



Supporting Information

for

Dialkylaminoalkylation of β -ketosulfones via ring-opening of 3-sulfonylpyrrolidines

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Experimental section, characterization data and copies of spectra

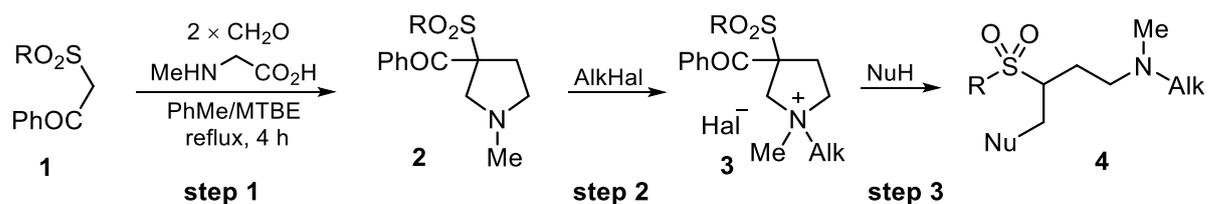
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1. Materials and methods:

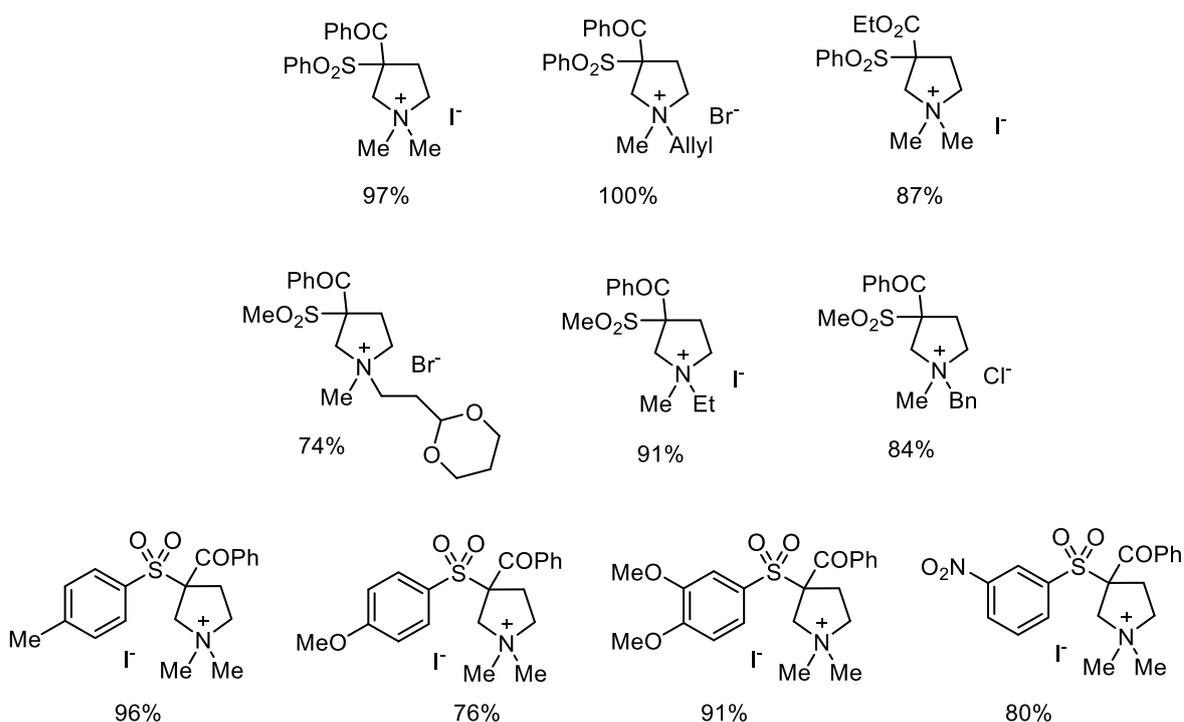
Starting materials, reagents, and solvents were purchased from commercial sources and used as received unless stated otherwise. All solvents used were dried and distilled per standard procedures. Dry cesium carbonate was applied. Alkyl halogenides were obtained from the commercial sources and were used after distillation. Starting ketosulfones are known compounds and were prepared according to the literature procedures. Purification of the reaction products was carried out by flash column chromatography using silica gel (40–63 μm , ASTM). A mixture of chloroform/ethanol (95%) was used as eluent. Analytical studies were carried out using equipment at the Center for Joint Use ‘Spectroscopy and Analysis of Organic Compounds’ at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch) and the Laboratory of Complex Investigations and Expert Evaluation of Organic Materials of the Center for Joint Use at the Ural Federal University. ^1H and ^{13}C NMR spectra were recorded at 400/500 and 126 MHz, respectively; CDCl_3 was used as solvents. The chemical shifts are reported in ppm relative to internal standard TMS or to residual signals of the solvent for ^{13}C (CDCl_3 , 77.16 ppm). The HRMS spectra were obtained using TOF mass spectrometer. Electrospray ionization with direct sample inlet (flow rate 240 $\mu\text{L/h}$) was used. The mass spectrometer was operating in positive mode in the mass range of 50–1550 Da.

2. General procedure:



Step 1: A mixture of β -ketosulfone (4.0 mmol, 1.0 equiv), finely ground *N*-methylglycine (427 mg, 4.8 mmol, 1.2 equiv) and paraformaldehyde (300 mg, 10.0 mmol of formaldehyde, 2.5 equiv) was refluxed in a mixture of dried PhMe (17 mL) and MTBE (3 mL) in a 75 mL round-bottom flask fitted with a Dean-Stark trap (filled with PhMe) for 4 h. The resulting mixture was cooled to room temperature and undissolved unreacted excess of *N*-methylglycine was filtered off. (**NOTE:** at this step pyrrolidines **2** can be isolated if needed via an acid-base work-up to provide analytically pure compounds. See **acid-base work-up procedure** below).

Step 2: Corresponding alkyl halide (6.0 mmol, 1.5 equiv) was added dropwise at room temperature to the resulting solution under constant stirring and the stirring continued overnight at room temperature for 15–24 h in case of methyl iodide, ethyl iodide and allyl bromide. In case of benzyl chloride and 2-(2-bromoethyl)-1,3-dioxane the reaction was carried out at 70 °C for 7 days. The formed precipitate was filtered, washed with PhMe several times and dried at 65 °C to give corresponding ammonium salt **3**. Ammonium salt was used further without additional purification.



Step 3:

Procedure for the ring-cleavage with alcohol (products 4a–f,h–k) or mercaptan (products 4q–t):

Corresponding quaternary ammonium salt (0.5 mmol, 1.0 equiv), dry cesium carbonate (341 mg, 1.05 mmol, 2.1 equiv), MeOH (4 mL) were sequentially added to the 10 mL pressure microwave vial equipped with magnetic stirrer. Vial was sealed with cap and heated in an oil bath at 65 °C for 24 h under vigorous stirring.

In case of mercaptan products 4q–t: butane-1-thiol (3.0 equiv, 1.5 mmol) or thiophenol (2.0 equiv, 1.0 mmol) were added to the starting mixture.

Procedure for the ring-cleavage with amine (products 4g,i–p):

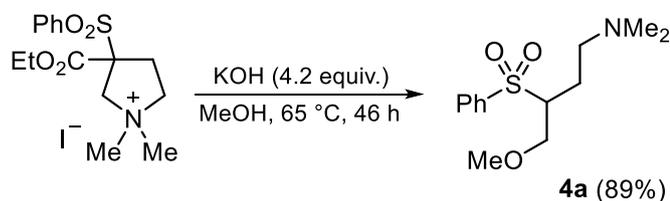
Corresponding quaternary ammonium salt (0.5 mmol, 1.0 equiv), dry cesium carbonate (341 mg, 1.05 mmol, 2.1 equiv), CH₃CN (4 mL) and amine (1.3–5.0 equiv) were sequentially added to the 10 mL pressure microwave vial equipped with magnetic stirrer. Vial was sealed with cap and heated in an oil bath at 80 °C for 24 h under vigorous stirring.

Work-up: The vial was cooled to room temperature and opened in a fume hood. The mixture was diluted with water (15 mL), extracted with CH₂Cl₂ (3 × 10 mL). Combined organic extracts were washed with water (3 × 10 mL), brine (10 mL), dried over sodium sulfate and evaporated under reduced pressure to give the desired product 4. The latter was purified by a column chromatography or the acid-base work-up.

Acid-base work-up for the isolation of pyrrolidines 2 and purification of products 4a,c–j,r:

The residue was extracted with cold 2 M HCl (12 mL). Water phase was washed with PhMe (2 × 7 mL), basified with NaHCO₃ to pH = 8–9 and extracted with CH₂Cl₂ (3 × 7 mL). Combined organic extracts were washed with H₂O (10 mL), brine (10 mL) and dried over anhydrous Na₂SO₄. Solvent was evaporated in vacuo and the product, if necessary, was purified by column chromatography.

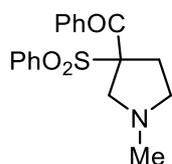
Procedure for the ring opening of the 3-ethoxycarbonylpyrrolidine:



Corresponding quaternary ammonium salt (0.5 mmol, 1.0 equiv), MeOH (2 mL) and solution of KOH (118 mg, 2.1 mmol, 4.2 equiv) in MeOH (2 mL) were sequentially added to the 10 mL pressure microwave vial equipped with magnetic stirrer. Vial was sealed with cap and heated in an oil bath at 65 °C for 46 h under constant stirring. Followed by the usual **work-up**. The product 4a was isolated in 89% yield and 77% overall yield. NMR data was in match with the product 4a obtained via **general procedure**.

3. Analytical data of products

(1-Methyl-3-(phenylsulfonyl)pyrrolidin-3-yl)(phenyl)methanone (2a)



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one according to the **general procedure** and isolated by an **acid-base work-up**.

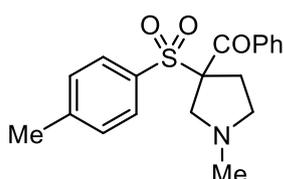
Brown viscous oil. Yield: 1276 mg (97%).

^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.6$ Hz, 2H, CO PhH -2,6), 7.73 (d, $J = 8.5$ Hz, 2H, SO $_2$ PhH-2,6), 7.66 (t, $J = 7.5$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 3.45 (d, $J = 10.7$ Hz, 1H, 2-CHH), 3.25 (d, $J = 10.7$ Hz, 1H, 2-CHH), 3.04–2.94 (m, 1H), 2.77–2.65 (m, 3H), 2.31 (s, 3H, NMe).

^{13}C NMR (126 MHz, CDCl_3) δ 196.1 (C=O), 136.0 (C), 135.6 (C), 134.4 (CH), 133.1 (CH), 130.5 (2CH), 130.3 (2CH), 128.9 (2CH), 128.3 (2CH), 83.0 (3-C), 62.1 (CH $_2$ N), 56.1 (NCH $_2$), 41.7 (NMe), 33.4 (CH $_2$).

HRMS (ESI) calcd for ($\text{C}_{18}\text{H}_{20}\text{NO}_3\text{S}$) $^+$ [M+H] $^+$: 330.1158, found: 330.1170.

(1-Methyl-3-tosylpyrrolidin-3-yl)(phenyl)methanone (2b)



Synthesized from 1-phenyl-2-tosylethan-1-one according to the **general procedure** and isolated by an **acid-base work-up**.

Light brown solid, mp 125–127 °C. Yield: 1139 mg (83%).

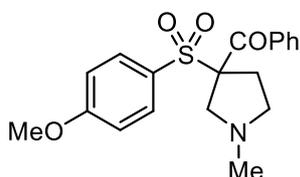
^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H, SO $_2$ ArH-2,6), 7.60 (d, $J = 8.4$ Hz, 2H, SO $_2$ ArH-3,5), 7.56 (t, $J = 7.4$ Hz, 1H, PhH-4), 7.46 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 7.30 (d, $J = 8.1$ Hz, 2H, CO PhH -2,6), 3.42 (d, $J = 10.6$ Hz, 1H, 2-CHH), 3.21 (d, $J = 10.6$ Hz, 1H, 2-CHH), 3.00–2.95 (m, 1H), 2.73–2.62 (m, 3H), 2.44 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 196.4 (C=O), 145.5 (C), 135.7 (C), 133.0 (CH), 130.5 (2CH), 130.3 (2CH), 129.5 (2CH), 128.3 (2CH), 83.0 (3-C), 62.2 (CH $_2$ N), 56.2 (NCH $_2$), 41.7 (NMe), 33.4 (CH $_2$), 21.8 (ArMe).

One C is masked.

HRMS (ESI) calcd for ($\text{C}_{19}\text{H}_{22}\text{NO}_3\text{S}$) $^+$ [M+H] $^+$: 344.1315, found: 344.1320.

(3-((4-Methoxyphenyl)sulfonyl)-1-methylpyrrolidin-3-yl)(phenyl)methanone (2c)



Synthesized from 2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one according to the **general procedure** and isolated by an **acid-base work-up**.

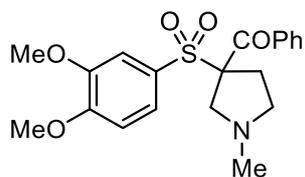
Light yellow solid, mp 82–83 °C. Yield: 1364 mg (95%).

^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.6$ Hz, 2H, CO PhH -2,6), 7.64 (d, $J = 9.0$ Hz, 2H, SO $_2$ ArH-2,6), 7.55 (t, $J = 7.4$ Hz, 1H, CO PhH -4), 7.45 (t, $J = 7.7$ Hz, 2H, CO PhH -3,5), 6.95 (d, $J = 9.0$ Hz, 2H, SO $_2$ ArH-3,5), 3.87 (s, 3H, OMe), 3.42 (d, $J = 10.6$ Hz, 1H, 2-CHH), 3.20 (d, $J = 10.6$ Hz, 1H, 2-CHH), 3.00–2.93 (m, 1H), 2.73–2.61 (m, 3H), 2.29 (s, 3H, NMe).

^{13}C NMR (126 MHz, CDCl_3) δ 196.6 (C=O), 164.3 (C-O), 135.8 (C), 133.0 (CH), 132.5 (2CH), 130.5 (2CH), 128.3 (2CH), 127.3 (C), 114.1 (2CH), 83.1 (3-C), 62.3 (CH $_2$ N), 56.2 (NCH $_2$), 55.8 (OMe), 41.8 (NMe), 33.5 (CH $_2$).

HRMS (ESI) calcd for (C₁₉H₂₂NO₄S)⁺ [M+H]⁺: 360.1264, found: 360.1275.

(3-((3,4-Dimethoxyphenyl)sulfonyl)-1-methylpyrrolidin-3-yl)(phenyl)methanone (2d)



Synthesized from 2-((3,4-dimethoxyphenyl)sulfonyl)-1-phenylethan-1-one according to the **general procedure** and isolated by an **acid-base work-up**.

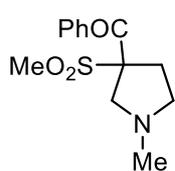
Light yellow amorphous solid. Yield: 1354 mg (87%).

¹H NMR (500 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 2H, C_{OPh}H-2,6), 7.56 (t, *J* = 7.4 Hz, 1H, C_{OPh}H-4), 7.46 (t, *J* = 7.7 Hz, 2H, C_{OPh}H-3,5), 7.36 (dd, *J* = 8.5, 2.1 Hz, 1H, SO₂ArH-6), 7.10 (d, *J* = 2.1 Hz, 1H, SO₂ArH-2), 6.92 (d, *J* = 8.5 Hz, 1H, SO₂ArH-5), 3.95 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.41 (d, *J* = 10.7 Hz, 1H, 2-CHH), 3.25 (d, *J* = 10.7 Hz, 1H, 2-CHH), 2.99–2.93 (m, 1H), 2.74–2.64 (m, 3H), 2.30 (s, 3H, NMe).

¹³C NMR (126 MHz, CDCl₃) δ 196.0 (C=O), 154.0 (C-O), 148.9 (C-O), 135.6 (C), 133.0 (CH), 130.6 (2CH), 128.3 (2CH), 127.6 (C), 124.6 (CH), 112.5 (CH), 110.4 (CH), 83.3 (3-C), 62.2 (CH₂N), 56.3, 56.1, 41.8 (NMe), 33.7 (CH₂).

HRMS (ESI) calcd for (C₂₀H₂₄NO₅S)⁺ [M+H]⁺: 390.1370, found: 390.1373.

(1-Methyl-3-(methylsulfonyl)pyrrolidin-3-yl)(phenyl)methanone (2e)



Synthesized from 2-(methylsulfonyl)-1-phenylethan-1-one according to the **general procedure** and isolated by an **acid-base work-up**.

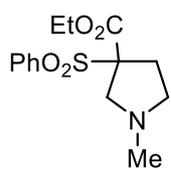
Yellow solid, mp 74–76 °C. Yield: 961 mg (90%).

¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.6 Hz, 2H, C_{OPh}H-2,6), 7.55 (t, *J* = 7.4 Hz, 1H, C_{OPh}H-4), 7.45 (t, *J* = 7.8 Hz, 2H, C_{OPh}H-3,5), 3.65 (d, *J* = 10.5 Hz, 1H, 2-CHH), 3.21 (d, *J* = 10.6 Hz, 1H, 2-CHH), 2.98 (s, 3H, SO₂Me), 2.89–2.83 (m, 1H), 2.79–2.72 (m, 2H), 2.69–2.62 (m, 1H), 2.34 (s, 3H, NMe).

¹³C NMR (126 MHz, CDCl₃) δ 198.2 (C=O), 135.7 (C), 133.1 (CH), 130.1 (2CH), 128.4 (2CH), 81.6 (3-C), 62.0 (CH₂N), 56.1 (NCH₂), 41.6 (NMe), 37.8 (SO₂Me), 32.9 (CH₂).

HRMS (ESI) calcd for (C₁₃H₁₈NO₃S)⁺ [M+H]⁺: 268.1002, found: 268.1001.

Ethyl 1-methyl-3-(phenylsulfonyl)pyrrolidine-3-carboxylate (2f)



Synthesized from ethyl 2-(phenylsulfonyl)acetate according to the **general procedure** and isolated by an **acid-base work-up**.

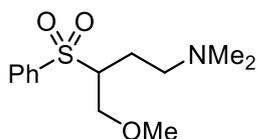
Light yellow oil. Yield: 1033 mg (87%).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.5 Hz, 2H, SO₂PhH-2,6), 7.68 (t, *J* = 7.5 Hz, 1H, SO₂PhH-4), 7.55 (t, *J* = 7.8 Hz, 2H, SO₂PhH-3,5), 4.11 (q, *J* = 7.1 Hz, 2H, CO₂CH₂CH₃), 3.34 (d, *J* = 10.3 Hz, 1H, 2-CHH), 3.04 (d, *J* = 10.3 Hz, 1H, 2-CHH), 2.86 (td, *J* = 7.9, 3.8 Hz, 1H), 2.77–2.61 (m, 2H), 2.58–2.51 (m, 2H), 2.35 (s, 3H, NMe), 1.17 (t, *J* = 7.1 Hz, 3H, CO₂CH₂CH₃).

¹³C NMR (126 MHz, CDCl₃) δ 168.0 (CO₂Et), 137.0 (C), 134.3 (CH), 130.0 (2CH), 129.0 (2CH), 78.4 (3-C), 62.9, 60.6, 55.8 (CH₂N), 41.7 (NMe), 30.9 (CH₂), 13.8 (COOCH₂CH₃).

HRMS (ESI) calcd for (C₁₄H₂₀NO₄S)⁺ [M+H]⁺: 298.1108, found: 298.1117.

4-Methoxy-*N,N*-dimethyl-3-(phenylsulfonyl)butan-1-amine (4a)



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and methanol as nucleophile. Product was purified by an **acid-base work-up**.

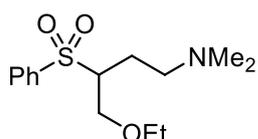
Light yellow oil. Yield: 112 mg (83%).

¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, *J* = 8.6, 1.3 Hz, 2H, PhH-2,6), 7.64 (t, *J* = 7.4 Hz, 1H, PhH-4), 7.55 (t, *J* = 7.7 Hz, 2H, PhH-3,5), 3.69 (d, *J* = 4.8 Hz, 2H, CH₂OMe), 3.45–3.40 (m, 1H, CHSO₂Ph), 3.21 (s, 3H, OMe), 2.41 (dt, *J* = 12.2, 7.7 Hz, 1H, CHHNMe₂), 2.33 (ddd, *J* = 12.2, 7.3, 5.4 Hz, 1H, CHHNMe₂), 2.15 (s, 6H, NMe₂), 2.17–2.08 (m, 1H), 1.84–1.76 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 138.9 (C), 133.6 (CH), 128.99 (2CH), 128.97 (2CH), 69.3 (CH₂OMe), 62.6, 58.9, 56.2, 45.2 (NMe₂), 23.7 (CH₂).

HRMS (ESI) calcd for (C₁₃H₂₂NO₃S)⁺ [M+H]⁺: 272.1315, found: 272.1316.

4-Ethoxy-*N,N*-dimethyl-3-(phenylsulfonyl)butan-1-amine (4b)



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and ethanol as nucleophile. Ring-opening reaction was performed in ethanol at 80 °C for 36 h. Product was purified by column

chromatography (eluent: chloroform/ethanol, 100/4; *R_f* (chloroform/ethanol, 100/4) = 0.14).

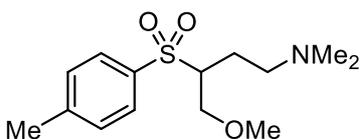
Light yellow oil. Yield: 106 mg (74%).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.6 Hz, 2H, PhH-2,6), 7.63 (t, *J* = 7.4 Hz, 1H, PhH-4), 7.53 (t, *J* = 7.6 Hz, 2H, PhH-3,5), 3.73 (dd, *J* = 10.6, 5.2 Hz, 1H, CHHOEt), 3.70 (dd, *J* = 10.6, 4.8 Hz, 1H, CHHOEt), 3.45–3.40 (m, 1H, CHSO₂Ph), 3.34 (q, *J* = 7.0 Hz, 1H, OCHHCH₃), 3.33 (q, *J* = 7.0 Hz, 1H, OCHHCH₃), 2.41 (dt, *J* = 12.3, 7.6 Hz, 1H, CHHNMe₂), 2.34 (ddd, *J* = 12.3, 7.3, 5.4 Hz, 1H, CHHNMe₂), 2.16 (s, 6H, NMe₂), 2.20–2.11 (m, 1H), 1.78 (ddd, *J* = 14.1, 7.2, 5.4 Hz, 1H), 0.99 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃).

¹³C NMR (126 MHz, CDCl₃) δ 139.2 (C), 133.5 (CH), 129.0 (2CH), 128.9 (2CH), 67.4, 66.7, 62.7, 56.4, 45.3 (NMe₂), 23.8 (CH₂), 14.9 (OCH₂CH₃).

HRMS (ESI) calcd for (C₁₄H₂₄NO₃S)⁺ [M+H]⁺: 286.1471, found: 286.1476.

4-Methoxy-*N,N*-dimethyl-3-tosylbutan-1-amine (4c)



Synthesized from 1-phenyl-2-tosylethan-1-one, applying methyl iodide as alkylating agent and methanol as nucleophile. Product was purified by an **acid-base work-up**.

Light brown oil. Yield: 98 mg (69%).

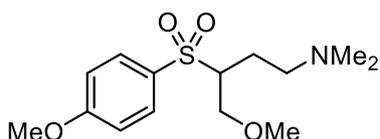
¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8.1 Hz, 2H, PhH-2,6), 7.34 (d, *J* = 8.1 Hz, 2H, PhH-3,5), 3.68 (dd, *J* = 10.5, 4.9 Hz, 1H, CHHOMe), 3.65 (dd, *J* = 10.5, 4.9 Hz, 1H, CHHOMe), 3.42–3.36 (m, 1H,

CHSO₂Tol), 3.22 (s, 3H, OMe), 2.44 (s, 3H, ArCH₃), 2.50–2.37 (m, 2H), 2.20 (s, 6H, NMe₂), 2.16–2.09 (m, 1H), 1.83 (ddd, *J* = 13.8, 7.8, 5.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 144.7, 135.8, 129.7 (2CH), 129.0 (2CH), 69.4 (CH₂OMe), 62.5, 59.0, 56.2, 45.1 (NMe₂), 23.7 (CH₂), 21.7 (CH₃).

HRMS (ESI) calcd for (C₁₄H₂₄NO₃S)⁺ [M+H]⁺: 286.1471, found: 286.1469.

4-Methoxy-3-((4-methoxyphenyl)sulfonyl)-*N,N*-dimethylbutan-1-amine (4d)



Synthesized from 2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and methanol as nucleophile.

Product was purified by an **acid-base work-up**.

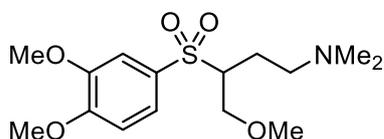
Light yellow oil. Yield: 81 mg (54%).

¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 9.0 Hz, 2H, ArH-2,6), 7.00 (d, *J* = 9.0 Hz, 2H, ArH-3,5), 3.88 (s, 3H, OMe), 3.68 (d, *J* = 4.8 Hz, 2H, CH₂OMe), 3.39–3.33 (m, 1H, CHSO₂Ar), 3.23 (s, 3H, CH₂OMe), 2.40 (dt, *J* = 12.2, 7.6 Hz, 1H, CHHNMe₂), 2.33 (dt, *J* = 12.2, 6.3 Hz, 1H, CHHNMe₂), 2.15 (s, 6H, NMe₂), 2.14–2.04 (m, 1H), 1.77 (dddd, *J* = 12.6, 8.5, 7.3, 5.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 163.8 (C), 131.2 (2CH), 130.3 (C), 114.3 (2CH), 69.5 (CH₂OMe), 62.7, 59.0, 56.3, 55.8, 45.2 (NMe₂), 23.8 (CH₂).

HRMS (ESI) calcd for (C₁₄H₂₄NO₄S)⁺ [M+H]⁺: 302.1421, found: 302.1428.

3-((3,4-Dimethoxyphenyl)sulfonyl)-4-methoxy-*N,N*-dimethylbutan-1-amine (4e)



Synthesized from 2-((3,4-dimethoxyphenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and methanol as nucleophile. Product was purified by an **acid-base work-up**.

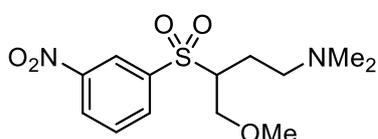
Light yellow viscous oil. Yield: 93 mg (56%).

¹H NMR (500 MHz, CDCl₃) δ 7.51 (dd, *J* = 8.5, 2.1 Hz, 1H, ArH-6), 7.34 (d, *J* = 2.1 Hz, 1H, ArH-2), 6.97 (d, *J* = 8.5 Hz, 1H, ArH-5), 3.96 (s, 3H, OMe), 3.94 (s, 3H, OMe), 3.69 (d, *J* = 4.8 Hz, 2H, CH₂OMe), 3.41–3.36 (m, 1H, CHSO₂Ar), 3.26 (s, 3H, OMe), 2.40 (dt, *J* = 12.3, 7.6 Hz, 1H, CHHNMe₂), 2.32 (ddd, *J* = 12.3, 7.4, 5.3 Hz, 1H, CHHNMe₂), 2.16 (s, 6H, NMe₂), 2.13–2.06 (m, 1H), 1.80 (dddd, *J* = 12.5, 8.4, 7.3, 5.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 153.4 (C), 149.1 (C), 130.3 (C), 123.1 (CH), 111.2 (CH), 110.6 (CH), 69.4 (CH₂OMe), 62.8, 59.0, 56.4 (OMe), 56.33 (OMe), 56.29 (OMe), 45.3 (NMe₂), 23.9 (CH₂).

HRMS (ESI) calcd for (C₁₅H₂₆NO₅S)⁺ [M+H]⁺: 332.1526, found: 332.1524.

4-Methoxy-*N,N*-dimethyl-3-((3-nitrophenyl)sulfonyl)butan-1-amine (4f)



Synthesized from 2-((3-nitrophenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and methanol as nucleophile.

Product was purified by an **acid-base work-up** and column

chromatography (eluent: chloroform/ethanol, 100/4; *R_f* (chloroform/ethanol, 100/4) = 0.1).

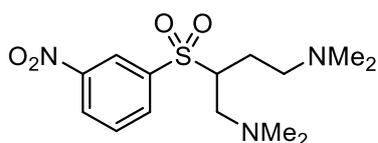
Brown oil. Yield: 33 mg (21%).

^1H NMR (400 MHz, CDCl_3) δ 8.76 (t, $J = 1.8$ Hz, 1H, ArH), 8.48 (ddd, $J = 8.3, 2.2, 1.0$ Hz, 1H, ArH), 8.22 (ddd, $J = 7.8, 1.7, 1.1$ Hz, 1H, ArH), 7.74 (t, $J = 8.0$ Hz, 1H, ArH), 3.82 (dd, $J = 10.6, 3.3$ Hz, 1H, CHHOMe), 3.68 (dd, $J = 10.6, 5.6$ Hz, 1H, CHHOMe), 3.55–3.49 (m, 1H, CHSO_2Ph), 3.18 (s, 3H, OMe), 2.46–2.30 (m, 2H), 2.23–2.14 (m, 1H), 2.19 (s, 6H, NMe_2), 1.74–1.64 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 148.2 (C), 141.8 (C), 134.7 (CH), 130.0 (CH), 128.0 (CH), 124.7 (CH), 69.0 (CH_2OMe), 63.4, 58.8, 55.9, 45.3 (NMe_2), 23.2 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{13}\text{H}_{21}\text{N}_2\text{O}_5\text{S})^+$ $[\text{M}+\text{H}]^+$: 317.1166, found: 317.1165.

N^1, N^1, N^4, N^4 -tetramethyl-2-((3-nitrophenyl)sulfonyl)butane-1,4-diamine (4g)



Synthesized from 2-((3-nitrophenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and 33% aqueous solution of dimethylamine as nucleophile (5.0 equiv, 2.5 mmol of NHMe_2). Product

was purified by an **acid-base work-up** and column chromatography (eluent: chloroform/ethanol, 100/12; R_f (chloroform/ethanol, 100/12) = 0.15).

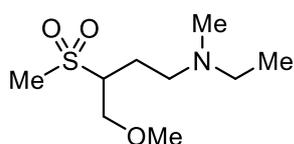
Brown oil. Yield: 40 mg (24%).

^1H NMR (400 MHz, CDCl_3) δ 8.78 (t, $J = 1.8$ Hz, 1H, ArH), 8.46 (ddd, $J = 8.2, 2.2, 1.0$ Hz, 1H, ArH), 8.23 (ddd, $J = 7.8, 1.6, 1.0$ Hz, 1H, ArH), 7.74 (t, $J = 8.0$ Hz, 1H, ArH), 3.52 (ddd, $J = 12.3, 7.6, 4.8$ Hz, 1H, CHSO_2Ph), 2.76 (dd, $J = 13.2, 7.6$ Hz, 1H), 2.45–2.41 (m, 2H), 2.38 (dd, $J = 13.2, 5.9$ Hz, 1H), 2.31–2.21 (m, 1H), 2.19 (s, 6H, NMe_2), 1.98 (s, 6H, $\text{N}'\text{Me}_2$), 1.71 (dt, $J = 13.5, 6.2$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 148.1 (C), 142.5 (C), 134.3 (CH), 130.0 (CH), 127.7 (CH), 124.4 (CH), 60.4, 58.9, 56.2, 45.3 (NMe_2), 45.0 ($\text{N}'\text{Me}_2$), 24.8 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{14}\text{H}_{24}\text{N}_3\text{O}_4\text{S})^+$ $[\text{M}+\text{H}]^+$: 330.1482, found: 330.1487.

N -Ethyl-4-methoxy- N -methyl-3-(methylsulfonyl)butan-1-amine (4h)



Synthesized from 2-(methylsulfonyl)-1-phenylethan-1-one, applying ethyl iodide as alkylating agent and methanol as nucleophile. Product was purified by an **acid-base work-up**.

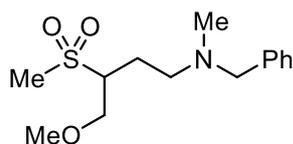
Light yellow oil. Yield: 45 mg (40%).

^1H NMR (500 MHz, CDCl_3) δ 3.83 (dd, $J = 10.5, 2.8$ Hz, 1H, CHHOMe), 3.70 (dd, $J = 10.5, 6.3$ Hz, 1H, CHHOMe), 3.37 (s, 3H, OMe), 3.22–3.17 (m, 1H, CHSO_2Me), 2.93 (s, 3H, SO_2Me), 2.54–2.36 (m, 4H), 2.28–2.18 (m, 1H), 2.21 (s, 3H, NMe), 1.76 (dddd, $J = 14.3, 9.5, 6.8, 5.1$ Hz, 1H), 1.04 (t, $J = 7.1$ Hz, 3H, NCH_2CH_3).

^{13}C NMR (126 MHz, CDCl_3) δ 69.6 (CH_2OMe), 62.2, 59.2, 53.7, 51.3, 41.33, 41.25, 22.1 (CH_2), 12.2 (CH_3).

HRMS (ESI) calcd for $(\text{C}_9\text{H}_{22}\text{NO}_3\text{S})^+$ $[\text{M}+\text{H}]^+$: 224.1315, found: 224.1323.

***N*-Benzyl-4-methoxy-*N*-methyl-3-(methylsulfonyl)butan-1-amine (4i)**



Synthesized from 2-(methylsulfonyl)-1-phenylethan-1-one, applying benzyl chloride as alkylating agent (reaction was performed at 70 °C for 7 days) and methanol as nucleophile. Product was purified by an **acid-base work-up**.

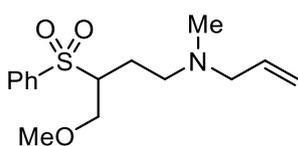
Yellow oil. Yield: 95 mg (67%).

¹H NMR (400 MHz, CDCl₃) δ 7.34–7.23 (m, 5H, PhH), 3.69 (dd, *J* = 10.6, 2.6 Hz, 1H, CHHOMe), 3.60 (d, *J* = 13.0 Hz, 1H, NCHHPh), 3.47 (dd, *J* = 10.6, 6.2 Hz, 1H, CHHOMe), 3.39 (d, *J* = 13.0 Hz, 1H, NCHHPh), 3.26 (s, 3H, OMe), 3.28–3.21 (m, 1H, CHSO₂Me), 2.90 (d, *J* = 0.5 Hz, 3H, SO₂Me), 2.53 (ddd, *J* = 12.5, 9.5, 5.8 Hz, 1H, CHHNMeBn), 2.41 (ddd, *J* = 12.5, 6.2, 4.6 Hz, 1H, CHHNMeBn), 2.28 (ddd, *J* = 14.0, 6.0, 3.4 Hz, 1H), 2.24 (s, 3H, NMe), 1.78–1.68 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 139.1 (C), 129.2 (2CH), 128.4 (2CH), 127.3 (CH), 69.0 (CH₂OMe), 62.6, 62.0, 59.1, 53.1, 42.0, 41.3, 22.0 (CH₂).

HRMS (ESI) calcd for (C₁₄H₂₄NO₃S)⁺ [M+H]⁺: 286.1471, found: 286.1471.

***N*-Allyl-4-methoxy-*N*-methyl-3-(phenylsulfonyl)butan-1-amine (4j)**



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying allyl bromide as alkylating agent and methanol as nucleophile. Product was purified by an **acid-base work-up**.

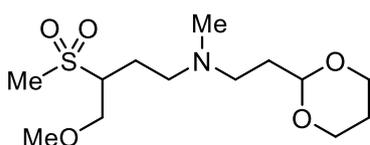
Yellow oil. Yield: 101 mg (68%).

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.6 Hz, 1H, PhH-2,6), 7.64 (t, *J* = 7.4 Hz, 1H, PhH-4), 7.55 (t, *J* = 7.6 Hz, 1H, PhH-3,5), 5.76 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H, NCH₂CH=), 5.16–5.08 (m, 2H, NCH₂CH=CH₂), 3.71 (dd, *J* = 9.3, 3.4 Hz, 1H, CHHOMe), 3.67 (dd, *J* = 9.3, 3.4 Hz, 1H, CHHOMe), 3.46–3.39 (m, 1H), 3.21 (s, 3H, OMe), 2.96 (dd, *J* = 13.6, 6.3 Hz, 1H, NCHHCH=), 2.89 (dd, *J* = 13.6, 6.8 Hz, 1H, NCHHCH=), 2.47 (ddd, *J* = 12.4, 7.9, 7.0 Hz, 1H, CHHNMeAllyl), 2.39 (ddd, *J* = 12.4, 7.2, 5.2 Hz, 1H, CHHNMeAllyl), 2.17–2.08 (m, 1H), 2.12 (s, 3H, NMe), 1.78 (dddd, *J* = 14.1, 8.6, 7.0, 5.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 139.0 (C), 135.6 (CH), 133.6 (CH), 129.0 (2CH), 117.6 (CH₂=), 69.2 (CH₂OMe), 62.6, 60.8, 58.9, 53.6, 41.7, 23.4 (CH₂).

HRMS (ESI) calcd for (C₁₅H₂₄NO₃S)⁺ [M+H]⁺: 298.1471, found: 298.1466.

***N*-(2-(1,3-Dioxan-2-yl)ethyl)-4-methoxy-*N*-methyl-3-(methylsulfonyl)butan-1-amine (4k)**



Synthesized from 2-(methylsulfonyl)-1-phenylethan-1-one, applying 2-(2-bromoethyl)-1,3-dioxane as alkylating agent (reaction was performed at 70 °C for 7 days) and methanol as nucleophile.

Brown viscous oil. Yield: 91 mg (59%).

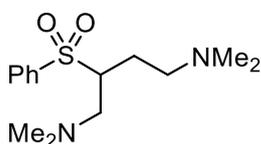
¹H NMR (400 MHz, CDCl₃) δ 4.59 (t, *J* = 5.2 Hz, 1H, OCHO), 4.09 (ddd, *J* = 6.4, 5.4, 1.6 Hz, 2H), 3.84 (dd, *J* = 10.6, 2.6 Hz, 1H, CHHOMe), 3.75 (tt, *J* = 11.9, 2.6 Hz, 2H), 3.68 (dd, *J* = 10.6, 6.1 Hz, 1H, CHHOMe), 3.37 (s, 3H, OMe), 3.25–3.18 (m, 1H), 2.92 (s, 3H, MeSO₂), 2.53–2.39 (m, 4H), 2.26–2.17 (m, 1H), 2.20 (s, 3H, NMe), 2.07 (qt, *J* = 13.3, 5.0 Hz, 1H), 1.80–1.70 (m, 3H), 1.33 (dddd, *J* = 13.5, 3.8, 2.5,

1.3 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 101.0 (OCHO), 69.3 (CH_2OMe), 67.0 (2OCH_2), 62.0, 59.2, 54.2, 52.3, 41.6, 41.3, 33.0, 25.9, 22.2.

HRMS (ESI) calcd for $(\text{C}_{13}\text{H}_{28}\text{NO}_5\text{S})^+$ $[\text{M}+\text{H}]^+$: 310.1683, found: 310.1685.

***N*¹,*N*¹,*N*⁴,*N*⁴-Tetramethyl-2-(phenylsulfonyl)butane-1,4-diamine (4l)**



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and 33% aqueous solution of dimethylamine as nucleophile (5.0 equiv, 2.5 mmol of NHMe_2).

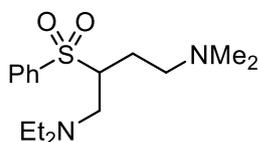
Brown oil. Yield: 138 mg (97%).

^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.6$ Hz, 2H, PhH-2,6), 7.63 (t, $J = 7.4$ Hz, 1H, PhH-4), 7.55 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 3.39 (dq, $J = 8.4, 5.3$ Hz, 1H, CHSO_2Ph), 2.65 (dd, $J = 12.8, 5.0$ Hz, 1H), 2.41 (dd, $J = 12.8, 8.4$ Hz, 1H), 2.40–2.35 (m, 2H), 2.14 (s, 6H, NMe_2), 2.09 (s, 6H, $\text{N}'\text{Me}_2$), 2.12–2.05 (m, 1H), 1.80 (td, $J = 13.6, 6.5$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 139.0 (C), 133.5 (CH), 129.0 (2CH), 128.9 (2CH), 60.3, 58.7, 56.6, 45.5 (NMe_2), 45.3 ($\text{N}'\text{Me}_2$), 25.8 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_2\text{S})^+$ $[\text{M}+\text{H}]^+$: 285.1631, found: 285.1633.

***N*¹,*N*¹-Diethyl-*N*⁴,*N*⁴-dimethyl-2-(phenylsulfonyl)butane-1,4-diamine (4m)**



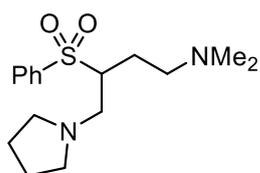
Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and diethylamine (4.0 equiv, 2.0 mmol) as nucleophile. Brown oil. Yield: 117 mg (75%).

^1H NMR (400 MHz, CDCl_3) δ 7.91–7.89 (m, 2H, PhH-2,6), 7.63 (tt, $J = 7.4, 1.3$ Hz, 1H, PhH-4), 7.55 (t, $J = 7.5$ Hz, 2H, PhH-3,5), 3.37 (dq, $J = 8.8, 5.5$ Hz, 1H, CHSO_2Ph), 2.81 (dd, $J = 13.2, 4.6$ Hz, 1H, CHHNEt_2), 2.49 (dd, $J = 13.2, 8.8$ Hz, 1H, CHHNEt_2), 2.47–2.26 (m, 6H), 2.15 (s, 6H, NMe_2), 2.16–2.06 (m, 1H), 1.90–1.80 (m, 1H), 0.84 (t, $J = 7.1$ Hz, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$).

^{13}C NMR (126 MHz, CDCl_3) δ 139.3 (C), 133.5 (CH), 129.0 (2CH), 128.8 (2CH), 60.3, 56.9, 53.0, 46.8 (2C), 45.3 (2C), 25.5 (CH_2), 11.4 ($\text{N}(\text{CH}_2\text{CH}_3)_2$).

HRMS (ESI) calcd for $(\text{C}_{16}\text{H}_{29}\text{N}_2\text{O}_2\text{S})^+$ $[\text{M}+\text{H}]^+$: 313.1944, found: 313.1945.

***N,N*-Dimethyl-3-(phenylsulfonyl)-4-(pyrrolidin-1-yl)butan-1-amine (4n)**



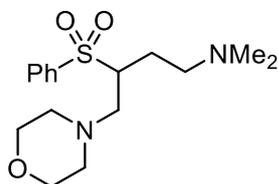
Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and pyrrolidine (4.0 equiv, 2.0 mmol) as nucleophile. Brown oil. Yield: 141 mg (91%).

^1H NMR (500 MHz, CDCl_3) δ 7.91–7.89 (m, 2H, PhH-2,6), 7.62 (tt, $J = 7.4, 1.2$ Hz, 1H, PhH-4), 7.53 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 3.42 (dq, $J = 8.2, 5.5$ Hz, 1H, CHSO_2Ph), 2.81 (dd, $J = 12.5, 5.5$ Hz, 1H), 2.65 (dd, $J = 12.5, 8.2$ Hz, 1H), 2.42–2.36 (m, 4H), 2.29–2.24 (m, 2H), 2.15 (s, 6H, NMe_2), 2.18–2.09 (m, 1H), 1.87–1.79 (m, 1H), 1.61–1.55 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 139.4 (C), 133.4 (CH), 128.9 (2CH), 128.8 (2CH), 61.0, 56.8, 55.1, 53.9 (2 NCH₂), 45.3 (NMe₂), 25.4 (CH₂), 23.7 (2CH₂).

HRMS (ESI) calcd for ($\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$)⁺ [M+H]⁺: 311.1788, found: 311.1791.

***N,N*-Dimethyl-4-morpholino-3-(phenylsulfonyl)butan-1-amine (4o)**



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and morpholine (4.0 equiv, 2.0 mmol) as nucleophile.

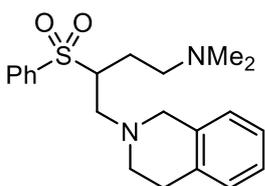
Brown oil. Yield: 153 mg (94%).

^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 2H, PhH-2,6), 7.64 (t, $J = 7.4$ Hz, 1H, PhH-4), 7.55 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 3.53–3.47 (m, 1H, CHSO₂Ph), 3.47–3.39 (m, 4H, CH₂OCH₂), 2.77 (dd, $J = 13.1, 6.1$ Hz, 1H), 2.46–2.36 (m, 2H), 2.43 (dd, $J = 13.1, 7.3$ Hz, 1H), 2.34–2.17 (m, 5H), 2.16 (s, 6H, NMe₂), 1.76 (td, $J = 13.0, 6.5$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 139.6 (C), 133.5 (CH), 129.0 (2CH), 128.8 (2CH), 66.8 (CH₂OCH₂), 58.9, 58.0, 56.4, 53.6 (CH₂NCH₂), 45.3 (NMe₂), 25.1 (CH₂).

HRMS (ESI) calcd for ($\text{C}_{16}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$)⁺ [M+H]⁺: 327.1737, found: 327.1740.

4-(3,4-Dihydroisoquinolin-2(*1H*)-yl)-*N,N*-dimethyl-3-(phenylsulfonyl)butan-1-amine (4p)



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and 1,2,3,4-tetrahydroisoquinoline (1.3 equiv, 0.65 mmol) as nucleophile. Product was purified by column chromatography (eluent: chloroform/ethanol, from 100/0 to 100/3; R_f (chloroform/ethanol, 100/3) = 0.22).

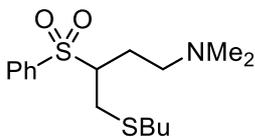
Brown amorphous solid. Yield: 125 mg (67%).

^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 2H, PhH-2,6), 7.55 (t, $J = 7.4$ Hz, 1H, PhH-4), 7.46 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 7.11–7.05 (m, 2H), 7.01 (dd, $J = 6.2, 2.1$ Hz, 1H), 6.92 (dd, $J = 6.2, 2.1$ Hz, 1H), 3.63–3.58 (m, 1H, CHSO₂Ph), 3.56 (d, $J = 14.7$ Hz, 1H, ^{THIQ}NCHH), 3.43 (d, $J = 14.7$ Hz, 1H, ^{THIQ}NCHH), 2.93 (dd, $J = 13.0, 5.5$ Hz, 1H), 2.72–2.59 (m, 4H), 2.59–2.53 (m, 1H), 2.45–2.37 (m, 2H), 2.20 (dtd, $J = 12.3, 7.1, 5.2$ Hz, 1H), 2.13 (s, 6H, NMe₂), 1.89–1.81 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 139.3 (C), 134.5 (C), 134.2 (C), 133.5 (CH), 129.0 (2CH), 128.8 (2CH), 128.6 (CH), 126.5 (CH), 126.2 (CH), 125.7 (CH), 59.7, 57.4, 56.6, 56.1, 50.9, 45.3 (NMe₂), 29.1 (CH₂), 25.4 (CH₂).

HRMS (ESI) calcd for ($\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$)⁺ [M+H]⁺: 373.1944, found: 373.1950.

4-(Butylthio)-*N,N*-dimethyl-3-(phenylsulfonyl)butan-1-amine (4q)



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and butane-1-thiol (3.0 equiv, 1.5 mmol) as nucleophile.

Product was purified by column chromatography (eluent: chloroform/ethanol, 100/5; R_f (chloroform/ethanol, 100/5) = 0.7).

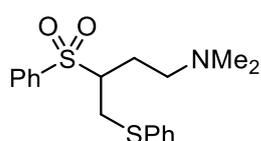
Light orange oil. Yield: 100 mg (61%).

^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 8.5$ Hz, 2H, PhH-2,6), 7.67 (t, $J = 7.4$ Hz, 1H, PhH-4), 7.58 (t, $J = 7.7$ Hz, 2H, PhH-3,5), 3.38 (dtd, $J = 9.4, 5.7, 3.3$ Hz, 1H, CHSO_2Ph), 3.03 (dd, $J = 13.6, 3.3$ Hz, 1H, CHHSBu), 2.56 (dd, $J = 13.6, 9.9$ Hz, 1H, CHHSBu), 2.43 (t, $J = 7.3$ Hz, 2H, SCH_2Pr), 2.47–2.36 (m, 2H, CH_2NMe_2), 2.16 (s, 6H, NMe_2), 2.10–2.02 (m, 1H), 1.96 (tdd, $J = 12.6, 7.1, 5.2$ Hz, 1H), 1.48–1.41 (m, 2H), 1.37–1.29 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H, $\text{S}(\text{CH}_2)_3\text{CH}_3$).

^{13}C NMR (126 MHz, CDCl_3) δ 137.9 (C), 133.9 (CH), 129.4 (2CH), 129.0 (2CH), 61.7, 56.5 (CH_2NMe_2), 45.3 (NMe_2), 32.3 (CH_2), 31.3 (CH_2), 30.9 (CH_2), 25.8 (CH_2), 22.0 (CH_2), 13.7 ($\text{S}(\text{CH}_2)_3\text{CH}_3$).

HRMS (ESI) calcd for $(\text{C}_{16}\text{H}_{28}\text{NO}_2\text{S}_2)^+$ $[\text{M}+\text{H}]^+$: 330.1556, found: 330.1570.

***N,N*-Dimethyl-3-(phenylsulfonyl)-4-(phenylthio)butan-1-amine (4r)**



Synthesized from 1-phenyl-2-(phenylsulfonyl)ethan-1-one, applying methyl iodide as alkylating agent and thiophenol (2.0 equiv, 1.0 mmol) as nucleophile. Product was purified by an **acid-base work-up**.

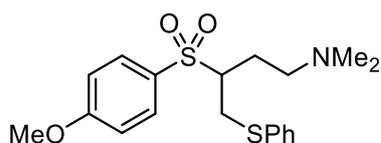
Brown oil. Yield: 145 mg (83%).

^1H NMR (500 MHz, CDCl_3) δ 7.86 (dd, $J = 8.3, 1.1$ Hz, 2H, SO_2PhH -2,6), 7.67 (t, $J = 7.5$ Hz, 1H, SO_2PhH -4), 7.56 (t, $J = 7.8$ Hz, 2H, SO_2PhH -3,5), 7.24–7.15 (m, 5H, SPhH), 3.48 (dd, $J = 13.9, 3.2$ Hz, 1H, PhSCHH), 3.33 (dddd, $J = 9.7, 6.0, 5.3, 3.2$ Hz, 1H, CHSO_2Ph), 2.89 (dd, $J = 13.9, 9.7$ Hz, 1H, PhSCHH), 2.41–2.34 (m, 2H, CH_2NMe_2), 2.17–2.10 (m, 1H), 2.13 (s, 6H, NMe_2), 2.00 (dtd, $J = 12.7, 7.2, 5.2$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 137.8 (C), 134.7 (C), 133.9 (CH), 129.9 (2CH), 129.4 (2CH), 129.3 (2CH), 129.0 (2CH), 126.9 (CH), 61.2, 56.5 (CH_2NMe_2), 45.3 (NMe_2), 33.1, 25.7 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{18}\text{H}_{24}\text{NO}_2\text{S}_2)^+$ $[\text{M}+\text{H}]^+$: 350.1243, found: 350.1251.

3-((4-Methoxyphenyl)sulfonyl)-*N,N*-dimethyl-4-(phenylthio)butan-1-amine (4s)



Synthesized from 2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and thiophenol (2.0 equiv, 1.0 mmol) as nucleophile. Product was purified by column chromatography (eluent: chloroform/ethanol, from 100/0 to 100/5; R_f (chloroform/ethanol, 100/5) = 0.33).

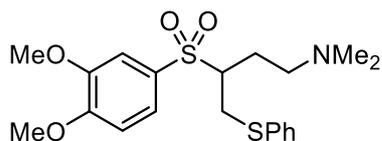
Yellow viscous oil. Yield: 165 mg (87%).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.9$ Hz, 2H, SO_2ArH -2,6), 7.24–7.17 (m, 5H, SPhH), 7.01 (d, $J = 8.9$ Hz, 2H, SO_2ArH -3,5), 3.90 (s, 3H, OMe), 3.49 (dd, $J = 13.8, 3.1$ Hz, 1H, PhSCHH), 3.30–3.23 (m, 1H, CHSO_2Ar), 2.87 (dd, $J = 13.8, 9.9$ Hz, 1H, PhSCHH), 2.40 (t, $J = 7.3$ Hz, 2H, CH_2NMe_2), 2.15 (s, 6H, NMe_2), 2.16–2.07 (m, 1H), 1.98 (dtd, $J = 12.5, 7.3, 5.3$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 164.1 (C-O), 134.9 (C), 131.2 (2CH), 129.8 (2CH), 129.3 (2CH), 129.2 (C), 126.9 (CH), 114.6 (2CH), 61.6 (CHSO_2), 56.6, 55.9, 45.3 (NMe_2), 33.2 (SCH_2), 25.8 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{19}\text{H}_{26}\text{NO}_3\text{S}_2)^+$ $[\text{M}+\text{H}]^+$: 380.1349, found: 380.1355.

3-((3,4-Dimethoxyphenyl)sulfonyl)-*N,N*-dimethyl-4-(phenylthio)butan-1-amine (4t)



Synthesized from 2-((3,4-dimethoxyphenyl)sulfonyl)-1-phenylethan-1-one, applying methyl iodide as alkylating agent and thiophenol (2.0 equiv, 1.0 mmol) as nucleophile. Product was purified by column chromatography (eluent: chloroform/ethanol, from 100/1 to 100/4; R_f

(chloroform/ethanol, 100/4) = 0.21).

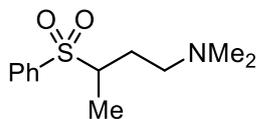
Yellow viscous oil. Yield: 135 mg (66%).

^1H NMR (500 MHz, CDCl_3) δ 7.48 (dd, $J = 8.4, 2.1$ Hz, 1H, $\text{SO}_2\text{ArH-6}$), 7.24 (d, $J = 2.1$ Hz, 1H, $\text{SO}_2\text{ArH-2}$), 7.23–7.16 (m, 5H, SPhH), 6.97 (d, $J = 8.4$ Hz, 1H, $\text{SO}_2\text{ArH-5}$), 3.97 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.45 (dd, $J = 13.9, 3.1$ Hz, 1H, PhSCHH), 3.21–3.25 (m, 1H, CHSO_2Ar), 2.89 (dd, $J = 13.9, 9.8$ Hz, 1H, PhSCHH), 2.42 (t, $J = 7.1$ Hz, 2H, CH_2NMe_2), 2.17 (s, 6H, NMe_2), 2.21–2.12 (m, 1H), 2.01 (dtd, $J = 12.5, 7.3, 5.4$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 153.7 (C-O), 149.5 (C-O), 134.8 (C), 130.0 (2CH), 129.23 (C), 129.20 (2CH), 126.9 (CH), 123.2 (CH), 110.9 (CH), 110.8 (CH), 61.6 (CHSO_2), 56.5 (NCH_2), 56.41 (OMe), 56.40 (OMe), 45.3 (NMe_2), 33.3 (SCH₂), 25.6 (CH_2).

HRMS (ESI) calcd for $(\text{C}_{20}\text{H}_{28}\text{NO}_4\text{S}_2)^+ [\text{M}+\text{H}]^+$: 410.1454, found: 410.1469.

N,N-Dimethyl-3-(phenylsulfonyl)butan-1-amine (5)



N,N-Dimethyl-3-(phenylsulfonyl)-4-(phenylthio)butan-1-amine (4r) (175 mg, 0.5 mmol) was dissolved in anhydrous THF (5.0 mL) and LiAlH_4 (76 mg, 2.0 mmol, 4.0 equiv) was added in small portions at room temperature. The resulting

suspension was stirred at 25 °C for 20 h. Few drops of H_2O /THF mixture (v/v 1/1) was carefully added to the resulting mixture, following by an addition of brine (5 mL) and 40% aqueous NaOH solution (5 mL) and then it was extracted with DCM (2×10 mL). Combined DCM extracts were washed with H_2O (2×10 mL), brine (10 mL), dried over Na_2SO_4 and evaporated under reduced pressure to give pure product.

Yellow viscous oil. Yield: 93 mg (77%).

^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.6$ Hz, 2H, $\text{SO}_2\text{PhH-2,6}$), 7.65 (t, $J = 7.5$ Hz, 1H, $\text{SO}_2\text{PhH-4}$), 7.56 (t, $J = 7.7$ Hz, 2H, $\text{SO}_2\text{PhH-3,5}$), 3.24 (dq, $J = 10.2, 6.9, 3.9$ Hz, 1H, CHSO_2Ph), 2.38 (ddd, $J = 12.0, 8.7, 7.2$ Hz, 1H, CHHNMe_2), 2.27 (ddd, $J = 12.0, 7.5, 3.9$ Hz, 1H, CHHNMe_2), 2.22–2.13 (m, 1H), 2.14 (s, 6H, NMe_2), 1.52–1.45 (m, 1H), 1.27 (d, $J = 6.9$ Hz, 3H, CH_3).

^{13}C NMR (126 MHz, CDCl_3) δ 137.5 (C), 133.7 (CH), 129.2 (2CH), 129.1 (2CH), 57.8, 55.9, 45.3 (NMe_2), 27.1 (CH_2), 13.19 (CH_3).

HRMS (ESI) calcd for $(\text{C}_{12}\text{H}_{20}\text{NO}_2\text{S})^+ [\text{M}+\text{H}]^+$: 242.1209, found: 242.1215.

