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Supporting Information

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# Supporting Information

## *Novel Route towards Bicyclo[1.1.1]pentane Sulfoxides from a Benchstable Starting Material*

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## Contents

# 1. General Remarks

## 1.1 Preparative Work

The starting materials, solvents and reagents were purchased from ABCR, ACROS, ALFA AESAR, CARBOLUTION, CHEMPUR, MERCK, TCI, THERMO FISHER SCIENTIFIC, SIGMA ALDRICH, or BLDPHARM and used without further purification.

All reactions containing air- and moisture-sensitive compounds were performed under an argon atmosphere using oven-dried glassware applying Schlenk techniques. Liquids were added *via* steel cannulas, and solids were added directly in powdered form.

Reactions were performed at room temperature if no other information is supplied.

Solvents were removed at 45 °C with a rotary evaporator under reduced pressure. For solvent mixtures each solvent was measured volumetrically. If no other information is supplied, saturated, aqueous solutions of inorganic salts were used.

Crude products were purified *via* flash chromatography using MERCK silica gel 60 (0.040 × 0.063 mm, 230 – 400 mesh ASTM), quartz sand (glowed and purified with hydrochloric acid), MACHEREY-NAGEL preparative TLC plates SIL G-200 coated with silica gel 60 with fluorescent indicator and BIO RAD-Bio-Beads S-X1 Support with 1% cross-linkage, 40 – 80 µm bead sizefor the exclusion range 600 – 14,000 MW. Therefore, the eluents were distilled or used directly in *p.a.* quality bought from MERCK, RIEDEL-DE HAËN, FISHER SCIENTIFIC.

## 1.2 Solvents and Reagents

Solvents of technical quality were purified by distillation or with the solvent purification system MB SPS5 from MBRAUN before use. Solvents of the grade *p.a.* were purchased (ACROS, FISHER SCIENTIFIC, SIGMA ALDRICH, ROTH) and were used without further purification. Absolute solvents were dried, using the solvent purification system MB SPS5 and were stored under argon afterwards or were purchased from a commercial supplier.

## 1.3 Analytics and Equipment

### Nuclear Magnetic Resonance (NMR)

All NMR spectra were recorded using the following machines:

**$^{1}$H NMR**: BRUKER *Avance 400* (400 MHz), BRUKER *Advance III 400* (400 MHz), BRUKER *Avance DRX 500* (500 MHz). The chemical shift $\delta$ is expressed in parts per million (ppm) where the residual signal of the solvent was used as reference: acetone-$d_6$ ($\delta$ = 3.31 ppm), $CDCl_3$ ($\delta$ = 7.26 ppm), methanol-$d_4$ ($\delta$ = 2.50 ppm), or deuterium oxide-$d_2$ ($\delta$ = 4.79 ppm).[1] The spectra were analyzed according to first order.

**$^{13}$C NMR:** BRUKER *Avance 400* (100 MHz), BRUKER *Advance III 400* (100 MHz), BRUKER *Avance DRX 500* (125 MHz). The chemical shift $\delta$ is expressed in parts per million (ppm) where the residual signal of the solvent was used as reference: acetone-$d_6$ ($\delta$ = 29.5 ppm), $CDCl_3$ ($\delta$ = 77.0 ppm) or methnaol-$d_4$ ($\delta$ = 49.0 ppm).[1] The spectra were $^{1}$H-decoupled and characterization of the $^{13}$C NMR-spectra ensured through the DEPT-technique (DEPT = Distortionless Enhancement by Polarization Transfer) and are stated as follows: DEPT: "+" = primary or secondary carbon atoms (positive DEPT-signal), "–" = secondary carbon atoms (negative DEPT-signal), $C_q$ = quaternary carbon atoms (no DEPT-signal).

**$^{19}$F NMR:** BRUKER *Avance 400* (376 MHz), BRUKER *Avance DRX 500* (470 MHz). The chemical shift $\delta$ is expressed in parts per million (ppm).

All spectra were obtained at room temperature. NMR-solvents were obtained from EURISOTOP and SIGMA ALDRICH: chloroform-$d_1$, deuterium oxide-$d_2$, methanol-$d_4$. For central symmetrical signals the midpoint and for multiplets the range of the signal region are given. The multiplicities of the signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, br = broad singlet, m = multiplet, b = broad, and combinations thereof. All coupling constants '*J*' are stated as modulus in Hertz [Hz]. In some cases the signals were assigned using $^{1}$H-$^{13}$C-HSQC (Heteronuclear Single Quantum Coherence) and $^{1}$H-$^{13}$C-HMBC (Heteronuclear Multiple Quantum Correlation) techniques.

**Infrared spectroscopy (IR)**

**IR-spectra** were recorded on a BRUKER *Alpha P* and a PERKINELMER *Spectrum 100 FT-IR*. Measurements of all samples were conducted *via* attenuated total reflection (ATR). The position of the absorption bands is given as wavenumber $\tilde{\nu}$ with the unit [cm$^{-1}$].

**Melting Points (MP)**

**MP** were measured on a STANFORD RESEARCH SYSTEMS *OptiMelt MPA100* with a heating rate of 2 °C/min and are uncorrected.

**Mass Spectrometry (GC-MS, EI-MS, FAB-MS, ESI-MS, HRMS)**

**GC-MS** (Gas chromatography–mass spectrometry). The measurements were recorded with an AGILENT TECHNOLOGIES *model 6890N* (electron impact ionization), equipped with a AGILENT 19091S-433 column (5% phenyl methyl siloxane, 30 m, 0.25 µm) and a 5975B VL MSD detector with a turbo pump. Helium was used as a carrier gas.

**EI-MS** and **FAB-MS**. The measurements were recorded with a FINNIGAN *MAT 95* (70 eV). Ionization was achieved through either EI (electron ionization), FAB (fast atom bombardment).

**ESI-MS**. The measurements were recorded with a THERMOFISHER *QExactive Plus* (4 kV) with a ThermoFisher LT Orbitrap XL. Ionization was achieved through ESI (electrospray ionization).

**HR-MS** (high resolution-mass spectra). The measurements were either recorded with the FINNIGAN *MAT 95* (EI/FAB) or with the THERMOFISHER *QExactive Plus* (ESI). The following abbreviations were used: calcd. = expected value (calculated); found = value found in analysis.

Notation of molecular fragments is given as mass to charge ratio (*m/z*); the intensities of the signals are noted in percent relative to the base signal (100%). As abbreviation for the ionized molecule $[M]^+$ is used. Characteristic fragmentation peaks are given as $[M–fragment]^+$ and $[fragment]^+$.

**Thin layer chromatography (TLC)**

All reactions were monitored by TLC using silica gel coated aluminium plates (MERCK, silica gel 60, $F_{254}$). The detection was performed with UV light (254 nm) and/or dipped into a solution of Seebach reagent (2.5% phosphor molybdic acid, 1.0% Cerium(IV) sulfate tetrahydrate and 6.0% sulfuric acid in water, dipping solution) or potassium permanganate (1.5 g $KMnO_4$, 10 g $K_2CO_3$ and 1.25 mL 10% NaOH in 200 mL water, dipping solution) and heated with a heat gun.

**Analytical scales**

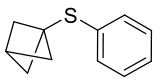
A balance from SATORIUS (*LC 620 S*) was used for mass determination.

## 2. Syntheses and Characterizations

### Tricyclo[1.1.1]pentane (**2**)

In a flame-dried round-bottomed flask that has been purged with argon 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (5.00 g, 16.8 mmol, 1.00 equiv.) was dissolved in diethyl ether (22.3 mL) and cooled to –40 °C. A 1.9 M phenyllithium solution in dibutyl ether (2.83 g, 17.7 mL, 33.7 mmol, 1.90M, 2.00 equiv.) was added dropwise under vigorous stirring. After complete addition, the mixture was allowed to warm to 0 °C and stirred at this temperature for 2 h. The reaction flask was attached to an argon purged rotavap with dry ice condenser. The receiving flask was cooled to –78 °C and the product was distilled together with diethyl ether. The water bath was set to 20 °C and the pressure was slowly reduced from 500 mbar to 20 mbar. A solution of 1 in $Et_2O$ was obtained and stored at –78 °C under argon atmosphere. To quantify the concentration of 1 an aliquot was taken and reacted with thiophenol. With the calculated concentration the yield of tricyclo[1.1.1]pentane (**2**) could be determined retrospectively (850 mg, 21.4 mL, 12.9 mmol, 0.600M, 76% yield).

### 1-(Phenylthio)-bicyclo[1.1.1]pentane



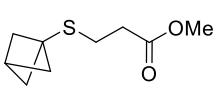

In an argon flushed 10 mL flask a thiophenol (162 mg, 150 µL, 1.47 mmol, 2.45 equiv.) in diethyl ether (1.00 mL) was added to 1.00 mL of the stock solution of tricyclo[1.1.1]pentane (**2**) (unknown concentration). The reaction was stirred for 15 min at room temperature. The mixture was diluted with 10 mL n-pentane and washed with 10 mL of a 1.00M NaOH solution. The organic phase was dried over $Na_2SO_4$, filtrated and the solvent was removed under reduced pressure to obtain the 1-(phenylthio)-bicyclo[1.1.1]pentane (105 mg, 596 µmol, 100%) as a yellow oil. The turnover of this reaction is assumed to be quantitative to calculate the concentration of the solution of tricyclo[1.1.1]pentane.

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.47–7.44 (m, 2H, $H_{aromatic}$), 7.34–7.28 (m, 3H, $H_{aromatic}$), 2.73 (s, 1H, $C(CH_2)_3CH$), 1.96 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 134.2 ($C_q$, $C_{aromatic}S$), 133.6 (+, $C_{aromatic}$), 128.9 (+, $C_{aromatic}$), 127.6 (+, $C_{aromatic}$), 54.1 (–, $C(CH_2)_3CH$), 45.8 ($C_q$, $C(CH_2)_3CH$), 28.8 (+, $C(CH_2)_3CH$) ppm. Following DOI: https://dx.doi.org/10.14272/AXGWEHWIGICNLX-UHFFFAOYSA-N.1 [2]

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-AXGWEHWIGI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/AXGWEHWIGICNLX-UHFFFAOYSA-N.2

**Methyl 3-(1-bicyclo[1.1.1]pentylthio) propionate** (**4**)




In an argon flushed 10 mL flask a methyl 3-sulfanylpropanoate (14.7 g, 13.5 mL, 122 mmol, 1.30 equiv.) in diethyl ether (125.00 mL) was added to tricyclo[1.1.1]pentane (**2**) (6.22 g, 157 mL, 94.1 mmol, 0.600M, 1.00 equiv.). The reaction was stirred for 15 min at room temperature. The mixture was diluted with 200 mL n-pentane and washed with 200 mL of a 1 M NaOH solution. The organic phase was dried over $Na_2SO_4$, filtrated and the solvent was removed under reduced pressure to obtain the methyl 3-(1-bicyclo[1.1.1]pentylthio) propionate (**4**) as a yellow oil in 80% yield (14.0 g, 75.2 mmol).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 3.71 (s, 3H, $CO_2CH_3$), 2.82–2.79 (m, 2H, $SCH_2$), 2.74 (s, 1H, $C(CH_2)_3CH$), 2.64–2.60 (m, 2H, $SCH_2CH_2$), 1.99 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 172.5(Cq, $CO_2CH_3$), 53.9 (3C, $C(CH_2)_3CH$), 51.9 (+, $CO_2CH_3$), 44.4 ($C_q$, $C(CH_2)_3CH$), 35.5 (–, $SCH_2CH_2$), 28.9 (+, $C(CH_2)_3CH$), 26.2 (–, $SCH_2CH_2$) ppm. Following DOI: https://dx.doi.org/10.14272/XVYUYMKGDFPRBJ-UHFFFAOYSA-N.1 [2]

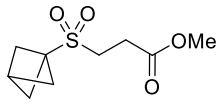
Additional information on the reaction details is available *via* the Chemotion repository:

https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XVYUYMKGDF-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.2

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/XVYUYMKGDFPRBJ-UHFFFAOYSA-N.3

The experimental data are consistent with the literature.[2]

**Methyl 3-(1-bicyclo[1.1.1]pentylsulfonyl) propionate** (**5**)



Methyl 3-(1-bicyclo[1.1.1]pentylthio) propionate (**4**) (14.0 g, 75.2 mmol, 1.00 equiv.) was dissolved in dichloromethane (140 mL) and cooled to 0 °C in an ice bath. 3-Chloroperbenzoic acid (34.0 g, 197 mmol, 2.62 equiv.) was added in portions and the mixture was stirred for 1 h at room temperature after complete addition. The reaction mixture was poured into 150 mL of sat. $Na_2S_2O_3$-solution. The precipitated 3-chloroperbenzoic acid was filtered off and washed with 50 mL of dichloromethane. The filtrate was poured into a separation funnel and the phases were separated. The organic layer was washed successively with 250 mL of a 1 M NaOH-solution. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The Methyl 3-(1-bicyclo[1.1.1]pentylsulfonyl) propionate (**5**) was isolated as a colorless oil in 55% yield (9.01 g, 41.3 mmol).

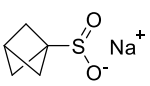
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 3.74 (s, 3H, $CO_2CH_3$), 3.27–3.23 (m, 2H, $SCH_2$), 2.88–2.84 (m, 2H, $SCH_2CH_2$), 2.80 (s, 1H, $C(CH_2)_3CH$), 2.28 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 171.1 (Cq, $CO_2CH_3$), 54.1, 52.6, 51.0 (3C, $C(CH_2)_3CH$), 45.1, 26.9, 26.2 ppm. Following DOI: https://dx.doi.org/10.14272/XBSQKZAIFINLLA-UHFFFAOYSA-N.1 [3]

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XBSQKZAIFI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.2

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/XBSQKZAIFINLLA-UHFFFAOYSA-N.3

The experimental data are consistent with the literature.[3]

**Sodium bicyclo[1.1.1]pentylsulfinate** (**Na-6**)



Methyl 3-(bicyclo[1.1.1]pentan-1-ylsulfonyl)propanoate (13.3 g, 61 mmol, 1.00 equiv.) was dissolved in tetrahydrofuran (130 mL) and stirred at 21 °C. Sodium methanolate (3.29 g, 11.3 mL, 5.4 M, 61 mmol, 1.00 equiv.) was added to the solution and a pale yellow solid precipitated. After

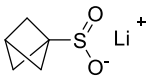
complete addition the reaction mixture was stirred at 21 °C for 20 min. The solvent and the formed acrylate were evaporated under reduced pressure. The sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) was isolated as a yellow solid in 96% yield (857 mg, 6.20 mmol).

**$^1$H NMR** (400 MHz, $D_2O$) $\delta$ = 2.68 (s, 1H, $C(CH_2)_3CH$), 1.88 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $D_2O$) $\delta$ = 57.2 ($C_q$, $C(CH_2)_3CH$), 47.2 (–, 3C, $C(CH_2)_3CH$), 25.8 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2978, 2959, 2904, 2873, 1205, 1190, 1017, 990, 933, 898, 860, 779, 664, 584, 524, 477, 397 $cm^{-1}$. – **HRMS** (ESI, positive, $[C_5H_9O_2{}^{32}S]^+$): calcd 133.0318, found 133.0314.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-KHFMOUFAUH-UHFFFADPSC-NUHFF-MUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/KHFMOUFAUHOHJO-UHFFFAOYSA-M.1

**Lithium bicyclo[1.1.1]pentylsulfinate** (**Li-6**)



The sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (1.00 g, 6.49 mmol, 1.00 equiv.) was dissolved in water (2mL). Then, the solution was acidified by adding 1.00M HCl (pH = 1) and poured into a separation funnel. The aqueous phase was washed three times with 15ml ethyl acetate. The organic layer was collected and dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The residue was solved in tetrahydrofuran (15.0 mL) and lithium hydroxide (155 mg, 6.49 mmol, 1.00 equiv.) in water (2.00 mL) was added to the solution and a pale yellow solid precipitated. After complete addition, the reaction mixture was stirred at 21 °C for 20 min. The solvent was removed under reduced pressure. The lithium bicyclo[1.1.1]pentylsulfinate (**Li-121**) was isolated as a yellow solid in 96% yield (857 mg, 6.20 mmol).

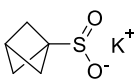
**$^1$H NMR** (400 MHz, $D_2O$) $\delta$ = 2.67 (s, 1H, $C(CH_2)_3CH$), 1.86 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $D_2O$) $\delta$ = 57.3 ($C_q$, $C(CH_2)_3CH$), 47.2 (–, 3C, $C(CH_2)_3CH$), 25.9 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2980, 2949, 2907, 2870, 1579, 1562, 1448, 1205, 1190, 984, 943, 938, 901, 866, 663, 594, 548, 527, 476,

455, 402 $cm^{-1}$. – **HRMS** (ESI, positive, $[C_5H_7LiO_2S]^+$): calcd 139.0400, found 139.0397.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-QTLFBDINSW-UHFFFADPSC-NUHFF-MUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/QTLFBDINSWAZHO-UHFFFAOYSA-M.1

**Potassium bicyclo[1.1.1]pentylsulfinate** (**K-6**)



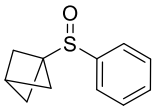
Methyl 3-(1-bicyclo[1.1.1]pentanylsulfonyl)propanoate (**5**) (1.36 g, 6.22 mmol, 1.00 equiv.) was dissolved in tetrahydrofuran (14 mL) and stirred at 21 °C. Potassium *tert*-butoxide in tetrahydrofuran (698 mg, 2.49 mL, 6.22 mmol, 2.50M, 1.00 equiv.) was added to the solution and a pale yellow solid precipitated. After complete addition, the reaction mixture was stirred at 21 °C for 20 min. The solvent and the formed acrylate were evaporated under reduced pressure. The potassium bicyclo[1.1.1]pentylsulfinate (**K-6**) was isolated as a yellow solid in 67% yield (715 mg, 4.20 mmol).

**$^1$H NMR** (400 MHz, $D_2O$) $\delta$ = 2.67 (s, 1H, $C(CH_2)_3CH$), 1.87 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $D_2O$) $\delta$ = 57.3 ($C_q$, $C(CH_2)_3CH$), 47.2 (–, 3C, $C(CH_2)_3CH$), 25.9 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2978, 2956, 2905, 2873, 1203, 1024, 1017, 972, 933, 899, 877, 860, 779, 693, 660, 602, 578, 544, 524, 480 $cm^{-1}$. – **HRMS** (ESI, positive, $[C_5H_7KO_2S]^+$): calcd 170.9877, found 170.9874.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-VIRDEPYHHG-UHFFFADPSC-NUHFF-MUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/VIRDEPYHHGDCIH-UHFFFAOYSA-M.1

**Bicyclo[1.1.1]pentyl phenyl sulfoxide** (**8a**)



1 mmol Scale

Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (154 mg, 1.00 mmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (2.00 mL) under argon. Chloro(trimethyl)silane (163 mg, 190 µL, 1.50 mmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Phenylmagnesium bromide (181 mg, 1.00 mL, 1.00 mmol, 1.00M, 1.00 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 5:1). The Bicyclo[1.1.1]pentyl phenyl sulfoxide (**8a**) was isolated as a colorless solid in 79% yield (152 mg, 791 µmol).

5 mmol Scale

Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (771 mg, 5.00 mmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (20.00 mL) under argon. Chloro(trimethyl)silane (815 mg, 950 µL, 7.50 mmol, 1.50 equiv.) was added and the mixture was heated to 70 °C for 3 h. Phenylmagnesium bromide (905 mg, 5.00 mL, 5.00 mmol, 1.00M, 1.00 equiv.) was added and the reaction was stirred for 3 h at 70 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 5:1). The Bicyclo[1.1.1]pentyl phenyl sulfoxide (**8a**) was isolated as a colorless solid in 23% yield (221 mg, 115 µmol).

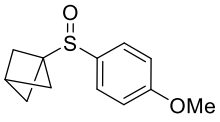
**$R_f$** (cyclohexane/ethyl acetate 5:1) = 0.3. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.55–7.49 (m, 5H, $H_{aromatic}$), 2.83 (s, 1H, $C(CH_2)_3CH$), 1.93–1.87 (m, 6H, $C(CH_2)_3CH$) ppm. Following DOI: https://dx.doi.org/10.14272/IGEMWXAPJBWLLG-UHFFFAOYSA-N.1

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-IGEMWXAPJB-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/IGEMWXAPJBWLLG-UHFFFAOYSA-N.2

The experimental data are consistent with the literature.[4]

**Bicyclo[1.1.1]pentyl 4-methoxyphenyl sulfoxide** (**8b**)



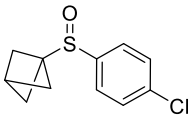

Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. (4-Methoxyphenyl)magnesium bromide (116 mg, 550 µL, 550 µmol, 1.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 2:1). The bicyclo[1.1.1]pentyl 4-methoxyphenyl sulfoxide (**8b**) was isolated as a yellow oil in 68% yield (76.0 mg, 342 µmol).

**$R_f$** (cyclohexane/ethyl acetate 2:1) = 0.10. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.49–7.45 (m, 2H, *H*$_{aromatic}$), 7.04–7.00 (m, 2H, *H*$_{aromatic}$), 3.86 (s, 3H, OC*H*$_3$), 2.82 (s, 1H, C(CH$_2$)$_3$C*H*), 1.89 (s, 6H, C(C*H*$_2$)$_3$CH) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 161.8 ($C_q$, *C*$_{aromatic}$), 132.6 ($C_q$, *C*$_{aromatic}$), 126.0 (+, 2C, *C*$_{aromatic}$H), 114.4 (+, 2C, *C*$_{aromatic}$H), 55.5 ($C_q$, *C*(CH$_2$)$_3$CH), 55.5 (+, O*C*H$_3$), 48.7 (–, 3C, C(*C*H$_2$)$_3$CH), 27.7 (+, C(CH$_2$)$_3$*C*H) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3452, 2969, 2915, 2880, 2840, 1594, 1493, 1460, 1407, 1302, 1248, 1203, 1130, 1085, 1026, 868, 830, 796, 773, 557, 524, 493, 463, 441, 387 cm$^{-1}$. – **MS** (EI, 70 eV, 50 °C): *m/z* (%) = 222 (2) $[M]^+$, 169 (4) $[C_8H_8O_2S + H]^+$, 156 (14) $[C_7H_7O_2S + H]^+$, 155 (8) $[C_7H_7O_2S]^+$, 139 (6) $[C_7H_7OS]^+$, 108 (3) $[C_7H_7O + H]^+$, 100 (13) $[C_5H_7S]^+$, 67 (3) $[C_5H_7]^+$. – **HRMS** *(m/z)*: $[C_{12}H_{14}O_2S]^+$ calcd 222.0715, found 222.0714.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-IFBUZUJIVR-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/IFBUZUJIVRGJML-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl 4-chlorophenyl sulfoxide** (**8c**)



Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. 4-Chlorophenylmagnesium bromide (119 mg, 550 µL, 550 µmol, 1.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 4:1). The bicyclo[1.1.1]pentyl 4-chlorophenyl sulfoxide (**8c**) was isolated as a yellow solid in 53% yield (60.0 mg, 265 µmol).

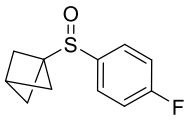
**$R_f$** (cyclohexane/ethyl acetate 4:1) = 0.10. – **MP**: 120 °C. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.51–7.49 (m, 2H, , $H_{aromatic}$), 7.48–7.46 (m, 2H, $H_{aromatic}$), 2.85 (s, 1H, $C(CH_2)_3CH$), 1.93–1.87 (m, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 140.2 ($C_q$, $C_{aromatic}$), 137.0 ($C_q$, $C_{aromatic}$), 129.2 (+, 2C, $C_{aromatic}H$), 125.5 (+, 2C, $C_{aromatic}H$), 55.3 ($C_q$, $C(CH_2)_3CH$), 48.8 (–, 3C, $C(CH_2)_3CH$), 27.7 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 2990, 2970, 2917, 2880, 2853, 1639, 1574, 1473, 1451, 1390, 1310, 1292, 1276, 1256, 1203, 1171, 1129, 1109, 1085, 1078, 1040, 1010, 938, 901, 881, 868, 823, 773, 754, 739, 701, 679, 664, 649, 633, 626, 602, 588, 579, 558, 538, 510, 475, 443, 414, 407 $cm^{-1}$. – **MS** (EI, 70 eV, 20 °C): *m/z* (%) = 226/228 (0.11/0.25) $[M]^+$, 160/162 (15/18) $[C_6H_4ClOS + H]^+$, 143/145 (1/5) $[C_6H_4ClS]^+$, 112/114 (2/8) $[C_6H_4Cl + H]^+$, 111/113 (2/3) $[C_6H_4Cl]^+$, 100 (14) $[C_5H_7S$

+ H]$^+$, 67, (19) [$C_5H_7$]$^+$. – **HRMS** *(m/z)*: [$C_{11}H_{11}ClOS$]$^+$ calcd 226.0219, found 226.0218.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-PRXXLNBZQI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/PRXXLNBZQITSKP-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl 4-fluorophenyl sulfoxide** (**8d**)



Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. 4-Fluorophenylmagnesium bromide (110 mg, 550 µL, 550 µmol, 1.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 2:1). The bicyclo[1.1.1]pentyl 4-fluorophenyl sulfoxide (**8d**) (83.5 mg, 397 µmol, 79% yield) was isolated as a yellow solid in 79% yield (83.0 mg, 395 µmol).

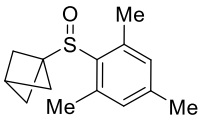
**$R_f$** (cyclohexane/ethyl acetate 2:1) = 0.18. – **MP**: 139 °C. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 7.54–7.50 (m, 2H, $H_{aromatic}$), 7.23–7.18 (m, 2H, $H_{aromatic}$), 2.83 (s, 1H, $C(CH_2)_3CH$), 1.88 (s, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 164.3 ($C_q$, d, $J$ = 250.9 Hz, $C_{aromatic}F$), 137.2 ($C_q$, d, $J$ = 3.1 Hz, $C_{aromatic}S$), 126.3 (+, d, $J$ = 8.7 Hz, 2C, $C_{aromatic}H$), 116.3 (+, d, $J$ = 22.5 Hz, 2C, $C_{aromatic}H$), 55.5 ($C_q$, $C(CH_2)_3CH$), 48.9 (–, 3C, $C(CH_2)_3CH$), 27.9 (+, $C(CH_2)_3CH$) ppm. – **$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ = –109.03 ppm. – **IR** (ATR): $\tilde{\nu}$ = 2987, 2917, 2877, 1588, 1487, 1400, 1289, 1203, 1149, 1132, 1082, 1033, 1010, 939, 884, 870, 826, 772, 557, 541, 513, 492, 467, 411, 387 cm$^{-1}$. – **MS** (EI, 70 eV, 30 °C): *m/z* (%) = 144 (100) [$C_6H_4FOS$ + H]$^+$, 143 (16) [$C_6H_4FOS$]$^+$, 127 (11) [$C_6H_4FS$]$^+$, 115 (9) [$C_5H_7OS$]$^+$, 96 (38) [$C_6H_4F$ + H]$^+$, 95

(14) $[C_6H_4F]^+$, 67 (100) $[C_5H_7]^+$, 55 (4) $[C_4H_7]^+$. – **HRMS** *(m/z)*: $[C_{11}H_{11}FOS]^+$ calcd 210.0515, found 234.1078.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZVCVKIGEBR-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/ZVCVKIGEBRIMGX-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl mesityl sulfoxide** (**8e**)




Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Mesitylmagnesium bromide (123 mg, 550 µL, 550 µmol, 1.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 4:1). The bicyclo[1.1.1]pentyl mesityl sulfoxide (**8e**) was isolated as a yellow solid in 54% yield (63.0 mg, 269 µmol).

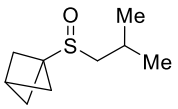
$\mathbf{R_f}$ (cyclohexane/ethyl acetate 4:1) = 0.13. – **MP**: 70 °C. – **$^1$H NMR** (400 MHz, $CD_3OD$) $\delta$ = 6.95 (s, 2H, $H_{aromatic}$), 2.84 (s, 1H, $C(CH_2)_3CH$), 2.46 (br, 6H, $CH_3$), 2.30 (s, 3H, $CH_3$), 2.10–2.08 (m, 3H, $C(CH)_3CH$), 2.05–2.02 (m, 3H, $C(CH)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CD_3OD$) $\delta$ = 142.9 (+, 2C, $C_{aromatic}H$), 132.8 ($C_q$, $C_{aromatic}$), 55.4 ($C_q$, , $C(CH_2)_3CH$), 51.8 (–, 3C, $C(CH_2)_3CH$), 29.2 (+, $C(CH_2)_3CH$), 21.2 (+, $CH_3$), 19.9 (+, 2C, $CH_3$) ppm. Due to peak broadening (3C) are missing. – **IR** (ATR): $\tilde{\nu}$ = 2987, 2965, 2911, 2876, 2853, 1599, 1567, 1504, 1445, 1404, 1380, 1290, 1200, 1128, 1108, 1061, 1040, 1024, 955, 942, 931, 914, 884, 866, 775, 714, 615, 567, 544, 510, 479, 425, 390, 377 $cm^{-1}$. – **MS** (EI, 70 eV, 40 °C): *m/z* (%) = 234 (2) $[M]^+$, 193 (5) $[C_{11}H_{13}OS]^+$, 168 (15) $[C_9H_{11}OS + H]^+$, 120 (12) $[C_9H_{11} + H]^+$, 119 (12)

$[C_9H_{11}]^+$, 115 (2) $[C_5H_7OS]^+$, 100 (13) $[C_5H_7S + H]^+$, 67 (7) $[C_5H_7]^+$. – **HRMS** *(m/z)*: $[C_{14}H_{18}OS]^+$ calcd 234.1078, found 234.1078.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XXXLXGIKCR-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/XXXLXGIKCRQFEA-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl *iso*butyl sulfoxide** (**8f**)




Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Isobutylmagnesium bromide (88.7 mg, 275 µL, 550 µmol, 2.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 1:2). The bicyclo[1.1.1]pentyl isobutyl sulfoxide (**8f**) (41.4 mg, 238 µmol, 48% yield) was isolated as a yellow oil in 48% yield (41.4 mg, 238 µmol).

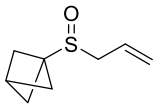
**$R_f$** (cyclohexane/ethyl acetate 1:2) = 0.14. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 2.90 (s, 1H, $C(CH_2)_3CH$), 2.57–2.53 (m, 1H, $SCH_2CH$), 2.26–2.18 (m, 2H, $SCH_2$), 2.14–2.12 (m, 3H, $CH_3$), 2.09–2.05 (m, 3H, $CH_3$), 1.13–1.09 (m, 6H, $C(CH_2)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 58.8 (–, $SCH_2$), 53.8 ($C_q$, $C(CH_2)_3CH$), 49.1 (–, 3C, $C(CH_2)_3CH$), 27.6 (+, $C(CH_2)_3CH$), 23.4 (+, $SCH_2CH$), 23.0 (+, $CH_3$), 21.6 (+, $CH_3$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3471, 3461, 3446, 3438, 3431, 3427, 3420, 3411, 3404, 2966, 2917, 2881, 2850, 2085, 2077, 2053, 2010, 1997, 1946, 1908, 1878, 1868, 1857, 1849, 1840, 1820, 1803, 1795, 1783, 1775, 1764, 1737, 1721, 1703, 1687, 1655, 1636, 1585, 1578, 1571, 1561, 1544, 1528, 1517, 1503, 1492, 1452, 1422, 1394, 1377, 1307, 1293, 1259, 1205, 1167, 1135, 1108, 1074, 1024, 928, 890,

868, 840, 799, 728, 720, 686, 662, 626, 611, 581, 552, 517, 507, 487, 473, 452, 445, 429, 416, 401, 381 $cm^{-1}$. – **MS** (EI, 70 eV, 20 °C): *m/z* (%) = 172 (3) $[M]^+$, 129 (1) $[C_6H_9OS]^+$, 116 (5) $[C_5H_7OS + H]^+$, 106 (24) $[C_4H_9OS + H]^+$, 99 (6) $[C_5H_7S]^+$, 89 (4) $[C_4H_9S]^+$, 67 (100) $[C_5H_7]^+$, 57 (30) $[C_4H_9]^+$, 55 (7) $[C_4H_7]^+$. – **HRMS** *(m/z)*: $[C_9H_{16}OS]^+$ calcd 172.0922, found 172.0923.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-FGVVTABWTL-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/FGVVTABWTLNBPX-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl allyl sulfoxide** (**8g**)



Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Allylmagnesium bromide (79.9 mg, 550 µL, 550 µmol, 1.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 1:1). The bicyclo[1.1.1]pentyl allyl sulfoxide (**8g**) was isolated as a yellow oil in 19% yield (15.0 mg, 96.0 µmol).

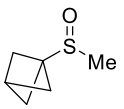
$\mathbf{R_f}$ (cyclohexane/ethyl acetate 1:1) = 0.13. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 5.95–5.84 (m, 1H, $SCH_2CHCH_2$), 5.42–5.41 (m, 1H, $SCH_2CHCHH$), 5.38–5.37 (m, 1H, $SCH_2CHCHH$), 3.34 (m, 2H, $SCH_2$), 2.90 (s, 1H, $C(CH_2)_3CH$), 2.17–2.14 (m, 3H, $C(CHH)_3CH$), 2.12–2.10 (m, 3H, $C(CHH)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 126.5 (+, $SCH_2CHCH_2$), 122.9 (–, $SCH_2CHCH_2$), 54.3 (–, $SCH_2$), 53.9 ($C_q$, $C(CH_2)_3CH$), 49.7(–, 3C, $C(CH_2)_3CH$), 27.8 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3442, 2966, 2917, 2881, 2850, 1636, 1452, 1422, 1377, 1307, 1259, 1205, 1135, 1108, 1074, 1024, 928, 868, 799, 720, 662, 581, 552, 487, 401, 381 $cm^{-1}$. – **MS**

(EI, 70 eV, 20 °C): *m/z* (%) = 156 (2) $[M]^+$, 115 (1) $[C_5H_7OS]^+$, 90 (20) $[C_3H_5OS + H]^+$, 87 (1) $[C_4H_6S + H]^+$, 73 (37) $[C_3H_5S]^+$, 67 (100) $[C_5H_7]^+$, 55 (2) $[C_4H_7]^+$. – **HRMS** *(m/z)*: $[C_8H_{12}OS]^+$ calcd 156.0609, found 156.0608.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-YCWZATQZUI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/YCWZATQZUIPZOB-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl methyl sulfoxide** (**8h**)



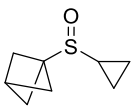

Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (308 mg, 2.00 mmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (4.00 mL) under argon. chloro(trimethyl)silane (326 mg, 381 µL, 3.00 mmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Methylmagnesium bromide (477 mg, 1.33 mL, 4.00 mmol, 3.00M, 2.00 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (ethyl acetate/methanol; 19:1). The bicyclo[1.1.1]pentyl methyl sulfoxide (**8h**) was isolated as a yellow solid in 22% yield (58.0 mg, 445 µmol).

**$R_f$** (ethyl acetate/methanol 19:1) = 0.27. – **MP:** 60 °C. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 2.92 (s, 1H, $C(CH_2)_3CH$), 2.44 (s, 3H, $SCH_3$), 2.15–2.12 (m, 3H, $C(CHH)_3CH$), 2.09–2.06 (m, 3H, $C(CHH)_3CH$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 54.3($C_q$, $C(CH_2)_3CH$), 48.7(–, 3C, $C(CH_2)_3CH$), 35.3 (+, $SCH_3$), 27.2 (+, $C(CH_2)_3CH$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3418, 2969, 2917, 2883, 1718, 1655, 1451, 1421, 1377, 1299, 1259, 1205, 1137, 1109, 1069, 1023, 967, 941, 888, 868, 841, 800, 779, 748, 737, 715, 690, 611, 504, 472, 449, 382 $cm^{-1}$. – **MS** (EI, 70 eV, 30 °C): *m/z* (%) = 130 (6) $[M]^+$, 122 (11), 105 (16), 77 (8), 69 (6), 68 (7), 67 (100) $[C_5H_7]^+$, 66 (13), 65 (64), 64 (17), 63 (10) $[CH_3OS]^+$, 61 (6), 55 (5), 51 (10). – **HRMS** *(m/z)*: $[C_6H_{10}OS]^+$ calcd 130.0452, found 130.0453.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-BSGQGZZQIX-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/BSGQGZZQIXSUCA-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl cyclopropyl sulfoxide** (**8i**)



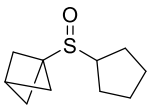
Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Cyclopropylmagnesium bromide (79.9 mg, 1.10 mL, 550 µmol, 0.500M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 1:4). The bicyclo[1.1.1]pentyl cyclopropyl sulfoxide (**8i**) was isolated as a yellow oil in 67% yield (52.0 mg, 333 µmol).

**$R_f$** (cyclohexane/ethyl acetate 1:4) = 0.09. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 2.89 (s, 1H, C($CH_2$)$_3$C*H*), 2.18–2.12 (m, 6H, C(C*H*$_2$)$_3$CH), 2.09–2.02 (m, 1H, SCH($CH_2$)$_2$), 1.17–1.10 (m, 1H, C*H*H), 1.01–0.87 (m, 2H, 2 × CH*H*), 0.77–0.70 (m, 1H, C*H*H) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 54.1 ($C_q$, *C*($CH_2$)$_3$CH), 49.7 (–, 3C, C(*C*$H_2$)$_3$CH), 28.0 (+, C($CH_2$)$_3$*C*H), 26.7 (+, S*C*H($CH_2$)$_2$), 2.0 (–, SCH*C*$H_2$CH$_2$), 1.5 (–, SCHCH$_2$*C*H$_2$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3435, 2989, 2970, 2917, 2880, 1718, 1647, 1639, 1449, 1425, 1414, 1286, 1258, 1205, 1135, 1112, 1037, 1014, 885, 870, 822, 782, 676, 613, 557, 541, 507, 499, 482 $cm^{-1}$. – **MS** (EI, 70 eV, 20 °C): *m/z* (%) = 156 (4) $[M]^+$, 90 (47) $[C_3H_5OS + H]^+$, 73 (28), 72 (5), 68 (5) $[C_5H_7 + H]^+$, 67 (100) $[C_5H_7]^+$, 66 (7), 65 (28). – **HRMS** *(m/z)*: $[C_8H_{12}OS]^+$ calcd 156.0610, found 156.0609.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WKEMTKKUQM-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/WKEMTKKUQMLXPX-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl cyclopentyl sulfoxide** (**8j**)



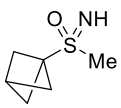
Sodium bicyclo[1.1.1]pentylsulfinate (**Na-6**) (77.1 mg, 500 µmol, 1.00 equiv.) was dissolved in 2-methyltetrahydrofuran (1.00 mL) under argon. Chloro(trimethyl)silane (81.5 mg, 95.2 µL, 750 µmol, 1.50 equiv.) was added and the mixture was heated to 50 °C for 1 h. Cyclopentylmagnesium Bromide (95.3 mg, 275 µL, 550 µmol, 2.00M, 1.10 equiv.) was added and the reaction was stirred for 1 h at 50 °C. The reaction was stopped with saturated $NH_4Cl$-solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were collected and were dried by the addition of $Na_2SO_4$. The mixture was filtered through a glass funnel and the solvent was evaporated under reduced pressure. The crude residue was adsorbed on a small amount of Celite and was purified *via* column chromatography (cyclohexane/ethyl acetate; 1:4). The bicyclo[1.1.1]pentyl cyclopentyl sulfoxide (**8j**) was isolated as a yellow oil in 46% yield (42.0 mg, 228 µmol).

**$R_f$** (cyclohexane/ethyl acetate 1:4) = 0.12. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 3.08–2.99 (m, 1H, SC*H*), 2.85 (s, 1H, C$(CH_2)_3$C*H*), 2.27–2.16(m, 1H, C*H*H), 2.11 (s, 6H, SC(C*H*$_2)_3$CH), 1.97–1.81 (m, 2H, CH*H*), 1.77–1.48 (m, 5H, C*H*H and 2 × C*H*$_2$) ppm. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 57.9 (+, S*C*H$(CH_2)_4$), 53.4 ($C_q$, *C*$(CH_2)_3$CH), 50.0 (–, 3C, C(*C*$H_2)_3$CH), 28.0 (+, C$(CH_2)_3$*C*H), 27.3 (–, *C*$H_2$), 26.3 (–, *C*$H_2$), 26.2 (–, *C*$H_2$), 25.7 (–, *C*$H_2$) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3452, 3445, 2965, 2915, 2870, 1718, 1638, 1449, 1265, 1205, 1135, 1111, 1023, 939, 891, 867, 778, 715, 554, 492 $cm^{-1}$. – **MS** (EI, 70 eV, 20 °C): *m/z* (%) = 184 (4) $[M]^+$, 118 (39) $[C_5H_9OS + H]^+$, 116 (10) $[C_5H_7OS + H]^+$, 101 (9), 100 (4), 99 (13), 69 (49) $[C_5H_9]^+$, 68 (27), 67 (100) $[C_5H_7]^+$, 65 (20). – **HRMS** *(m/z)*: $[C_{10}H_{16}OS]^+$ calcd 184.0923, found 184.0922.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-VNTMCSVVFA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/VNTMCSVVFAFNJR-UHFFFAOYSA-N.1

**Bicyclo[1.1.1]pentyl methyl sulfoximine** (**9**)




To a stirred solution of bicyclo[1.1.1]pentyl methyl sulfoxide (**8h**) (30.4 mg, 233 µmol, 1.00 equiv.) in methanol (1.00 mL) was added ammonium carbonate (89.7 mg, 934 µmol, 4.00 equiv.), followed by (diacetoxyiodo)benzene (226 mg, 700 µmol, 3.00 equiv.). After stirring for 30 min at 21 °C the solvent was removed under reduced pressure. The crude residue was adsorbed on a small amount of silica Celite and was purified *via* column chromatography (ethyl acetate/methanol; 19:1). The bicyclo[1.1.1]pentyl methyl sulfoximine (**9**) was isolated as a colorless solid in 80% yield (27.0 mg, 186 mmol).

**$R_f$** (ethyl acetate/methanol 19:1) = 0.16. – **MP:** 82 °C. – **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ = 2.90 (s, 3H, SC*H*$_3$), 2.82 (s, 1H, C(CH$_2$)$_3$C*H*), 2.23 (s, 6H, C(C*H*$_2$)$_3$CH) ppm. Due to peak broadening (1H) signal is missing. – **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ = 56.2 ($C_q$, *C*(CH$_2$)$_3$CH), 50.4 (–, 3C, C(*C*H$_2$)$_3$CH), 39.0 (+, S*C*H$_3$), 25.2 (+, C(CH$_2$)$_3$*C*H) ppm. – **IR** (ATR): $\tilde{\nu}$ = 3271, 2995, 2919, 2884, 1711, 1414, 1324, 1201, 1142, 1095, 1007, 953, 925, 888, 874, 779, 747, 545, 526, 469 cm$^{-1}$. – **MS** (EI, 70 eV, 20 °C): *m/z* (%) = 145 (4) $[M]^+$, 131 (13) $[C_5H_8NOS + H]^+$, 130 (2) $[C_5H_8NOS]^+$, 100 (3) $[C_5H_7S + H]^+$, 79 (15) $[CH_4NOS + H]^+$, 78 (1) $[CH_4NOS]^+$, 68 (6) $[C_5H_7 + H]^+$, 67 (100) $[C_5H_7]^+$, 55 (5) $[C_4H_7]^+$. – **HRMS** *(m/z)*: $[C_6H_{10}NOS]^+$ calcd 145.0561, found 145.0560.

Additional information on the reaction details is available *via* the Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-KBKAKKSPPN-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Additional information on the analysis of the target compound is available *via* the Chemotion repository: https://dx.doi.org/10.14272/KBKAKKSPPNJJTH-UHFFFAOYSA-N.1

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