ring formation

The synthesis of the corresponding starting materials for the 5-membered ring formation was performed following the procedure reported in literature^[2] and is outlined below (Scheme S-1)



Scheme S-1. Substrate synthesis for 5-membered ring formation.

Step 1: The corresponding nitrile (1 equiv.) was dissolved in dry THF (0.4 M) under an argon atmosphere. The solution was cooled to -78 °C and LDA (2 M, 1.0 equiv.) was added dropwise at this temperature. The reaction mixture was stirred for 30 min at -78 °C. Subsequently, the corresponding bromide (1.2 equiv.) was added and the reaction mixture was warmed to room temperature and stirred for an additional 12 h. Then, the reaction mixture was quenched by addition of a saturated solution of NH₄Cl and extracted with DCM (3 x). The combined organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was used without further purification for the next step.

Step 2: LiAlH₄ (3 equiv. based on the nitrile from step 1) was added to a two-neck flask with a stirring bar and a reflux condenser. Subsequently, Et_2O (0.25 M based on nitrile) was carefully added and the suspension was cooled to 0 °C. The crude product from step 1 was dissolved in a small volume of Et_2O and added dropwise to the suspension. Then, the reaction mixture was refluxed for 2 h after which the reaction was cooled again to 0 °C and quenched with a 10% aqueous solution of NaOH. The mixture was filtered over a pad of Na₂SO₄ and the solvent was removed under reduced pressure to yield the crude amine in quantitative yields.

Step 3: The crude amine from step 2 (1 equiv.) was dissolved in pyridine (0.4 M) and the solution was cooled to 0 °C. The corresponding sulfonylchloride was added in one portion and the reaction mixture was stirred for 12 h at room temperature. Then, the mixture was diluted with DCM and washed with a 5% aqueous solution of HCl (3 x). The organic layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The thus obtained crude product was further purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as eluents.

3. Variation of General Protocol 1 (GP 1.1)

For the synthesis of the required nitriles the first step of **GP 1** was replaced by a Suzuki coupling.^[3] Pd(OAc)₂ (6.9 mg, 0.031 mmol, 1 mol%), PPh₃ (16.0 mg, 0.061 mmol, 2 mol%), arylboronic acid (4.59 mmol, 1.5 equiv.) and K₃PO₄ (2.6 g, 12.24 mmol, 4 equiv.) were added to a flame-dried Schlenk tube. Dry toluene (10 mL) was added followed by addition of 2-(bromomethyl)benzonitrile (0.6 g, 3.06 mmol, 1 equiv.). The reaction mixture was stirred overnight at 80 °C and then quenched by addition of water. The mixture was extracted with Et₂O and the combined organic phases were washed with water, aqueous NaOH solution (1M), brine and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure and the crude product was directly used for the reduction of the nitrile (Step 2, **GP 1**).

4. General protocol (GP 2) for the synthesis of the substrates for 6membered ring formation

The synthesis of the corresponding starting materials for the 6-membered ring formation was performed following the procedure reported in literature^[4] and is outlined below (Scheme S-2).



Scheme S-2. Substrate synthesis for 6-membered ring formation.

Step 1: Diethyl malonate (1.05 equiv.) was added dropwise to a suspension of NaH (60% on mineral oil, 1.05 equiv.) in dry THF at 0 °C. After 15 min the corresponding benzyl bromide was added in one portion and the reaction mixture was refluxed for 1 h. Subsequently, the reaction was cooled and quenched by the addition of H₂O. The solvent was removed under reduced pressure and the crude product was dissolved in Et₂O and washed with H₂O. The aqueous layer was extracted with Et₂O and the combined organic layers were dried over Na₂SO₄. The crude product which was obtained after evaporation of the solvent was directly used in the next step.

Step 2: The diester (1.0 equiv.), NaCl (2.1 equiv.) and H_2O (2.1 equiv.) were dissolved in DMSO and stirred at reflux for 8 h. Then, the reaction mixture was cooled to room temperature, diluted with a aqueous solution of HCl (3 M) and extracted with ethyl acetate (3 x). The combined organic layers were washed with water, brine and dried over Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was filtered through a pad of silica to obtain the desired ester.

Step 3: The crude ester from step 2 was dissolved in dry THF and the solution was cooled to 0 °C. Then, LiAlH₄ (2 equiv.) was carefully added and the resulting suspension was stirred for 2 h at room temperature. After completion of the reaction time the mixture was cooled again to 0 °C and quenched by slow addition of a 10% aqueous solution of NaOH. Filtration over a pad of Na₂SO₄ and removal of the solvent under reduced pressure yielded the crude alcohol.

Step 4: The crude alcohol from step 3 and CBr_4 (1.05 equiv.) were dissolved in dry DCM. The solution was cooled to 0 °C and triphenylphosphine (1.05 equiv.) was added portion-wise. The reaction mixture was stirred at room temperature and monitored by TLC. After consumption of the starting material, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent.

Once the corresponding bromide was obtained, **GP 1** was followed to synthesize the substrates for the 6-membered ring formation.

5. General protocol (GP 3) for the electrochemical cyclization reaction

The corresponding substrate (0.2 mmol) and Bu_4NBF_4 (0.1 M) were dissolved in 10 mL 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) in an undivided cell. As cathode material, a platinum mesh (Alfa Aesar, 25 x 25 mm) was employed. A graphite rod (Alfa Aesar, d = 6.3 mm, immersion depth: 10 mm) served as anode material. The electrolysis was performed under constant current conditions (2.5 mA, 4 h 40 min) and a charge of 2.2 F was applied. After completion of the electrolysis, the solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluents.

6. General protocol (GP 4) for carbon-carbon bond formation with 2-hexafluoroisopropoxy pyrrolidine 9

A flame-dried Schlenk flask was charged with 2-hexafluoroisopropoxy pyrrolidine **9** (0.1 mmol, 1 equiv.) and dry diethyl ether (1 mL) under an argon atmosphere. The resulting solution was then cooled to -78 °C and the corresponding alkyl magnesium bromide reagent (1.2 equiv.) was added slowly at that temperature. The reaction mixture was stirred for 5 min at -78 °C, warmed to room temperature and stirred for 12 h at room temperature. The reaction was quenched by addition of a saturated aqueous NH₄Cl solution and the layers were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (hexane/ethyl acetate).

7. Electrochemical set-up

As experimental set-up, a stirring plate and a schlenk tube with a stir bar were used. The electrodes were fixed by a Teflon cap. As cathode material, a platinum mesh (Alfa Aesar, 25 x 25 mm) was employed. A graphite rod (Alfa Aesar, d = 6.3 mm, immersion depth: 10 mm) served as anode material (Figure S-1).





Figure S-1. Experimental set-up for anodic aliphatic C-H amination.

8. Cyclic voltammetric studies

Comparison of oxidation potentials of sulfonamide substrate 1f vs. pyrrolidine product 2f:

Sulfonamide substrate **1f** is irreversibly oxidized at a potential of 1.79 V vs. Ag/AgNO₃ while the corresponding pyrrolidine product **2f** is oxidized at a higher potential of 1.88 V vs. Ag/AgNO₃ ($\Delta E = 90$ mV). Thus, pyrrolidine products are efficiently formed (Figure S-2).



Figure S-2. Cyclic voltammetry of **1f** (3 mM, red line) and **2f** (3 mM, brown line). The voltammogram for the blank electrolyte is shown for comparison (black line). Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/0.01 M AgNO₃ in 0.1 M Bu₄NClO₄; scan rate: 50 mV s⁻¹; cut-off current density for oxidation defined as $j_{lim.} = 0.1 \text{ mA cm}^{-2}$.

Comparison of oxidation potentials of *N*-(5-(pyridin-3-yl)pentyl)benzenesulfonamide vs. 3-ethylpyridine:

By comparison of the oxidation potentials of N-(5-(pyridin-3-yl)pentyl)benzenesulfonamide and 3-ethylpyridine it is obvious, that sulfonamide oxidation occurs prior to oxidation of the electron-poor arene core (Figure S-3). The oxidation of the sulfonamide does not lead to product formation as demonstrated by an electrolysis with N-(5-(pyridin-3-yl)pentyl)benzenesulfonamide as substrate.



Figure S-3. Cyclic voltammetry of *N*-(5-(pyridin-3-yl)pentyl)benzenesulfonamide (3 mM, violet line) and 3-ethylpyridine (3 mM, orange line). The voltammogram for the blank electrolyte is shown for comparison (black line). Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/0.01 M AgNO₃ in 0.1 M Bu₄NClO₄; scan rate: 50 mV s⁻¹.

9. Mechanistic proposal for the C-C cleavage observed during electrochemical oxidation of alcohol 8

Upon electrochemical oxidation of alcohol **8**, the epoxide **I** is formed by trapping of the anodically generated benzylic cation. This step is expected to be more rapid than the direct piperidine formation. Epoxide **I** is opened by nucleophilic attack of the tosylamide leading to aminoalcohol **II**. This 1,2-aminoalcohol **II** undergoes C-C cleavage⁵ upon further anodic oxidation leading to benzaldehyde **III** and a *N*-tosyliminium ion **IV**, which is trapped by the solvent HFIP (Scheme S-3).



Scheme S-3. Mechanistic proposal for C-C cleavage observed during electrochemical oxidation of alcohol **8**.

10. Analytical data starting materials 5-membered rings

N-(2,2-dimethyl-4-phenylbutyl)-4-methylbenzenesulfonamide (1a)

 ${\bf 1a}$ was synthesized according to ${\bf GP}~{\bf 1}.$ The NMR data match those previously reported in literature. $^{[2]}$

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.79-7.74 (m, 2H), 7.35-7.25 (m, 4H), 7.22-7.13 (m, 3H), 4.65 (bs, 1H), 2.76 (d, *J*=6.9 Hz, 2H), 2.57-2.48 (m, 2H), 2.44 (s, 3H), 1.56-1.49 (m, 2H), 0.95 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 142.7, 137.1, 129.8, 128.5, 128.4, 127.2, 125.9, 53.0, 41.6, 34.2, 30.4, 25.1, 21.6.

N-(2,2-dimethyl-4-phenylbutyl)-4-nitrobenzenesulfonamide (1b)

1b was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 8.40-8.27 (m, 2H), 8.03-7.97 (m, 2H), 7.41-7.04 (m, 5H), 4.58 (bs, 1H), 2.89-2.76 (m, 2H), 2.56-2.45 (m, 2H), 1.56-1.41 (m, 2H), 0.94 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ = 150.1, 146.0, 142.4, 128.6, 128.4, 128.3, 126.1, 124.5, 53.3, 41.5, 34.4, 30.4, 25.0.

N-(2,2-dimethyl-4-phenylbutyl)methanesulfonamide (1c)

1c was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[6]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.34-7.28 (m, 2H), 7.24-7.17 (m, 3H), 4.42 (bs, 1H), 2.98 (d, J=6.9 Hz, 2H), 2.95 (s, 3H), 2.65-2.54 (m, 2H), 1.66-1.54 (m, 2H), 1.03 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.6, 128.6, 128.4, 126.0, 53.1, 41.7, 40.1, 34.3, 30.5, 25.0.

N-(2,2-Dimethyl-4-phenylbutyl)-2-(trimethylsilyl)ethane-1-sulfonamide (1d)



1d was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (500 MHz, CDCl₃): δ = 7.35-7.27 (m, 2H), 7.23-7.18 (m, 3H), 4.26 (t, *J*=6.9 Hz, 1H), 3.02-2.90 (m, 4H), 2.66-2.57 (m, 2H), 1.62-1.52 (m, 2H), 1.06-0.98 (m, 8H), 0.07 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ = 142.7, 128.6, 128.4, 126.0, 53.3, 48.6, 41.7, 34.4, 30.5, 25.0, 10.8, -1.9.

4-methyl-N-((1-phenethylcyclohexyl)methyl)benzenesulfonamide (1e)

1e was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.78-7.72 (m, 2H), 7.37-7.22 (m, 4H), 7.20-7.10 (m, 3H), 2.82 (s, 2H), 2.41-2.36 (m, 5H), 1.65-1.52 (m, 2H), 1.46-1.18 (m, 10H).

¹³C NMR (**75 MHz, CDCl**₃): δ = 143.5, 142.9, 137.1, 129.9, 128.5, 128.5, 127.2, 125.9, 49.3, 37.5, 36.2, 33.6, 29.3, 26.2, 21.7, 21.4.

4-Methyl-N-(4-phenylbutyl)benzenesulfonamide (1f)

Ph

1f was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.75 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.33-7.22 (m, 4H), 7.21-7.14 (m, 1H), 7.13-7.08 (m, 2H), 4.67 (bs, 1H), 2.95 (q, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.70-1.43 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ = 143.5, 141.9, 137.1, 129.8, 128.5, 127.2, 126.0, 43.2, 35.4, 29.2, 28.3, 21.6.

N-(2,2-Dimethyl-4-phenylbutyl)benzamide (1g)



1g was synthesized according to **GP 1** applying the first two steps. Then, the crude amine (1 equiv.) and pyridine (1.5 equiv.) were dissolved in dry CH_2Cl_2 and cooled to 0 °C. Subsequently, benzoyl chloride (1.5 equiv.) was slowly added at 0 °C. The reaction mixture was then warmed to room temperature and stirred overnight at room temperature. The solvent was evaporated under reduced pressure. The thus obtained crude product was further purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as eluents. The product was obtained as a white solid (69%). The NMR data match those previously reported in literature.^[6]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.78-7.71 (m, 2H), 7.54-7.40 (m, 3H), 7.32-7.24 (m, 2H), 7.22-7.14 (m, 3H), 6.13 (bs, 1H), 3.38 (d, *J* = 6.4 Hz, 2H), 2.72-2.59 (m, 2H), 1.66-1.54 (m, 2H), 1.04 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 167.7, 142.9, 135.0, 131.4, 128.6, 128.5, 128.4, 126.8, 125.8, 49.3, 42.2, 34.9, 30.6, 25.1.

N-(2,2-Dimethyl-4-phenylbutyl)-2,2,2-trifluoroacetamide (1h)



1h was synthesized according to **GP 1** applying the first two steps. Then, the crude amine (1 equiv.) and pyridine (1.2 equiv.) were dissolved in dry CH_2Cl_2 and cooled to 0 °C.

Subsequently, trifluoroacetic anhydride (1.2 equiv.) was slowly added at 0 °C. The reaction mixture was then warmed to room temperature and stirred overnight at room temperature. The solvent was evaporated under reduced pressure. The thus obtained crude product was further purified by column chromatography on silica gel using *n*-hexane and ethyl acetate as eluents. The product was obtained as a white solid (44%). The NMR data match those previously reported in literature.^[6]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.32-7.27 (m, 2H), 7.22-7.16 (m, 3H), 6.19 (bs, 1H), 3.25 (d, *J* = 6.5 Hz, 2H), 2.65-2.58 (m, 2H), 1.58-1.52 (m, 2H), 1.00 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 157.6 (q, *J* = 36.6 Hz), 142.5, 128.7, 128.4, 126.1, 116.1 (d, *J* = 288.1 Hz), 49.4, 42.0, 34.9, 30.6, 25.0.

¹⁹F NMR (375 MHz, CDCl₃): δ = -75.9.

N-(2,2-dimethyl-4-(*p*-tolyl)butyl)-4-methylbenzenesulfonamide (1i)



1i was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.04 (q, *J* = 8.1 Hz, 4H), 4.56 (t, *J* = 6.7 Hz, 1H), 2.73 (d, *J* = 6.9 Hz, 2H), 2.50-2.43 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 1.53-1.42 (m, 2H), 0.92 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.4, 139.6, 137.1, 135.3, 129.8, 129.2, 128.3, 127.2, 53.0, 41.8, 34.1, 29.9, 25.1, 21.6, 21.1.

N-(4-(4-Fluorophenyl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide (1j)



1j was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (400 MHz, CDCl₃): δ = 7.77-7.73 (m, 2H), 7.32-7.26 (m, 2H), 7.10-7.03 (m, 2H), 6.92 (t, *J* = 8.1 Hz, 2H), 2.73 (s, 2H), 2.54-2.43 (m, 2H), 2.41 (s, 3H), 1.51-1.42 (m, 2H), 0.91 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 161.3 (d, *J* = 243.2 Hz), 143.5, 138.3, 137.1, 129.8, 129.7 (d, *J* = 7.7 Hz), 127.2, 115.2 (d, *J* = 21.2 Hz), 52.9, 41.7, 34.1, 29.6, 25.1, 21.6. ¹⁹F NMR (375 MHz, CDCl₃): δ = -118.1. N-(4-(4-chlorophenyl)-2,2-dimethylbutyl)-4-methylbenzenesulfonamide (1k)



1k was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.32-7.27 (m, 2H), 7.23-7.17 (m, 2H), 7.10-7.03 (m, 2H), 4.66 (t, *J* = 6.9 Hz, 1H), 2.72 (d, *J* = 6.9 Hz, 2H), 2.52-2.43 (m, 2H), 2.42 (s, 3H), 1.53-1.40 (m, 2H), 0.91 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 141.1, 137.1, 131.5, 129.9, 129.8, 128.5, 127.2, 52.9, 41.4, 34.2, 29.8, 25.1, 21.7.

N-(2,2-dimethyl-4-(m-tolyl)butyl)-4-methylbenzenesulfonamide (1)



1I was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[6]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.74 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.01-6.91 (m, 3H), 4.57 (bs, 1H), 2.73 (s, 2H), 2.50-2.43 (m, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 1.56-1.43 (m, 2H), 0.92 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.4, 142.6, 138.1, 137.1, 129.8, 129.2, 128.4, 127.2, 126.6, 125.4, 53.0, 41.7, 34.2, 30.3, 25.1, 21.6, 21.5.

4-Methyl-N-(2-(4-methylbenzyl)benzyl)benzenesulfonamide (1m)



1m was synthesized according to **GP 1.1**. The NMR data match those previously reported in literature.^[6]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.76-7.70 (m, 2H), 7.35-7.30 (m, 2H), 7.30-7.24 (m, 2H), 7.23-7.15 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.97-6.92 (m, 2H), 4.83 (t, *J* = 6.2 Hz, 1H), 4.08 (d, *J* = 6.0 Hz, 2H), 3.95 (s, 2H), 2.49 (s, 3H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 139.3, 137.1, 136.6, 135.6, 134.3, 130.7, 129.7, 129.6, 129.2, 128.5, 128.2, 127.2, 126.8, 44.9, 38.1, 21.5, 21.0.

4-Methyl-N-(2-(4-chlorobenzyl)benzyl)benzenesulfonamide (1n)



1n was synthesized according to **GP 1.1**. White solid, 66%.

¹H NMR (300 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.28 - 7.15 (m, 5H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 2H), 4.33 (t, *J* = 6.1 Hz, 1H), 3.99 (d, *J* = 6.0 Hz, 2H), 3.92 (s, 2H), 2.45 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.8, 138.9, 138.7, 136.5, 134.2, 132.2, 131.0, 130.0, 129.9, 129.9, 128.8, 128.7, 127.4, 45.2, 37.9, 21.7.

IR v (cm⁻¹): 3280, 1598.

mp: 119-120 °C.

HRMS: Mass calculated for C₂₁H₂₀NNaO₂S: 408.0795, found: 408.0795.

4-Methyl-N-(2-(4-fluorobenzyl)benzyl)benzenesulfonamide (10)



1o was synthesized according to **GP 1.1**. White solid, 67%.

¹**H NMR (400 MHz, CDCl₃):** δ = 7.75-7.60 (m, 2H), 7.32-7.22 (m, 3H), 7.21-7.18 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.99-6.85 (m, 4H), 4.38 (bs, 1H), 4.00 (d, *J* = 4.1 Hz, 2H), 3.92 (s, 2H), 2.44 (s, 3H).

¹³**C NMR (100 MHz, CDCl₃):** δ = 161.5 (d, *J* = 244.6 Hz), 143.7, 139.2, 136.6, 135.8, 135.8, 134.2, 130.9, 130.1, 130.0, 129.9, 129.9, 128.6, 127.4, 127.3, 115.4 (d, *J* = 21.2 Hz), 45.2, 37.8, 21.7.

¹⁹F NMR (375 MHz, CDCl₃): δ = -116.93.

IR v (cm⁻¹): 3247, 1598, 1505.

mp: 115-117 °C.

HRMS: Mass calculated for C₂₁H₂₀FNNaO₂S: 392.1091, found: 392.1088.

4-Methyl-N-(2-(4-(trifluoromethyl)benzyl)benzyl)benzenesulfonamide (1p)



1p was synthesized according to **GP 1.1**. White solid, 50%.

¹H NMR (300 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.32-7.24 (m, 3H), 7.24-7.17 (m, 2H), 7.16-7.08 (m, 3H), 4.38 (bs, 1H), 4.03 (s, 2H), 3.99 (d, *J* = 6.1 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 144.4, 143.8, 138.4, 136.5, 134.2, 131.1, 130.0, 129.9, 129.0, 128.9, 128.8, 128.5, 127.5, 127.3, 126.1, 125.5 (q, *J* = 3.7 Hz), 122.5, 45.3, 38.3, 21.7.

¹⁹F NMR (375 MHz, CDCl₃): δ = -62.5.

IR v (cm⁻¹): 3285, 1617, 1598.

mp: 133-134 °C.

HRMS: Mass calculated for $C_{22}H_{20}F_3NNaO_2S$: 442.1059, found: 442.1059.

4-Methyl-N-(2-(4-(tert-butyl)benzyl)benzyl)benzenesulfonamide (1q)



1q was synthesized according to GP 1.1. White solid, 62%.

¹**H NMR (500 MHz, CDCl₃):** δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.33-7.30 (m, 2H), 7.30-7.27 (m, 3H), 7.26-7.24 (m, 1H), 7.23-7.22 (m, 2H), 7.21-7.17 (m, 2H), 6.96-6.90 (m, 2H), 4.17 (t, *J* = 6.1 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 2H), 3.93 (s, 2H), 2.47 (s, 3H), 1.33 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ = 149.4, 143.6, 139.5, 137.2, 136.8, 134.4, 131.1, 130.1, 129.8, 128.5, 128.3, 127.4, 127.1, 125.6, 45.2, 38.3, 34.5, 31.5, 21.7.

IR v (cm⁻¹): 2385, 2958, 1596.

mp: 114-116 °C.

HRMS: Mass calculated for C₂₅H₂₉NNaO₂S: 430.1811, found: 430.1808.

4-Methyl-N-(2-(thiophen-2-ylmethyl)benzyl)benzenesulfonamide (1r)



1r was synthesized according to **GP 1.1**. The NMR data match those previously reported in literature.^[6]

¹H NMR (300 MHz, CDCl₃): δ = 7.69 (d, J = 8.3 Hz, 2H), 7.34-7.18 (m, 6H), 7.13 (dd, J = 5.2, 1.2 Hz, 1H), 6.88 (dd, J = 5.2, 3.4 Hz, 1H), 6.62-6.58 (m, 1H), 4.25 (bs, 1H), 4.10 (s, 2H), 4.07 (s, 2H), 2.44 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.7, 143.6, 138.9, 136.6, 134.1, 130.6, 130.1, 129.9, 128.8, 127.6, 127.4, 127.0, 125.3, 124.3, 45.1, 33.1, 21.7.

N-(2-(benzofuran-2-ylmethyl)benzyl)-4-methylbenzenesulfonamide (1s)



1s was synthesized according to **GP 1.1**.

¹H NMR (500 MHz, CDCl₃): δ = 7.71-7.65 (m, 2H), 7.46-7.43 (m, 1H), 7.40-7.35 (m, 1H), 7.25-7.19 (m, 7H), 7.19-7.15 (m, 1H), 6.25 (d, *J* = 1.0 Hz, 1H), 4.71 (bs, 1H), 4.16 (d, *J* = 4.3 Hz, 2H), 4.02 (s, 2H), 2.40 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 156.9, 155.0, 143.7, 136.5, 135.9, 134.2, 130.9, 130.1, 129.8, 128.8, 128.7, 127.7, 127.3, 123.8, 122.8, 120.6, 111.0, 103.6, 45.2, 31.8, 21.7.
 IR v (cm⁻¹): 3267, 3063, 2855, 1599.
 mp: 100-101 °C.

HRMS: Mass calculated for C₂₃H₂₁NNaO₃S: 414.1134, found: 414.1149.

3,4,5,6-tetrahydro-2*H*-benzo[*g*][1,2]thiazocine 1,1-dioxide (1t)



1t was synthesized according to the literature and the NMR data match those previously reported.^[2]

¹**H NMR (500 MHz, CDCl₃)**: δ = 7.99 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.32-7.28 (m, 2H), 4.54 (bs, 1H), 3.44-3.39 (m, 2H), 3.34 (t, *J* = 6.7 Hz, 2H), 1.87 (p, *J* = 6.6 Hz, 2H), 1.55-1.48 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ = 142.2, 140.0, 132.8, 132.1, 128.0, 126.6, 41.8, 30.7, 29.5, 27.4.

N-2-(2,3-Dihydro-1H-inden-2-yl)ethyl)-4-methylbenzenesulfonamide (1u)



1u was synthesized according to **GP 1** starting from the known amine^[7] applying step 3.The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.84-7.72 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.21-7.07 (m, 4H), 4.52 (bs, 1H), 3.13-2.91 (m, 4H), 2.60-2.40 (m, 6H), 1.69 (q, *J* = 7.1 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃): δ = 143.6, 142.9, 137.0, 129.9, 127.3, 126.4, 124.5, 42.3, 39.0, 37.4, 35.6, 21.7.

4-Methyl-*N*-(1-methyl-4-phenylbutyl)benzenesulfonamide (1v)



1v was synthesized according to **GP 1** starting from the known amine^[8] applying step 3. Brown oil, 9%.

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.76 (d, J = 8.3 Hz, 2H), 7.31-7.23 (m, 4H), 7.23-7.15 (m, 1H), 7.11-7.07 (m, 2H), 4.32 (d, J = 8.3 Hz, 1H), 3.42-3.29 (m, 1H), 2.51 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H), 1.64-1.47 (m, 2H), 1.47-1.34 (m, 2H), 1.02 (d, J = 6.6 Hz, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.3, 142.0, 138.4, 129.8, 128.5, 128.4, 127.2, 125.9, 50.0, 37.2, 35.5, 27.4, 22.0, 21.7.

HRMS: Mass calculated for C₁₈H₂₃NNaO₂S: 340.1342, found: 340.1332. **IR v (cm⁻¹):** 3278, 2930, 1598.

4-Methyl-N-(2-methyl-4-phenylbutyl)benzenesulfonamide (1w)

Ph

1w was synthesized according to **GP 1**. The NMR data match those previously reported in literature.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.82-7.70 (m, 2H), 7.34-7.24 (m, 4H), 7.22-7.17 (m, 1H), 7.15-7.10 (m, 2H), 2.89 (dd, *J* = 12.5, 5.7 Hz, 1H), 2.80 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.69-2.47 (m, 2H), 2.44 (s, 3H), 1.76-1.54 (m, 2H), 1.49-1.34 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.3, 142.0, 137.0, 129.7, 128.4, 128.3, 127.1, 125.8, 48.9, 35.7, 33.0, 32.8, 21.5, 17.4.

4-Methyl-*N*-(2-ethyl-4-phenylbutyl)benzenesulfonamide (1x)

1x was synthesized according to GP 1. Colorless oil, 51%.

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.33-7.22 (m, 4H), 7.21-7.14 (m, 1H), 7.14-7.08 (m, 2H), 4.34 (bs, 1H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.57-2.47 (m, 2H), 2.42 (s, 3H), 1.62-1.50 (m, 2H), 1.49-1.24 (m, 3H), 0.82 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 142.2, 137.1, 129.8, 128.5, 128.4, 127.2, 126.0, 45.7, 38.9, 32.9, 32.9, 24.0, 21.7, 10.8.

HRMS: Mass calculated for C₁₉H₂₆NO₂S: 332.1679, found: 332.1673. **IR v (cm⁻¹):** 3280, 2928, 1603.

11. Analytical data starting materials 6-membered rings

N-(2,2-Dimethyl-5-phenylpentyl)-4-methylbenzenesulfonamide (5a)

5a was synthesized according to **GP 1** using (3-Bromopropyl)benzene as starting material. The NMR data match those previously reported in literature.^[4]

¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.34-7.31 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.15 (m, 3H), 4.38 (s, 1H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.56-1.45 (m, 2H), 1.29-1.21 (m, 2H), 0.85 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 142.5, 137.2, 129.8, 128.5, 128.4, 127.2, 125.9, 53.0, 39.2, 36.6, 33.9, 25.9, 25.0, 21.6.

4-Methyl-N-((3-Phenylpropyl)cyclohexyl)methyl)benzenesulfonamide (5b)



5b was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.76 (d, *J* = 8.4 Hz, 2H), 7.35-7.24 (m, 4H), 7.24-7.19 (m, 1H), 7.18-7.12 (m, 2H), 4.37 (bs, 1H), 2.75 (d, *J* = 6.4 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.49-1.16 (m, 14H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.4, 142.6, 137.1, 129.8, 128.4, 128.5, 127.2, 125.9, 49.1, 36.6, 35.9, 34.9, 33.6, 26.2, 24.7, 21.7, 21.4.

2-Bromo-N-(2,2-dimethyl-5-phenylpentyl)benzenesulfonamide (5c)



5c was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 8.14 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52-7.38 (m, 2H), 7.33-7.25 (m, 2H), 7.24-7.14 (m, 3H), 5.07 (t, *J* = 6.8 Hz, 1H), 2.62 (d, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.65-1.45 (m, 2H), 1.34-1.22 (m, 2H), 0.87 (s, 6H).

¹³C NMR (125 MHz, CDCl₃): δ = 142.4, 138.8, 135.1, 133.8, 131.8, 128.5, 128.5, 128.0, 126.0, 119.7, 53.1, 39.2, 36.6, 33.9, 25.9, 25.1.

N-(5-(4-(tert-Butyl)phenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (5d)



5d was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.72 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.2 Hz, 4H), 7.08 (d, J = 8.3 Hz, 2H), 4.26 (bs, 1H), 2.67 (d, J = 6.9 Hz, 2H), 2.49 (t, J = 7.7 Hz, 2H), 2.42 (s, 3H), 1.56-1.54 (m, 2H), 1.54-1.41 (m, 2H), 1.31 (s, 9H), 1.28-1.19 (m, 2H), 0.83 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 148.7, 143.5, 139.4, 137.2, 129.8, 128.1, 127.2, 125.4, 53.1, 39.3, 36.1, 34.5, 33.9, 31.6, 25.9, 25.0, 21.7.

N-(5-([1,1'-Biphenyl]-4-yl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (5e)



5e was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.3 Hz, 2H), 7.61-7.57 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.47-7.40 (m, 2H), 7.36-7.27 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.41 (t, *J* = 6.8 Hz, 1H), 2.69 (d, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 1.59-1.45 (m, 2H), 1.31-1.21 (m, 2H), 0.85 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 141.6, 141.2, 138.9, 137.2, 129.8, 128.9, 128.9, 127.2, 127.2, 127.1, 53.0, 39.2, 36.3, 33.9, 25.8, 25.1, 21.7.

N-(5-(4-Chlorophenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (5f)



5f was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.32-7.27 (m, 2H), 7.26-7.20 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.56 (bs, 1H), 2.66 (d, *J* = 6.7 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.55-1.39 (m, 2H), 1.27-1.15 (m, 2H), 0.82 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 140.9, 137.1, 131.6, 129.8, 128.5, 127.2, 53.0, 39.0, 35.9, 33.9, 25.7, 25.0, 21.7.

N-(5-(4-Fluorophenyl-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (5g)



5g was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12-7.05 (m, 2H), 6.99-6.91 (m, 2H), 4.49 (bs, 1H), 2.71-2.62 (m, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.54-1.38 (m, 2H), 1.29-1.16 (m, 2H), 0.82 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ = 161.3 (d, *J* = 243.3 Hz), 143.5, 138.1 (d, *J* = 3.1 Hz), 137.2, 129.8, 129.8 (d, *J* = 9.3 Hz), 127.2, 115.1 (d, *J* = 20.9 Hz), 53.0, 39.0, 35.8, 33.9, 25.9, 25.0, 21.7.

¹⁹F NMR (375 MHz, CDCl₃): δ = -117.97 (ddd, J = 14.2, 8.8, 5.4 Hz).

4-(4,4-Dimethyl-5-((4-methylphenyl)sulfonamido)pentyl)phenyl benzoate (5h)



5h was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 8.21 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.68-7.60 (m, 1H), 7.55-7.46 (m, 2H), 7.34-7.29 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 4.46 (t, *J* = 6.9 Hz, 1H), 2.68 (d, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.57-1.43 (m, 2H), 1.30-1.21 (m, 2H), 0.84 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 165.5, 149.1, 143.5, 140.1, 137.1, 133.7, 130.3, 129.9, 129.8, 129.4, 128.7, 127.2, 121.6, 53.0, 39.1, 36.1, 33.9, 25.8, 25.0, 21.7.

N-2,2-dimethyl-5-(o-tolyl)pentyl)-4-methylbenzenesulfonamide (5i)



5i was synthesized according to **GP 2**. The NMR data match those previously reported in literature.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.32-7.28 (m, 2H), 7.16-7.05 (m, 4H), 4.50 (bs, 1H), 2.67 (d, *J* = 6.8 Hz, 2H), 2.56-2.47 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 1.54-1.35 (m, 2H), 1.34-1.22 (m, 2H), 0.84 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ = 143.4, 140.7, 137.2, 135.9, 130.3, 129.8, 128.8, 127.2, 126.0, 53.1, 39.5, 33.9, 25.0, 24.6, 21.6, 19.4.

N-(5-(3,5-dimethylphenyl)-2,2-dimethylpentyl)-4-methylbenzenesulfonamide (5j)

5j was synthesized according to GP 2. Obtained as a white solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.79-7.72 (m, 2H), 7.33-7.28 (m, 2H), 6.87-6.75 (m, 3H), 4.60 (t, *J* = 6.8 Hz, 1H), 2.67 (d, *J* = 6.8 Hz, 2H), 2.48-2.41 (m, 5H), 2.30 (s, 6H), 1.51-1.42 (m, 2H), 1.28-1.18 (m, 2H), 0.84 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 142.5, 137.9, 137.2, 129.8, 127.6, 127.2, 126.3, 53.0, 39.3, 36.5, 33.9, 26.0, 25.0, 21.6, 21.4.

IR v (cm⁻¹): 3273, 2958, 2933, 2868, 1603.

mp: 86-88 °C.

HRMS: Mass calculated for C₂₂H₃₂NO₂S: 374.2148, found: 374.2143.

N-(2-Benzylphenethyl)-4-methylbenzenesulfonamide (5k)



 $\mathbf{5k}$ was synthesized according to the literature and the NMR data match those previously reported. $^{[4]}$

¹H NMR (300 MHz, CDCl₃): δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.30-7.24 (m, 3H), 7.24-7.11 (m, 5H), 7.11-7.02 (m, 3H), 4.32 (bs, 1H), 3.95 (s, 2H), 3.09-2.99 (m, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 140.6, 139.0, 137.0, 136.3, 131.2, 129.9, 129.8, 128.7, 128.6, 127.2, 127.1, 126.3, 43.5, 39.1, 33.0, 21.7.

4-methyl-N-((1,2,3,4-tetrahydronaphthalen-1-yl)methyl)benzenesulfonamide (5l)



5I was synthesized from the corresponding known amine^[9] by applying the last step of **GP1**.

¹H NMR (500 MHz, CDCl₃): δ = 7.78 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.13-7.04 (m, 4H), 5.12-5.07 (m, 1H), 3.23-3.17 (m, 1H), 3.16-3.08 (m, 1H), 3.00-2.91 (m, 1H), 2.75-2.69 (m, 2H), 2.44 (s, 3H), 1.93-1.86 (m, 1H), 1.86-1.81 (m, 1H), 1.81-1.74 (m, 1H), 1.72-1.65 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 143.4, 137.9, 137.0, 136.5, 129.7, 129.4, 128.6, 127.1, 126.4, 125.8, 48.2, 37.6, 29.5, 25.4, 21.5, 19.3. IR v (cm⁻¹): 3286, 2929, 1598. mp: 107-108 °C.

HRMS: Mass calculated for $C_{18}H_{20}NO_2S$: 314.1220, found: 314.1219.

N-(3-(2,3-Dihydro-1H-inden-2-yl)propyl)-4-methylbenzenesulfonamide (5m)



The required amine was synthesized according to an adaption of a previously reported procedure^[7] and was tosylated by applying the last step of **GP 1**. The NMR data match those previously reported in literature.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.19-7.08 (m, 4H), 4.33 (t, *J* = 6.2 Hz, 1H), 3.04-2.92 (m, 4H), 2.50 (dd, *J* = 15.4, 7.9 Hz, 2H), 2.43 (s, 3H), 2.41-2.28 (m, 1H), 1.64-1.41 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ = 143.6, 143.3, 137.1, 129.9, 127.3, 126.3, 124.5, 43.5, 39.8, 39.3, 32.7, 28.6, 21.7.

4-Methyl-N-(3-(1,2,3,4-tetrahydronaphthalen-2-yl)propyl)benzenesulfonamide (5n)



The required amine was synthesized according to an adaption of a previously reported procedure^[7] and was tosylated by applying the last step of **GP 1**. **5n** was obtained as a white solid.

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.34-7.28 (m, 2H), 7.11-6.99 (m, 4H), 4.62 (bs, 1H), 3.00-2.93 (m, 2H), 2.83-2.68 (m, 3H), 2.42 (s, 3H), 2.37-2.27 (m, 1H), 1.89-1.79 (m, 1H), 1.68-1.51 (m, 3H), 1.39-1.25 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.5, 137.2, 136.8, 136.4, 129.8, 129.2, 128.9, 127.2, 125.7, 125.6, 43.6, 36.1, 33.9, 33.3, 29.4, 29.1, 27.2, 21.6.

IR v (cm⁻¹): 3284, 2926, 2901, 2845, 1596.

mp: 66-68 °C.

HRMS: Mass calculated for C₂₀H₂₆NO₂S: 344.1679, found: 344.1676.

4-Methyl-N-(2-methyl-5-phenylpentyl)benzenesulfonamide (50)



50 was synthesized according to **GP 1** using (3-Bromopropyl)benzene as starting material. The NMR data match those previously reported in literature.^[4]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.77-7.68 (m, 2H), 7.33-7.24 (m, 4H), 7.20-7.15 (m, 1H), 7.15-7.11 (m, 2H), 4.52 (bs, 1H), 2.87-2.80 (m, 1H), 2.77-2.69 (m, 1H), 2.57-2.49 (m, 2H), 2.42 (s, 3H), 1.65-1.54 (m, 2H), 1.54-1.45 (m, 1H), 1.40-1.29 (m, 1H), 1.16-1.06 (m, 1H), 0.86 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.4, 142.4, 137.2, 129.8, 128.5, 128.4, 127.2, 125.9, 49.1, 36.1, 33.6, 33.2, 28.7, 21.6, 17.5.

4-Methyl-N-(2-ethyl-5-phenylpentyl)benzenesulfonamide (5p)



5p was synthesized according to **GP 1** using (3-Bromopropyl)benzene as starting material. The NMR data match those previously reported in literature.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.3 Hz, 2H), 7.32-7.23 (m, 4H), 7.22-7.16 (m, 1H), 7.16-7.10 (m, 2H), 4.30 (bs, 1H), 2.84 (t, *J* = 6.1 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 2.42 (s, 3H), 1.55-1.45 (m, 2H), 1.44-1.34 (m, 1H), 1.34-1.21 (m, 4H), 0.78 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.5, 142.4, 137.1, 129.8, 128.5, 128.4, 127.3, 125.9, 45.8, 39.3, 36.2, 30.7, 28.4, 24.0, 21.7, 10.8.

4-Nitro-*N*-(2-((1,1,1-trifluoro-*N*-phenethylmethyl)sulfonamido)ethyl)benzenesulfonamide (5q)



5q was synthesized according to a literature known procedure and the NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 8.37 (d, J = 8.9 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.38-7.23 (m, 3H), 7.22-7.16 (m, 2H), 4.94 (t, J = 6.1 Hz, 1H), 3.63-3.46 (m, 4H), 3.17 (q, J = 6.3 Hz, 2H), 2.99-2.89 (m, 2H).

¹³C NMR (**75** MHz, CDCl₃): δ = 150.4, 145.5, 136.8, 129.1, 128.9, 128.4, 127.4, 124.7, 51.7, 49.1, 41.9, 35.5.

¹⁹F NMR (375 MHz, CDCl₃): δ = -75.0.

12. Analytical data for 5-membered ring products

4,4-Dimethyl-2-phenyl-1-tosylpyrrolidine (2a)

2a was obtained as a colorless oil (85%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.53 (d, *J* = 8.3 Hz, 2H), 7.29-7.24 (m, 4H), 7.24-7.18 (m, 3H), 4.70 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.44 (dd, *J* = 10.4, 1.5 Hz, 1H), 3.34 (dd, *J* = 10.4, 0.8 Hz, 1H), 2.39 (s, 3H), 2.02 (ddd, *J* = 12.8, 7.3, 1.5 Hz, 1H), 1.72 (dd, *J* = 12.8, 9.4 Hz, 1H), 1.05 (s, 3H), 0.76 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.1, 143.0, 135.9, 129.4, 128.4, 127.5, 127.2, 126.6, 63.9, 62.0, 51.7, 38.3, 26.2, 25.8, 21.6.

4,4-Dimethyl-1-((4-nitrophenyl)sulfonyl)-2-phenylpyrrolidine (2b)



2b was obtained as a white solid (51%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹**H NMR (500 MHz, CDCl₃)**: δ = 8.11 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.20-7.14 (m, 3H), 7.12-7.09 (m, 2H), 4.86 (dd, J = 9.8, 7.2 Hz, 1H), 3.66 (dd, J = 10.0, 1.7 Hz, 1H), 3.30 (d, J = 10.0 Hz, 1H), 2.15 (ddd, J = 12.9, 7.2, 1.7 Hz, 1H), 1.79 (dd, J = 12.9, 9.8 Hz, 1H), 1.13 (s, 3H), 1.02 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 149.6, 145.9, 141.4, 128.5, 128.1, 127.8, 127.2, 123.8, 64.1, 61.9, 51.3, 38.6, 25.7, 25.7.

4,4-Dimethyl-1-(methylsulfonyl)-2-phenylpyrrolidine (2c)



2c was obtained as a white solid (73%) by applying **GP 3**. The NMR data match those previously reported.^[6]

¹H NMR (500 MHz, CDCl₃): δ = 7.39-7.35 (m, 4H), 7.31-7.26 (m, 1H), 4.92 (dd, J = 9.8, 7.3 Hz, 1H), 3.68 (dd, J = 10.2, 1.7 Hz, 1H), 3.30 (dd, J = 10.2, 0.8 Hz, 1H), 2.55 (s, 3H), 2.22 (ddd, J = 12.8, 7.3, 1.7 Hz, 1H), 1.85 (dd, J = 12.8, 9.8 Hz, 1H), 1.21 (s, 3H), 1.17 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 142.6, 128.8, 127.8, 126.9, 63.5, 61.5, 51.6, 40.7, 38.4, 25.8, 25.7.

4,4-Dimethyl-2-phenyl-1-((2-(trimethylsilyl)ethyl)sulfonyl)pyrrolidine (2d)



2d was obtained as a white solid (37%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.31 (m, 4H), 7.29-7.26 (m, 1H), 4.93 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.75 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.25 (d, *J* = 10.2 Hz, 1H), 2.47 (td, *J* = 13.9, 4.1 Hz, 1H), 2.28 (td, *J* = 13.9, 4.5 Hz, 1H), 2.22-2.15 (m, 1H), 1.89-1.78 (m, 1H), 1.19 (s, 3H), 1.15 (s, 3H), 0.82 (ddd, *J* = 20.8, 13.7, 4.2 Hz, 2H), -0.13 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.8, 128.8, 127.9, 127.2, 63.4, 62.4, 51.6, 50.4, 38.8, 25.6, 25.5, 10.1, -1.9.

3-Phenyl-2-tosyl-2-azaspiro[4.5]decane (2e)



2e was obtained as a white solid (89%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.59 (d, J = 8.3 Hz, 2H), 7.31-7.28 (m, 4H), 7.26-7.22 (m, 3H), 4.64 (dd, J = 9.4, 7.3 Hz, 1H), 3.64 (d, J = 10.8 Hz, 1H), 3.33 (d, J = 10.7 Hz, 1H), 2.42 (s, 3H), 2.13 (dd, J = 12.9, 7.3 Hz, 1H), 1.67 (dd, J = 12.9, 9.4 Hz, 1H), 1.47-1.41 (m, 4H), 1.38-1.26 (m, 4H), 1.07-0.98 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.2, 143.1, 135.6, 129.4, 128.4, 127.5, 127.2, 126.5, 63.2, 59.4, 49.7, 42.1, 36.5, 34.0, 26.0, 23.9, 22.9, 21.6.

2-Phenyl-1-tosylpyrrolidine (2f)



2f was obtained as a white solid (55%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.67 (d, J = 8.3 Hz, 2H), 7.34-7.17 (m, 7H), 4.78 (dd, J = 7.8, 3.6 Hz, 1H), 3.66-3.56 (m, 1H), 3.48-3.37 (m, 1H), 2.42 (s, 3H), 2.08-1.75 (m, 3H), 1.75-1.60 (m, 1H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.4, 143.2, 135.2, 129.7, 128.4, 127.6, 127.1, 126.3, 63.4, 49.5, 35.9, 24.1, 21.6.

(4,4-Dimethyl-2-phenylpyrrolidin-1-yl)(phenyl)methanone (2g)



2g was obtained in 65% yield (NMR) by applying **GP 3**. Product could not be separated from starting material by column chromatography. The NMR data match those previously reported.^[6]

¹H NMR (500 MHz, CDCl₃): δ = 7.66-7.60 (m, 2H), 7.45 (td, *J* = 7.7, 2.1 Hz, 3H), 7.39-7.33 (m, 4H), 5.36 (dd, *J* = 10.2, 7.7 Hz, 1H), 3.61 (d, *J* = 10.4 Hz, 1H), 3.42-3.37 (m, 1H), 2.26 (dd, *J* = 12.8, 7.7 Hz, 1H), 1.83-1.76 (m, 1H), 1.13 (s, 3H), 1.06 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 170.3, 143.6, 136.8, 130.4, 128.5, 128.3, 127.9, 126.9, 125.8, 64.2, 60.9, 49.4, 39.1, 25.6, 25.4.

1-(4,4-Dimethyl-2-phenylpyrrolidin-1-yl)-2,2,2-trifluoroethan-1-one (2h)



2h was obtained as a white solid (60%) by applying **GP 3**. The NMR data match those previously reported.^[6]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.38-7.32 (m, 2H), 7.29-7.26 (m, 1H), 7.24-7.19 (m, 2H), 5.13 (dd, J = 9.8, 7.8 Hz, 1H), 3.74 (dt, J = 10.9, 2.0 Hz, 1H), 3.53 (d, J = 10.9 Hz, 1H), 2.26 (ddd, J = 13.0, 7.8, 1.7 Hz, 1H), 1.76 (dd, J = 13.0, 9.8 Hz, 1H), 1.21 (s, 3H), 1.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 155.9 (d, J = 36.5 Hz), 141.7, 128.9, 127.5, 125.7, 116.4 (q, J = 287.9 Hz), 62.7, 60.6 (d, J = 2.8 Hz), 48.6, 39.0, 25.6, 25.5. ¹⁹F NMR (375 MHz, CDCl₃): δ = -71.61.

4,4-Dimethyl-2-(p-tolyl)-1-tosylpyrrolidine (2i)



2i was obtained as a white solid (84%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.58-7.49 (m, 2H), 7.24-7.12 (m, 4H), 7.09-7.04 (m, 2H), 4.65 (dd, J = 9.4, 7.2 Hz, 1H), 3.45-3.30 (m, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 1.99 (dd, J = 12.8, 7.2 Hz, 1H), 1.71 (dd, J = 12.8, 9.4 Hz, 1H), 1.05 (s, 3H), 0.74 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.1, 140.0, 136.8, 135.9, 129.4, 129.1, 127.5, 126.6, 63.7, 62.0, 51.6, 38.1, 26.3, 25.8, 21.6, 21.2.

2-(4-Fluorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2j)



2j was obtained as a white solid (83%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹H NMR (400 MHz, CDCl₃): δ = 7.58-7.50 (m, 2H), 7.27-7.20 (m, 4H), 6.97-6.90 (m, 2H), 4.67 (dd, J = 9.4, 7.2 Hz, 1H), 3.43 (dd, J = 10.4, 1.5 Hz, 1H), 3.33 (d, J = 10.4 Hz, 1H), 2.40 (s, 3H), 2.00 (ddd, J = 12.8, 7.2, 1.5 Hz, 1H), 1.68 (dd, J = 12.8, 9.4 Hz, 1H), 1.05 (s, 3H), 0.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 162.0 (d, J = 245.1 Hz), 143.3, 138.8 (d, J = 3.1 Hz), 135.8, 129.5, 128.2 (d, J = 8.1 Hz), 127.4, 115.2 (d, J = 21.6 Hz), 63.3, 61.9, 51.6, 38.2, 26.2, 25.7, 21.6.

¹⁹F NMR (375 MHz, CDCl₃): δ = -116.0.

2-(4-Chlorophenyl)-4,4-dimethyl-1-tosylpyrrolidine (2k)



2k was obtained as a slightly brown solid (52%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹H NMR (300 MHz, CDCl₃): δ = 7.59 (d, J = 8.2 Hz, 2H), 7.32-7.27 (m, 6H), 4.70 (dd, J = 9.3, 7.3 Hz, 1H), 3.47 (dd, J = 10.4, 1.4 Hz, 1H), 3.38 (d, J = 10.5 Hz, 1H), 2.45 (s, 3H), 2.04 (ddd, J = 12.8, 7.2, 1.4 Hz, 1H), 1.71 (dd, J = 12.8, 9.3 Hz, 1H), 1.09 (s, 3H), 0.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 143.4, 141.6, 135.6, 132.8, 129.5, 128.5, 128.0, 127.5, 63.3, 62.0, 51.5, 38.2, 26.2, 25.8, 21.6.

4,4-Dimethyl-2-(m-tolyl)-1-tosylpyrrolidine (2l)



2I was obtained as a yellow oil (63%) by applying **GP 3**. The NMR data match those previously reported.^[6]

¹H NMR (300 MHz, CDCl₃): δ = 7.57-7.48 (m, 2H), 7.22-6.97 (m, 6H), 4.69 (dd, J = 9.5, 7.2 Hz, 1H), 3.48 (dd, J = 10.4, 1.5 Hz, 1H), 3.33 (d, J = 10.3 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 2.01 (ddd, J = 12.8, 7.2, 1.5 Hz, 1H), 1.71 (dd, J = 12.8, 9.5 Hz, 1H), 1.06 (s, 3H), 0.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 143.0, 142.8, 137.8, 136.1, 129.3, 128.2, 127.9, 127.4, 127.2, 123.8, 63.9, 61.9, 51.7, 38.2, 26.1, 25.8, 21.6, 21.5.

1-(p-Tolyl)-2-tosylisoindoline (2m)



2m was obtained as a white solid (77%) by applying **GP 3**. The NMR data match those previously reported.^[6]

¹**H NMR (400 MHz, CDCl₃)**: δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.24-7.21 (m, 2H), 7.20-7.15 (m, 3H), 7.13-7.05 (m, 4H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.89-5.83 (m, 1H), 4.83-4.78 (m, 2H), 2.36 (s, 3H), 2.32 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.3, 141.2, 139.1, 137.6, 135.4, 135.2, 129.5, 129.2, 128.1, 128.0, 127.6, 127.5, 123.7, 122.5, 69.4, 54.1, 21.6, 21.2.

1-(4-Chlorophenyl)-2-tosylisoindoline (2n)



2n was obtained as a yellow oil (83%) by applying **GP 3**. ¹**H NMR (300 MHz, CDCl₃)**: δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.28-7.15 (m, 9H), 6.87 (dd, *J* = 7.5, 1.1 Hz, 1H), 5.88 (s, 1H), 4.91-4.79 (m, 2H), 2.39 (s, 3H). ¹³**C NMR (75 MHz, CDCl₃)**: δ = 143.7, 140.6, 140.5, 135.2, 135.1, 133.8, 129.7, 129.1, 128.7, 128.3, 128.2, 127.5, 123.7, 122.6, 68.8, 54.1, 21.6. **IR v (cm⁻¹)**: 2846, 1598. **HRMS**: Mass calculated for C₂₁H₁₈ClNNaO₂S: 406.0639, found: 406.0647.

1-(4-Fluorophenyl)-2-tosylisoindoline (20)



20 was obtained as a white solid (56%) by applying GP 3.

¹H NMR (400 MHz, CDCl₃): δ = 7.62-7.53 (m, 2H), 7.29-7.25 (m, 2H), 7.24-7.17 (m, 5H), 7.0-6.94 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.92 (s, 1H), 4.85 (s, 2H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 162.5 (d, *J* = 246.5 Hz), 143.6, 140.9, 137.9, 137.9, 135.4, 135.2, 129.7, 129.6, 129.5, 128.2 (d, *J* = 2.4 Hz), 127.5, 123.7, 122.6, 115.5 (d, *J* = 21.6 Hz), 68.8, 54.1, 21.6.

¹⁹F NMR (375 MHz, CDCl₃*d*): δ = -114.65.

IR v (cm⁻¹): 2923, 1603, 1508.

mp: 154-156 °C.

HRMS: Mass calculated for C₂₁H₁₈FNNaO₂S: 390.0934, found:390.0928.

2-Tosyl-1-(4-(trifluoromethyl)phenyl)isoindoline (2p)



2p was obtained as a yellow oil (56%) by applying **GP 3**.

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.56 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 2H), 7.23-7.16 (m, 3H), 6.87 (dd, *J* = 7.5, 1.1 Hz, 1H), 5.95 (s, 1H), 4.92-4.85 (m, 2H), 2.38 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 145.9, 143.8, 140.2, 135.2, 130.3, 129.9, 129.7, 128.5, 128.3, 128.1, 127.5, 126.0, 125.6 (q, *J* = 3.8 Hz), 123.7, 122.8, 122.4, 68.9, 54.3, 21.6.

¹⁹F NMR (375 MHz, CDCl₃): δ = -62.6.

IR v (cm⁻¹): 2926, 1718,1618, 1598.

HRMS: Mass calculated for C₂₂H₁₈F₃NNaO₂S: 440.0903, found: 440.0905.

1-(4-(tert-Butyl)phenyl)-2-tosylisoindoline (2q)



2q was obtained as an orange solid (62%) by applying GP 3.

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.47 (d, *J* = 8.3 Hz, 2H), 7.24-7.21 (m, 4H), 7.20-7.14 (m, 1H), 7.13-7.05 (m, 4H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.93 (s, 1H), 4.93-4.78 (m, 2H), 2.33 (s, 3H), 1.29 (s, 9H).

¹³C NMR (**75** MHz, CDCl₃): δ = 150.7, 143.1, 141.3, 138.6, 135.9, 135.3, 129.5, 128.1, 128.0, 127.5, 127.4, 125.4, 123.9, 122.5, 69.3, 54.0, 34.6, 31.5, 21.6.

mp: 170-171 °C.

IR ν (cm⁻¹): 2959.

HRMS: Mass calculated for C₂₅H₂₇NNaO₂S: 428.1655, found: 428.1656.

1-(Thiophen-2-yl)-2-tosylisoindoline (2r)



2r was obtained as a white solid (48%) by applying **GP 3** (I = 1 mA). The NMR data match those previously reported.^[6]

¹**H NMR (500 MHz, CDCl₃)**: δ = 7.60-7.56 (m, 2H), 7.30-7.28 (m, 1H), 7.27-7.22 (m, 2H), 7.22-7.17 (m, 3H), 7.13 (dd, J = 3.4, 1.2 Hz, 1H), 7.10-7.07 (m, 1H), 6.94 (dd, J = 5.1, 3.5 Hz, 1H), 6.35 (s, 1H), 4.84 (d, J = 13.5 Hz, 1H), 4.76 (dd, J = 13.6, 2.6 Hz, 1H), 2.38 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.4, 140.4, 135.8, 135.3, 129.6, 128.5, 128.1, 127.4, 126.5, 126.5, 126.1, 123.8, 122.6, 64.7, 53.3, 21.6.

1-(benzofuran-2-yl)-2-tosylisoindoline(2s)



2s was obtained as a white solid (67%) by applying **GP 3** (I = 1 mA).

¹**H NMR (500 MHz, CDCl₃):** δ = 7.54-7.49 (m, 3H), 7.32-7.27 (m, 2H), 7.22 (td, *J* = 7.1, 6.6, 1.9 Hz, 1H), 7.19-7.15 (m, 2H), 7.15-7.10 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 6.18 (d, *J* = 2.7 Hz, 1H), 4.95 (d, *J* = 13.2 Hz, 1H), 4.88 (dd, *J* = 13.2, 2.8 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 155.3, 155.1, 143.4, 137.6, 136.0, 135.5, 129.3, 128.6, 128.1, 127.9, 127.2, 124.3, 123.5, 122.8, 122.8, 121.3, 111.4, 105.6, 62.8, 53.8, 21.4.

IR v (cm⁻¹): 3023, 2921, 1599.

mp: 134-135 °C.

HRMS: Mass calculated for C₂₃H₁₉NNaO₃S: 412.0978, found: 412.0968.

1,2,3,9b-Tetrahydrobenzo[1,2-b]isothiazole-5,5-dioxide (2t)



2t was obtained in 30% yield (NMR) by applying **GP 3**. The product could not be separated from the starting material by column chromatography. The NMR data match those previously reported.^[2]

¹**H NMR (500 MHz, CDCl₃):** δ = 7.74 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 4.99 (t, *J* = 6.6 Hz, 1H), 3.83-3.79 (m, 1H), 3.39-3.36 (m, 1H), 2.48-2.40 (m, 1H), 2.03-1.96 (m, 1H), 1.95-1.90 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ = 140.1, 136.4, 133.3, 129.5, 124.0, 121.6, 65.2, 48.4, 32.6, 26.2.

1-Tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-b]pyrrole (2u)



2u was obtained as a white solid (87%) by applying **GP 3**. The NMR data match those previously reported.^[2]

¹**H NMR (500 MHz, CDCl₃)**: δ = 7.88-7.78 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.32-7.24 (m, 2H), 7.21-7.16 (m, 1H), 5.18 (d, *J* = 7.8 Hz, 1H), 3.40 (ddd, *J* = 10.3, 7.2, 4.4 Hz, 1H), 3.27 (ddd, *J* = 10.3, 8.7, 6.7 Hz, 1H), 3.05 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.81-2.70 (m, 2H), 2.47 (s, 3H), 1.91-1.83 (m, 1H), 1.63-1.53 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.6, 142.1, 141.0, 135.0, 129.8, 128.4, 127.8, 127.4, 126.9, 125.0, 68.8, 49.3, 41.9, 36.0, 31.5, 21.6.

2-methyl-5-phenyl-1-tosylpyrrolidine (2v)



2v was obtained as a white solid (46%, d.r. = 1.2:1) by applying **GP 3**. The NMR data of the major diastereoisomer (*anti*) is given.

¹H NMR (300 MHz, CDCl₃): δ = 7.69 (d, J = 8.3 Hz, 2H), 7.42-7.22 (m, 5H), 7.16-7.00 (m, 2H), 4.72 (t, J = 6.5 Hz, 1H), 3.92 (dq, J = 12.8, 6.4 Hz, 1H), 2.42 (s, 3H), 1.94-1.83 (m, 1H), 1.78-1.67 (m, 1H), 1.63-1.54 (m, 1H), 1.47 (d, J = 6.4 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ = 143.4, 143.0, 135.4, 129.7, 128.4, 127.1, 127.1, 126.4, 65.1, 57.4, 34.6, 32.3, 22.9, 21.7. IR v (cm⁻¹): 2928, 1596. HRMS: Mass calculated for C₁₈H₂₁NNaO₂S: 338.1185, found: 338.1180.

4-Methyl-2-phenyl-1-tosylpyrrolidine (2w)



2w was obtained as a white foam (67%, d.r. = 2.5:1) by applying **GP 3**. The NMR data of the major diastereoisomer (*anti*) is given which match those previously reported.^[2]

¹**H NMR (500 MHz, CDCl₃):** δ = 7.65-7.61 (m, 2H), 7.37-7.18 (m, 7H), 4.67 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.86 (ddd, *J* = 11.2, 7.3, 1.4 Hz, 1H), 3.11 (t, *J* = 10.8 Hz, 1H), 2.44 (s, 3H), 2.43-2.37 (m, 1H), 1.96-1.80 (m, 1H), 1.51 (ddd, *J* = 12.7, 11.4, 9.5 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.3, 143.1, 135.7, 129.6, 128.4, 127.6, 127.2, 126.4, 64.8, 56.8, 45.8, 33.5, 21.6, 16.6.

4-Ethyl-2-phenyl-1-tosylpyrrolidine (2x)

2x was obtained as a colorless oil (64%, d.r. 2:1) by applying **GP 3**. The NMR data of the major diastereoisomer (*anti*) is given.

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.34-7.20 (m, 6H), 4.64 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.89 (ddd, *J* = 11.1, 7.3, 1.3 Hz, 1H), 3.13 (dd, *J* = 11.1, 10.3 Hz, 1H), 2.43 (s, 3H), 1.80-1.63 (m, 1H), 1.56-1.45 (m, 1H), 1.41-1.17 (m, 3H), 0.90-0.79 (m, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.3, 143.1, 135.7, 129.6, 128.4, 127.5, 127.2, 126.4, 64.6, 55.3, 43.8, 40.6, 25.4, 21.6, 12.6.

IR v (cm⁻¹): 2961, 1598.

HRMS: Mass calculated for C₁₉H₂₃NNaO₂S: 352.1342, found: 352.1338.

N-(4-Cyclohexylbutyl)-4-methylbenzenesulfonamide (7a)

7a was prepared from the corresponding nitrile following **GP1**. ¹**H NMR (300 MHz, CDCl₃)**: δ = 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.48 (bs, 1H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.69-1.57 (m, 5H), 1.48-1.35 (m, 2H), 1.30-1.01 (m, 8H), 0.89-0.71 (m, 2H). ¹³**C NMR (75 MHz, CDCl₃)**: δ = 143.4, 137.2, 129.8, 127.2, 43.4, 37.6, 37.0, 33.4, 30.0, 26.8, 26.48, 23.9, 21.7. **mp**: 76-77 °C. **IR** v (cm⁻¹): 3288, 2918, 2845, 1597. **HRMS**: Mass calculated for C₁₇H₂₈NO₂S: 310.1835, found: 310.1843.

2-Phenyltetrahydrofuran (4a)



4a was obtained in 55% yield (NMR) by applying **GP 3**. The yield was determined by NMR using 1,3,5-trimethoxybenzene as internal standard due to the volatility of the compound. The NMR data match those reported in literature.^[10]

¹H NMR (500 MHz, CDCl₃): δ = 7.36-7.33 (m, 4H), 7.28-7.25 (m, 1H), 4.91 (t, *J* = 7.2 Hz, 1H), 4.11 (ddd, *J* = 8.5, 7.3, 6.4 Hz, 1H), 3.95 (td, *J* = 7.8, 6.3 Hz, 1H), 2.38-2.30 (m, 1H), 2.07-1.98 (m, 2H), 1.87-1.78 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.7, 26.2.

5-Phenyldihydrofuran-2(3*H*)-one (4b)



4b was obtained in 73% yield by applying **GP 3**. The NMR data match those reported in literature.^[11]

¹**H NMR (500 MHz, CDCl₃)**: δ = 7.42-7.37 (m, 2H), 7.36-7.32 (m, 3H), 5.55-5.49 (m, 1H), 2.72-2.62 (m, 3H), 2.25-2.13 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ = 177.0, 139.5, 128.9, 128.6, 125.4, 81.4, 31.1, 29.1.

N-(4-hydroxy-5-phenylpentyl)-4-methylbenzenesulfonamide (8)



¹H NMR (500 MHz, CDCl₃): δ = 7.76-7.71 (m, 2H), 7.34-7.28 (m, 4H), 7.25-7.21 (m, 1H), 7.18-7.14 (m, 2H), 3.82-3.71 (m, 1H), 3.02-2.91 (m, 2H), 2.76 (dd, J = 13.5, 4.3 Hz, 1H), 2.61 (dd, J = 13.5, 8.5 Hz, 1H), 2.42 (s, 3H), 1.70-1.53 (m, 3H), 1.49-1.38 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 143.4, 138.2, 137.2, 129.8, 129.5, 128.8, 127.2, 126.8, 72.4, 44.4, 43.3, 33.7, 26.1, 21.6. IR v (cm⁻¹): 3465, 3146, 2914, 1598. HRMS: Mass calculated for C₁₈H₂₂NO₃S: 332.1326, found: 332.1329.

2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-1-tosylpyrrolidine (9)

9 was obtained as a white solid (40%) by applying **GP 3**.

9 can also be obtained by a Shono oxidation from tosylated pyrrolidine. The electrolysis conditions are the following: graphite rod anode (d = 6.3 mm, immersion depth: 10 mm), platinum mesh cathode, 5 mA, 2.2 F, 10 mL 0.1 M HFIP/Bu₄NBF₄, 0.2 g (0.89 mmol) *N*-tosyl pyrrolidine. After the electrolysis, the solvent was evaporated under reduced pressure und the resulting crude product was further purified by column chromatography (hexane/ethyl acetate). **9** was obtained as a white solid (52%).
¹H NMR (400 MHz, CDCl₃): δ = 7.71-7.65 (m, 2H), 7.37-7.32 (m, 2H), 5.42 (d, *J* = 4.9 Hz, 1H), 5.13 (hept, *J* = 6.2 Hz, 1H), 3.57-3.51 (m, 1H), 3.11 (td, *J* = 10.0, 7.5 Hz, 1H), 2.44 (s, 3H), 2.18-1.98 (m, 2H), 1.88-1.75 (m, 1H), 1.38-1.20 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ = 144.6, 134.5, 130.2, 127.5, 91.7, 70.6 (p, *J* = 32.5 Hz), 48.2, 33.1, 22.8, 21.7.

¹⁹**F** NMR (**375** MHz, Chloroform-d): δ = -73.57 (q, J = 8.9 Hz), -74.12 (q, J = 8.8 Hz), -75.79 (s).

mp: 95-96 °C.

IR v (cm⁻¹): 2955, 1597.

HRMS: Mass calculated for C₁₄H₁₅F₆NNaO₃S: 414.0569, found: 414.0571.

X-Ray Analytical Data for Compound 9



 Table S-1. Crystal data and structure refinement for compound 9.

Identification code	CCDC 1841280	CCDC 1841280	
Empirical formula	C14 H15 F6 N O3 S	C14 H15 F6 N O3 S	
Formula weight	391.33	391.33	
Temperature	100(2) K		
Wavelength	0.71073 ≈		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 39.756(4)≈	$\alpha = 90\infty$.	
	b = 6.2412(7)≈	$\beta = 123.261(2)\infty$.	
	$c = 31.125(3) \approx$	$\gamma = 90\infty$.	
Volume	6457.8(12) ≈ ³		
Z	16		
Density (calculated)	1.610 Mg/m ³	1.610 Mg/m ³	
Absorption coefficient	0.280 mm ⁻¹	0.280 mm ⁻¹	
F(000)	3200	3200	
Crystal size	0.25 x 0.05 x 0.01 mm	0.25 x 0.05 x 0.01 mm ³	
Theta range for data collection	1.565 to 30.686∞.	1.565 to 30.686∞.	
Index ranges	-37<=h<=56,-8<=k<=8	-37<=h<=56,-8<=k<=8,-44<=l<=42	
Reflections collected	45043	45043	
Independent reflections	9922[R(int) = 0.0627]	9922[R(int) = 0.0627]	
Completeness to theta = 30.686∞	99.4%	99.4%	
Absorption correction	Multi-scan	Multi-scan	
Max. and min. transmission	0.997 and 0.767	0.997 and 0.767	
Refinement method	Full-matrix least-squar	Full-matrix least-squares on F ²	
Data / restraints / parameters	9922/ 0/ 453	9922/ 0/ 453	
Goodness-of-fit on F ²	1.071	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.	R1 = 0.0641, WR2 = 0.1453	
R indices (all data)	R1 = 0.1017, wR2 = 0.	R1 = 0.1017, $wR2 = 0.1599$	
Largest diff. peak and hole	0.522 and -0.629 e. \approx -3	$0.522 \text{ and } -0.629 \text{ e.}^{-3}$	

13. Analytical data for 6-membered ring products

5,5-Dimethyl-2-phenyl-1-tosylpiperidine (6a)



6a was obtained as a colorless oil (53%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (400 MHz, CDCl₃): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.25-1.19 (m, 4H), 7.19-7.13 (m, 3H), 5.23 (t, *J* = 4.1 Hz, 1H), 3.41 (d, *J* = 13.5 Hz, 1H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.40 (s, 3H), 2.13-2.05 (m, 2H), 1.30-1.17 (m, 2H), 0.80 (s, 3H), 0.79 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.9, 139.0, 138.7, 129.5, 128.5, 127.1, 127.1, 126.8, 55.5, 52.7, 32.6, 30.4, 28.7, 25.9, 24.2, 21.6.

3-Phenyl-2-tosyl-2-azaspiro[5.5]undecane (6b)



6b was obtained as a colorless oil (39%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.25-7.14 (m, 7H), 5.21 (t, *J* = 4.2 Hz, 1H), 3.73 (d, *J* = 13.6 Hz, 1H), 2.78 (d, *J* = 13.7 Hz, 1H), 2.39 (s, 3H), 2.10-2.01 (m, 2H), 1.47-1.24 (m, 8H), 1.22-1.03 (m, 4H).

¹³C NMR (**75** MHz, CDCl₃): δ = 142.8, 139.1, 138.6, 129.5, 128.5, 127.1, 127.0, 126.8, 56.1, 50.3, 37.9, 32.7, 31.9, 30.9, 26.6, 25.1, 21.7, 21.6, 21.5.

1-((2-Bromophenyl)sulfonyl)-5,5-dimethyl-2-phenylpiperidine (6c)



6c was obtained as a white solid (49%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 8.12-8.08 (m, 1H), 7.75-7.70 (m, 1H), 7.40-7.24 (m, 6H), 7.22-7.15 (m, 1H), 5.32 (dd, *J* = 5.4, 2.9 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.46-2.29 (m, 1H), 2.24-2.12 (m, 1H), 1.32-1.24 (m, 2H), 0.79 (s, 3H), 0.74 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 139.9, 139.0, 135.5, 133.3, 132.4, 128.6, 127.6, 127.0, 126.9, 120.5, 56.4, 53.3, 32.8, 30.7, 28.6, 25.5, 23.9.

2-(4-(tert-Butyl)phenyl)-5,5-dimethyl-1-tosylpiperidine (6d)



6d was obtained as a brownish oil (59%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.61 (d, J = 8.3 Hz, 2H), 7.25-7.16 (m, 4H), 7.07 (d, J = 7.9 Hz, 2H), 5.17 (t, J = 4.2 Hz, 1H), 3.40 (d, J = 13.4 Hz, 1H), 2.88 (d, J = 13.3 Hz, 1H), 2.39 (s, 3H), 2.11-2.03 (m, 2H), 1.31-1.19 (m, 11H), 0.81 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 149.7, 142.7, 138.6, 136.0, 129.5, 127.1, 126.8, 125.4, 55.4, 52.7, 34.5, 32.6, 31.5, 30.5, 28.7, 25.9, 24.3, 21.6.

2-([1,1'-Biphenyl]-4-yl)-5,5-dimethyl-1-tosylpiperidine (6e)



6e was obtained as a white solid (69%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.70 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.49 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.39-7.32 (m, 1H), 7.25-7.22 (m, 4H), 5.30 (d, *J* = 4.1 Hz, 1H), 3.47 (d, *J* = 13.4 Hz, 1H), 2.94 (d, *J* = 13.4 Hz, 1H), 2.42 (s, 3H), 2.20-2.11 (m, 2H), 1.41-1.21 (m, 3H), 0.84 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 142.9, 140.7, 139.7, 138.6, 138.1, 129.5, 128.9, 127.5, 127.4, 127.2, 127.1, 127.1, 55.4, 52.7, 32.7, 30.5, 28.7, 25.8, 24.2, 21.6.

2-(4-Chlorophenyl)-5,5-dimethyl-1-tosylpiperidine (6f)



6f was obtained as a white solid (49%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.26-7.18 (m, 4H), 7.09 (dd, *J* = 8.8, 1.0 Hz, 2H), 5.17 (t, *J* = 4.3 Hz, 1H), 3.39 (d, *J* = 13.5 Hz, 1H), 2.80 (d, *J* = 13.8 Hz, 1H), 2.41 (s, 3H), 2.11-2.00 (m, 2H), 1.27-1.16 (m, 2H), 0.79 (s, 3H), 0.77 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.1, 138.5, 137.6, 132.7, 129.6, 128.7, 128.5, 127.1, 55.1, 52.6, 32.6, 30.4, 28.6, 25.8, 24.2, 21.6.

2-(4-Fluorophenyl)-5,5-dimethyl-1-tosylpiperidine (6g)



6g was obtained as a white solid (64%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.64 (d, J = 8.3 Hz, 2H), 7.26-7.21 (m, 2H), 7.17-7.09 (m, 2H), 6.96-6.88 (m, 2H), 5.20-5.15 (m, 1H), 3.38 (d, J = 13.5 Hz, 1H), 2.82 (d, J = 13.5 Hz, 1H), 2.40 (s, 3H), 2.10-2.00 (m, 2H), 1.27-1.17 (m, 2H), 0.80 (s, 3H), 0.77 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ = 161.8 (d, J = 245.5 Hz), 143.0, 138.5, 134.7 (d, J = 3.2 Hz), 129.6, 128.8 (d, J = 8.0 Hz), 127.1, 115.4 (d, J = 21.2 Hz), 55.1, 52.6, 32.6, 30.5, 28.7, 26.0, 24.3, 21.6.

¹⁹**F NMR (375 MHz, CDCl₃)**: δ = -116.46 – -116.55 (m).

4-(5,5-Dimethyl-1-tosylpiperidin-2-yl)phenyl benzoate (6h)



6h was obtained as a white solid (29%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 8.21-8.17 (m, 2H), 7.69-7.60 (m, 3H), 7.55-7.48 (m, 2H), 7.25-7.18 (m, 3H), 7.10 (d, J = 8.7 Hz, 2H), 5.24 (t, J = 4.0 Hz, 1H), 3.43 (d, J = 13.8 Hz, 1H), 2.86 (d, J = 13.5 Hz, 1H), 2.40 (s, 3H), 2.17-2.06 (m, 2H), 1.39-1.16 (m, 2H), 0.81 (s, 6H).

¹³C NMR (**75** MHz, CDCl₃): δ = 165.2, 149.8, 143.0, 138.6, 136.6, 133.8, 130.3, 129.6, 128.7, 128.2, 127.1, 121.7, 55.1, 52.6, 32.6, 30.5, 28.7, 25.8, 24.2, 21.6.

5,5-Dimethyl-2-(o-tolyl)-1-tosylpiperidine (6i)



6i was obtained as a slightly yellow oil (50%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.33-7.22 (m, 2H), 7.08-6.98 (m, 4H), 6.89 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.81-6.74 (m, 1H), 5.08 (t, *J* = 5.8 Hz, 1H), 3.40-3.26 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.10-1.96 (m, 1H), 1.76-1.60 (m, 1H), 1.50-1.37 (m, 1H), 1.34-1.21 (m, 1H), 1.04 (s, 3H), 1.03 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 142.5, 140.1, 137.4, 134.9, 130.7, 129.0, 127.2, 126.9, 126.7, 125.4, 55.2, 54.0, 33.3, 30.7, 27.9, 25.8, 21.5, 19.7.

2-(3,5-dimethylphenyl)-5,5-dimethyl-1-tosylpiperidine (6j)



6j was obtained as a colorless oil (44%) by applying GP 3.

¹H NMR (500 MHz, CDCl₃): δ = 7.65-7.61 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.78 (s, 1H), 6.58 (s, 2H), 5.16 (t, J = 4.1 Hz, 1H), 3.45 (d, J = 13.2 Hz, 1H), 2.83 (d, J = 13.3 Hz, 1H), 2.40 (s, 3H), 2.16 (s, 6H), 2.11-2.07 (m, 2H), 1.28-1.20 (m, 2H), 0.91 (s, 3H), 0.81 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 142.7, 138.9, 138.8, 137.9, 129.5, 128.4, 127.1, 124.8, 55.4, 52.7, 32.8, 30.5, 28.7, 26.0, 24.2, 21.6, 21.5. IR v (cm⁻¹): 2952, 2919, 2865, 1601. HRMS: Mass calculated for C₂₂H₂₉NNaO₂S: 394.1811, found: 294.1815.

1-Phenyl-2-tosyl-1,2,3,4-tetrahydroisoguinoline (6k)



6k was obtained as a white solid (81%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.55 (d, *J* = 8.3 Hz, 2H), 7.30-7.17 (m, 5H), 7.16-7.11 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02-6.96 (m, 2H), 6.24 (s, 1H), 3.77 (dddd, *J* = 14.1, 6.5, 2.9, 1.2 Hz, 1H), 3.32 (ddd, *J* = 14.1, 10.9, 5.4 Hz, 1H), 2.76-2.52 (m, 2H), 2.32 (s, 3H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.1, 141.7, 137.8, 134.1, 133.9, 129.4, 129.1, 128.8, 128.5, 128.4, 127.7, 127.2, 127.2, 126.2, 59.3, 39.2, 26.8, 21.5.

10-tosyl-1,2,3,4-tetrahydro-1,4-(epiminomethano)naphthalene (6l)



6I was obtained as a white solid (40%) by applying **GP 3**.

¹**H NMR (500 MHz, CDCl₃):** δ = 7.48-7.44 (m, 2H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1H), 7.08-7.02 (m, 4H), 6.95 (d, *J* = 7.3 Hz, 1H), 4.93-4.90 (m, 1H), 3.61 (dd, *J* = 9.5 Hz, 2.3, 1H), 3.17-3.14 (m, 1H), 2.93 (dt, *J* = 9.4, 2.5 Hz, 1H), 2.34-2.27 (m, 4H), 1.88-1.82 (m, 1H), 1.50-1.40 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ = 142.9, 140.1, 139.0, 135.8, 129.3, 127.6, 127.4, 126.2, 123.7, 123.1, 52.5, 49.8, 34.8, 28.4, 22.9, 21.5.

mp: 118-120 °C.

IR v (cm⁻¹): 2933, 2872, 1598.

HRMS: Mass calculated for C₁₈H₂₀NO₂S: 314.1209, found:314.1206.

X-Ray Analytical Data for Compound 6I



 Table S-2.
 Crystal data and structure refinement for 6l.

Identification code	CCDC 1841279	
Empirical formula	C18 H19 N O2 S	
Formula weight	313.40	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9159(18)≈	$\alpha = 105.035(5)\infty$.
	b = 9.2280(19)≈	$\beta = 98.430(5)\infty$.
	c = 10.159(2)≈	$\gamma = 102.959(5)\infty$.
Volume	$767.9(3) \approx^3$	
Z	2	
Density (calculated)	1.356 Mg/m ³	
Absorption coefficient	0.218 mm ⁻¹	

F(000)	332
Crystal size	0.20 x 0.10 x 0.05 mm ³
Theta range for data collection	2.127 to 30.608∞.
Index ranges	-12<=h<=10,-9<=k<=13,-14<=l<=14
Reflections collected	7780
Independent reflections	4257[R(int) = 0.0218]
Completeness to theta = 30.608∞	90.200005%
Absorption correction	Multi-scan
Max. and min. transmission	0.989 and 0.761
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4257/ 0/ 200
Goodness-of-fit on F ²	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1008
R indices (all data)	R1 = 0.0476, wR2 = 0.1063
Largest diff. peak and hole	0.429 and -0.415 e. \approx^{-3}

1-Tosyl-2,3,4,4a,5,9b-hexahydro-1H-indeno[1,2-b]pyridine (6m)



6m was obtained as a white solid (54%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 4H), 5.40 (d, *J* = 6.3 Hz, 1H), 3.91-3.78 (m, 1H), 2.95 (dd, *J* = 15.3, 6.0 Hz, 1H), 2.81 (ddd, *J* = 14.4, 12.2, 2.8 Hz, 1H), 2.50-2.40 (m, 4H), 2.41-2.26 (m, 1H), 1.67-1.52 (m, 1H), 1.35-1.23 (m, 1H), 1.23-1.15 (m, 1H), 1.15-0.96 (m, 1H).

¹³C NMR (**75** MHz, CDCl₃): δ = 143.2, 141.2, 139.9, 138.8, 129.9, 127.6, 127.1, 126.9, 125.7, 124.0, 61.1, 41.4, 37.2, 37.1, 26.2, 23.3, 21.7.

1-Tosyl-1,2,3,4,4a,5,6,10b-octahydrobenzo[h]quinolone (6n)



6n was obtained as a white solid (48%) by applying GP 3.

¹H NMR (400 MHz, CDCl₃): δ = 7.87-7.74 (m, 2H), 7.50-7.44 (m, 1H), 7.37-7.31 (m, 2H), 7.23-7.14 (m, 2H), 7.13-7.04 (m, 1H), 5.21 (d, *J* = 5.2 Hz, 1H), 3.90-3.77 (m, 1H), 2.90-2.66 (m, 3H), 2.45 (s, 3H), 2.02-1.92 (m, 1H), 1.91-1.84 (m, 1H), 1.80-1.72 (m, 1H), 1.46-1.37 (m, 3H), 1.33-1.25 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 143.1, 139.3, 137.1, 134.0, 129.9, 129.0, 127.4, 127.1, 127.0, 126.8, 56.4, 41.0, 32.6, 27.6, 24.5, 24.4, 23.7, 21.7. mp: 117-122 °C. IR v (cm⁻¹): 2926, 2852.

HRMS: Mass calculated for C₂₀H₂₃NNaO₂S: 364.1342, found: 364.1344.

5-Methyl-2-phenyl-1-tosylpiperidine (60)



60 was obtained as a white solid (59%, d.r. = 1.7:1) by applying **GP 3**. The NMR data of the major diastereoisomer (*anti*) is given which match those previously reported.^[4]

¹H NMR (500 MHz, CDCl₃): δ = 7.61 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 4.4 Hz, 2H), 7.28-7.21 (m, 5H), 4.80 (t, *J* = 5.1 Hz, 1H), 3.55 (dd, *J* = 13.0, 3.8 Hz, 1H), 3.15 (dd, *J* = 12.9, 5.1 Hz, 1H), 2.43 (s, 3H), 2.06-1.96 (m, 2H), 1.87-1.81 (m, 1H), 1.54-.48 (m, 1H), 1.22-1.15 (m, 1H), 0.89 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 142.8, 140.0, 138.7, 129.3, 128.2, 127.3, 127.2, 126.8, 57.8, 49.2, 28.3, 27.4, 26.8, 21.5, 18.0.

5-Ethyl-2-phenyl-1-tosylpiperidine (6p)



6p was obtained as a colorless oil (49%, d.r. = 1.5:1) by applying **GP 3**. The NMR data of the major diastereoisomer (*anti*) is given which match those previously reported.^[4]

¹**H NMR (300 MHz, CDCl₃)**: δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.34-7.19 (m, 7H), 4.82 (t, *J* = 5.0 Hz, 1H), 3.49 (dd, *J* = 13.0, 3.8 Hz, 1H), 3.25 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.40 (s, 3H), 2.00-1.91 (m, 2H), 1.73-1.56 (m, 2H), 1.55-1.45 (m, 1H), 1.40-1.10 (m, 3H), 1.09-0.91 (m, 2H), 0.89-0.75 (m, 3H).

¹³C NMR (75 MHz, CDCl₃): δ = 142.9, 140.2, 138.9, 129.4, 128.4, 127.3, 127.0, 126.9, 57.9, 47.0, 35.6, 27.7, 26.7, 24.8, 21.6, 11.9.

1-((4-Nitrophenyl)sulfonyl)-2-phenyl-4-((trifluoromethyl)sulfonyl)piperazine (6q)



6q was obtained as a white solid (24%) by applying **GP 3**. The NMR data match those previously reported.^[4]

¹H NMR (300 MHz, CDCl₃): δ = 8.28 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.30-7.25 (m, 3H), 7.21-7.16 (m, 2H), 5.22 (s, 1H), 4.29 (d, *J* = 13.3 Hz, 1H), 3.93-3.78 (m, 2H), 3.63-3.53 (m, 1H), 3.48-3.24 (m, 2H).

¹³C NMR (**75** MHz, CDCl₃): δ = 150.3, 145.4, 134.8, 129.2, 128.8, 128.5, 127.4, 124.6, 49.2, 46.3, 41.8.

¹⁹F NMR (375 MHz, CDCl₃): δ = -74.1.

2-Methyl-1-tosylpyrrolidine (10a)

10a was obtained as as a white solid (90%) by applying **GP 4**. The NMR data match those previously reported.^[12]

¹H NMR (400 MHz, CDCl₃): δ = 7.74-7.70 (m, 2H), 7.32-7.28 (m, 2H), 3.76-3.65 (m, 1H), 3.46-3.40 (m, 1H), 3.18-3.11 (m, 1H), 2.42 (s, 3H), 1.89-1.76 (m, 1H), 1.72-1.64 (m, 1H), 1.57-1.44 (m, 2H), 1.31 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.3, 135.1, 129.7, 127.6, 56.2, 49.2, 33.6, 24.0, 23.0, 21.6.

2-Ethyl-1-tosylpyrrolidine (10b)

10b was obtained as as an unseparable mixture with the SM (65%) by applying **GP 4**. The NMR data match those previously reported.^[13]

¹H NMR **(500 MHz, CDCl₃)**: δ = 7.74-7.70 (m, 2H), 7.32-7.28 (m, 2H), 3.57-3.49 (m, 1H), 3.37 (ddd, *J* = 10.4 Hz, 7.1 Hz, 5.2 Hz, 1H), 3.19 (dt, *J* = 10.4 Hz, 7.3 Hz, 1H), 2.43 (s, 3H), 1.89-1.82 (m, 1H), 1.76 (dt, *J* = 12.1 Hz, 7.4 Hz, 1H), 1.58-1.54 (m, 2H), 1.51-1.45 (m, 2H), 0.91-0.87 (m, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.3, 135.3, 129.7, 127.6, 62.0, 49.1, 30.3, 29.3, 24.3, 21.6, 10.5.

2-Hexyl-1-tosylpyrrolidine (10c)



10c was obtained as as a colorless oil (61%) by applying **GP 4**. The NMR data match those previously reported.

¹**H NMR (500 MHz, CDCl₃)**: δ = 7.73-7.70 (m, 2H), 7.32-7.28 (m, 2H), 3.62-3.56 (m, 1H), 3.37 (ddd, *J* = 10.4 Hz, 7.1 Hz, 5.1 Hz, 1H), 3.19 (dt, *J* = 10.4 Hz, 7.2 Hz, 1H), 2.43 (s, 3H), 1.87-1.72 (m, 2H), 1.61-1.53 (m, 3H), 1.51-1.44 (m, 1H), 1.32-1.27 (m, 8H), 0.92-0.85 (m, 3H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.2, 135.3, 129.7, 127.7, 60.8, 49.0, 36.6, 32.0, 30.8, 29.4, 26.3, 24.3, 22.8, 21.6, 14.2.

IR v (cm⁻¹): 2926, 2857.

HRMS: Mass calculated for C₁₇H₂₇NNaO₂S: 332.1655, found: 332.1665.

2-Allyl-1-tosylpyrrolidine (10d)

10d was obtained as as a colorless oil (94%) by applying **GP 4**. The NMR data match those previously reported.^[14]

¹H NMR (500 MHz, CDCl₃): δ = 7.75-7.71 (m, 2H), 7.32-7.29 (m, 2H), 5.79 (ddt, *J* = 17.2 Hz, 10.2 Hz, 7.1 Hz, 1H), 5.11-5.04 (m, 2H), 3.66 (ddd, *J* = 12.9 Hz, 8.0 Hz, 3.9 Hz, 1H), 3.39 (ddd, *J* = 10.1 Hz, 7.0 Hz, 4.8 Hz, 1H), 3.17 (dt, *J* = 10.3 Hz, 7.3 Hz, 1H), 2.63-2.56 (m, 1H), 2.43 (s, 3H), 2.34-2.26 (m, 1H), 1.81-1.73 (m, 1H), 1.68-1.61 (m, 1H), 1.60-1.53 (m, 1H), 1.53-1.46 (m, 1H).

¹³C NMR (125 MHz, CDCl₃): δ = 143.4, 135.1, 134.8, 129.8, 127.7, 117.7, 59.8, 49.3, 41.0, 30.2, 24.1, 21.6.

N-(5-(Pyridin-3-yl)pentyl)benzenesulfonamide



¹H NMR (400 MHz, CDCl₃): δ = 8.42 (dd, J = 4.8, 1.7 Hz, 1H), 8.39 (d, J = 2.3 Hz, 1H), 7.87-7.84 (m, 2H), 7.60-7.43 (m, 4H), 7.20 (ddd, J = 7.8, 4.8, 0.9 Hz, 1H), 4.85 (bs, 1H), 2.97-2.91 (m, 2H), 2.55 (t, J = 7.7 Hz, 2H), 1.60-1.45 (m, 4H), 1.35-1.24 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 149.8, 147.3, 140.2, 137.6, 136.0, 132.6, 129.2, 127.1, 123.4, 43.13, 32.8, 30.6, 29.5, 26.1. mp: 70-71 °C. IR v (cm⁻¹): 3059, 2933, 2859. HRMS: Mass calculated for $C_{16}H_{21}N_2O_2S$: 305.1318, found: 305.1324.

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15. NMR spectra













S 56



S 57











S 62







S 65




















¹³C NMR CDCl₃, 125 MHz



























































¹³C NMR CDCl₃, 75 MHz









¹H NMR CDCl₃, 400 MHz


























¹H NMR CDCl₃, 300 MHz



¹³C NMR CDCl₃, 75 MHz











¹H NMR CDCl₃, 300 MHz



¹³C NMR CDCl₃, 75 MHz



¹¹F NMR CDCl₃, 375 MHz

----62.64



-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 f1 (ppm)





¹H NMR CDCl₃, 500 MHz





¹³C NMR CDCl₃, 125 MHz





¹H NMR CDCl₃, 500 MHz











160 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -6(f1 (ppm)



¹³C NMR CDCl₃, 75 MHz









¹H NMR CDCl₃, 500 MHz













S 133











¹H NMR CDCl₃, 300 MHz



¹³C NMR CDCl₃, 75 MHz





¹⁹F NMR CDCl₃, 375 MHz
















S 145



S 146



¹H NMR CDCl₃, 500 MHz







¹H NMR CDCl₃, 300 MHz







-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 f1 (ppm)



¹H NMR CDCl₃, 400 MHz















S 153



¹H NMR CDCl₃, 500 MHz



¹³C NMR CDCl₃, 125 MHz







¹H NMR CDCl₃, 400 MHz



¹³C NMR CDCl₃, 75 MHz

