SUPPORTING INFORMATION

One-pot Rhodium(I) Catalyzed Hydroboration of Alkenes - Radical Conjugate Addition

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Table of contents

General techniques	S2
Experimental methods and spectroscopic data of compounds:	
<i>O</i> - <i>tert</i> -Butyldimethylsilylcyclohex-2-en-1-ol (1)	S2
Methyl 3-(2-(<i>tert</i> -butyldimethylsilyloxy)cyclohexyl)-2-(2-pyridyl sulfanyl)propanoate (2)	S2
Methyl 3-(2-(<i>tert</i> -butyldimethylsilyloxy)cyclohexyl)propanoate (3)	S3
Methyl 3-[3-(<i>tert</i> -butyldimethylsilyloxy)cyclohexyl]-2-(2-pyridyl sulfanyl)propanoate (4)	S3
1- <i>tert</i> -Butyldimethylsilyloxy-3-(2-pyridylsulfanyl)cyclohexane	S4
Methyl 3-[3-(<i>tert</i> -Butyldimethylsilyloxy)cyclohexyl]propanoate (5)	S4
Methyl 5-(4-methyl-cyclohex-3-enyl)-2-(2-pyridylsulfanyl) hexanoate (7)	S5
1-Methyl-4-[1-methyl-2-(2-pyridylsulfanyl)ethyl]cyclohex-1-ene	S5
Methyl 5-(4-methyl-cyclohex-3-enyl)hexanoate (8)	S5
Methyl 3-[(1 <i>R</i> ,2 <i>R</i> ,4 <i>R</i>)-2-norbornyl]-2-(2-pyridylsulfanyl)propanoate (10)	S6
<i>exo</i> -5-(2-Pyridylsulfanyl)norbornane	S6
Methyl 3-[(1 <i>R</i> ,2 <i>R</i> ,4 <i>R</i>)-2-norbornyl]propanoate (11)	S6
Norborn-5-en-2,3-diol	S7
5,6-Isopropylidenedioxy-2-norbornene (12)	S7
Methyl-3-[(1 <i>R</i> ,2 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>R</i>)-5,6-isopropylidenedioxy-2-norbornyl]-2-(2-pyridylsulfanyl)propanoate	S7
<i>exo</i> -2,3-Isopropylidenedioxy- <i>exo</i> -5-(2-pyridylsulfanyl)norbornane	S8
Methyl 3-[(1 <i>R</i> ,2 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> ,6 <i>R</i>)-5,6-isopropylidenedioxy-2-norbornyl] propanoate (13)	S8
Methyl (5 <i>S</i>)-5,6,6-trimethyl-2-(2-pyridylsulfanyl)heptanoate	S8
(3 <i>R</i>)-2,2,3-Trimethyl-4-(2-pyridylsulfanyl)butane	S9
Methyl (5 <i>S</i>)-5,6,6-trimethyl-heptanoate (15)	S9
References	S9

General techniques. CH₂Cl₂ and benzene were freshly distilled from CaH₂ under N₂. Other reagents were obtained from commercial sources and used as received. Flash column chromatography (FC): Silica gel (0.063-0.200 mm; EtOAc and hexane as eluents. Thin-layer chromatography (TLC): silica gel analytical plates; detection either with UV or by dipping in a soln. of KMnO₄ (3 g), K₂CO₃ (20 g), NaOH 5% (3 mL) in H₂O (300 mL) and subsequent heating. Mp: not corrected; hot stage apparatus. Gas chromatography (GC): achiral column *OPTIMA 1701* (Macherey-Nagel) or the chiral column *PS 086*, β -cyclodextrine, 25% diacetoxy; retention times in min, ratio (%). NMR spectroscopy: Chemical shift δ in ppm relative to tetramethylsilane (δ = 0 ppm) or CHCl₃ for ¹H, (δ = 7.26 ppm) and CDCl₃ for ¹³C, (δ = 77.0 ppm). MS: CI (CH₄); m/z (%); FAB: in 2-nitrobenzyl alcohol with Ar at 8 KV. High resolution mass spectra (HRMS) were recorded on a FTICR mass spectrometer.

***O-tert*-Butyldimethylsilylcyclohex-2-en-1-ol (1).**¹ To a solution of TBDMSCl (850 mg, 5.6 mmol, 1.1 equiv) in CH₂Cl₂ (10 mL) was added successively DBU (0.91 mL, 6.2 mmol, 1.2 equiv) and cyclohex-2-en-1-ol (500 mg, 5.1 mmol, 1 equiv) dropwise at rt under N₂. The reaction mixture was stirred at rt overnight, treated with water and diluted with CH₂Cl₂. The organic phase was washed successively with 0.1 M HCl, aq. sat. NaHCO₃ and dried over MgSO₄. After concentration in vacuo, the crude product was purified by FC (hexane/AcOEt 98:2) to give **1** as a colorless oil (1.0 g, 92%). Physical and spectral data were in accordance with literature data.¹ ¹H NMR (360 MHz, CDCl₃) δ 5.71–5.62 (*m*, 1H), 5.68–5.51 (*m*, 1H), 4.20–4.10 (*m*, 1H), 2.00–1.62 (*m*, 4H), 1.54–1.38 (*m*, 2H), 0.82 (*s*, 9H), 0.00 (*s*, 6H).

Methyl 3-(2-(*tert*-butyldimethylsilyloxy)cyclohexyl)-2-(2-pyridylsulfanyl)propanoate (2). Prepared according to the general procedure A from **1** (640 mg, 3.0 mmol). FC (hexane/ EtOAc 95:5) gave **2** (136 mg, 11%) as a 2:2:1:1 mixture of four diastereomers. Colorless oil.

Mixture of the two major diastereomers (less polar): ¹H NMR (500 MHz, CDCl₃) δ 8.43–8.39 (*m*, 2H, two dias.), 7.49 (*ddd*, *J* = 1.9, 7.4, 8.0, 2H, two dias.), 7.23–7.19 (*m*, 2H, two dias.), 7.00 (*ddt*, *J* = 1.1, 5.0, 7.5, 2H, two dias.), 4.68–4.62 (*m*, 2H, two dias.), 4.06–4.00 (*m*, 1H, one dias.), 3.91–3.87 (*m*, 1H, one dias.), 3.72 (*s*, 6H, two dias.), 2.06 (*ddd*, *J* = 6.0, 7.8, 13.9, 1H, one dias.), 2.01–1.10 (*m*, 20H, two dias.), 1.02–0.91 (*m*, 1H, one dias.), 0.91 (*s*, 9H, one dias.), 0.89 (*s*, 9H, one dias.), 0.08 (*s*, 3H, one dias.), 0.07 (*s*, 3H, one dias.), 0.05 (*s*, 3H, one dias.), 0.03 (*s*, 3H, one dias.). ¹³C NMR (500 MHz, CDCl₃) δ 173.9 (two dias.), 157.8 (one dias.), 157.8 (one dias.), 149.7 (two dias.), 136.4 (two dias.), 122.6 (one dias.), 122.5 (one dias.), 120.1 (one dias.), 120.1 (one dias.), 69.7 (two dias.), 52.3 (two dias.), 44.3 (one dias.), 44.2 (one dias.), 40.1 (one dias.), 40.0 (one dias.), 39.9 (two dias.), 39.0 (one dias.), 38.5 (one dias.), 33.7 (one dias.), 33.4 (one dias.), 26.5 (two dias.), 25.9 (one dias.), 25.8 (one dias.), 25.3 (two dias.), 18.1 (two dias.), 25.9 (two dias.), 4.2 (one dias.), 4.8 (one dias.), 4.9 (one dias.).

Mixture of the two minor diastereomers (more polar): ¹H NMR (500 MHz, CDCl₃) δ 8.43–8.38 (*m*, 2H, two dias.), 7.52–7.46 (*m*, 2H, two dias.), 7.23–7.19 (*m*, 2H, two dias.), 7.02–6.96 (*m*, 2H, two dias.), 4.73 (*t*, *J* = 7.9, 1H, one dias.), 4.58 (*dd*, *J* = 5.2, 10.2, 1H, one dias.), 3.73 (*s*, 3H, one dias.), 3.72 (*s*, 3H, one dias.), 3.58–3.47 (*m*, 1H, one dias.), 3.27–3.21 (*m*, 1H, one dias.), 2.51 (*ddd*, *J* = 3.2, 10.3, 13.4, 1H, one dias.), 2.37 (*ddd*, *J* = 3.2, 10.5, 13.7, 1H, one dias.), 2.10–0.93 (*m*, 20H, two dias.), 0.90 (*s*, 9H, one dias.), 0.89 (*s*, 9H, one dias.), 0.06 (*s*, 3H, one dias.), 0.05

(*s*, 3H, one dias.), 0.03 (*s*, 3H, one dias.), 0.02 (*s*, 3H, one dias.). ^{13}C NMR (500 MHz, CDCl_3): 173.8 (one dias.), 173.8 (one dias.), 157.7 (one dias.), 157.6 (one dias.), 149.4 (one dias.), 149.3 (one dias.), 136.4 (one dias.), 136.4 (one dias.), 122.6 (one dias.), 122.5 (one dias.), 120.2 (two dias.), 71.6 (one dias.), 71.5 (one dias.), 52.7 (two dias.), 45.0 (one dias.), 44.6 (one dias.), 43.0 (one dias.), 42.7 (one dias.), 39.2 (one dias.), 39.1 (one dias.), 36.3 (one dias.), 36.2 (one dias.), 34.6 (two dias.), 32.2 (one dias.), 31.9 (one dias.), 26.2 (one dias.), 26.2 (one dias.), 24.3 (one dias.), 24.2 (one dias.), 20.3 (one dias.), 20.2 (one dias.), $\square$ 3.6 (one dias.), $\square$ 4.2 (one dias.), $\square$ 4.3 (one dias.).

Mixture of four diastereomers: IR (neat) $\square$ 2930, 2860, 1740, 1580, 1450, 1410, 1250, 1120, 1090, 880, 840, 770 cm^{-1} . MS (FAB-MS, matrix: NBA) m/z 410 (MH^+ , 98), 352 (100), 278 (48), 164 (54), 112 (80). Anal. Calcd for $\text{C}_{21}\text{H}_{35}\text{NO}_3\text{SSi}$ (409.66): C 61.57; H 8.61. Found: C 61.49; H 8.68.

Methyl 3-(2-(*tert*-butyldimethylsilyloxy)cyclohexyl)propanoate (3). Prepared according to the general procedure C from **2** (127 mg, 0.31 mmol). FC (hexane/EtOAc 98:2) gave **3** (80 mg, 86 %, *trans/cis* 2:1) (GC: 100 °C 10 min, 5 °C/min, OPTIMA 1701, retention times: *cis* = 37 min (35.5 %), *trans* = 38 min (64.5%)). Colorless oil.

trans-**3** (less polar, major): ^1H NMR (500 MHz, CDCl_3) $\square$ 4.03–4.00 (*m*, 1H), 3.66 (*s*, 3H), 2.30 (*t*, J = 8.0, 2H), 1.78–1.30 (*m*, 10H), 1.09 (*ddd*, J = 2.5, 11.2, 13.4, 1H), 0.88 (*s*, 9H), 0.02 (*s*, 6H). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 174.6, 66.9, 51.4, 40.1, 33.7, 32.3, 31.8, 31.1, 25.8, 20.0, 18.1, $\square$ 4.8.

cis-**3** (more polar, minor): ^1H NMR (500 MHz, CDCl_3) $\square$ 3.67 (*s*, 3H), 3.55–3.47 (*m*, 1H), 2.35–2.30 (*m*, 2H), 1.88–1.81 (*m*, 2H), 1.76–1.68 (*m*, 1H), 1.65–1.54 (*m*, 3H), 1.35–1.12 (*m*, 3H), 1.00–0.87 (*m*, 1H), 0.88 (*s*, 9H), 0.84–0.73 (*m*, 1H), 0.05 (*s*, 6H). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 174.72, 71.7, 51.8, 42.9, 36.38, 36.36, 32.2, 31.98, 31.95, 26.2, 24.3, 18.5, $\square$ 4.23, $\square$ 4.25.

Mixture of diastereomers: MS (CI, CH_4) m/z 301 (MH^+ , 10), 285 (20), 243 (63), 211 (21), 169 (100), 137 (18). IR (neat) $\square$ 2930, 2860, 1740, 1460, 1250, 1020, 840, 780 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{O}_3\text{Si}$ (300.5): C 63.95; H 10.73. Found: C 63.94; H 10.69

Methyl 3-[3-(*tert*-butyldimethylsilyloxy)cyclohexyl]-2-(2-pyridylsulfanyl)propanoate (4). Prepared according to the general procedure B from **1** (640 mg, 3.0 mmol). Hydroboration with $[\text{Rh}(\text{COD})\text{Cl}]_2$ and PPh_3 at rt overnight. FC (hexane/ EtOAc 95:5) gave **4** (843 mg, 69%) as a 1:1:1:1 mixture of four diastereomers and 1-*tert*-butyldimethylsilyloxy-3-(2-pyridylsulfanyl)cyclohexane (direct trapping) (86 mg, 9%) as a 1:1 mixture of two diastereomers. Colorless oil.

Mixture of two diastereomers, less polar): ^1H NMR (500 MHz, CDCl_3) $\square$ 8.41–8.38 (*m*, 2H, two dias.), 7.47 (*ddd*, J = 1.8, 7.3, 8.0, 1H, one dias.), 7.46 (*ddd*, J = 1.8, 7.3, 8.0, 1H, one dias.), 7.19 (*dt*, J = 1.0, 8.0, 1H, one dias.), 7.17 (*dt*, J = 1.0, 8.0, 1H, one dias.), 7.00 (*dt*, J = 1.1, 7.4, 1H, one dias.), 6.99 (*dt*, J = 1.1, 7.4, 1H, one dias.), 4.66–4.61 (*m*, 2H, two dias.), 4.04–3.98 (*m*, 2H, two dias.), 3.71 (*s*, 3H, one dias.), 3.71 (*s*, 3H, one dias.), 2.03–1.63 (*m*, 14H, two dias.), 1.48–1.30 (*m*, 4H, two dias.), 1.18–1.10 (*m*, 2H, two dias.), 1.02–0.86 (*m*, 2H, two dias.), 0.87 (*s*, 9H, one dias.), 0.82 (*s*, 9H, one dias.), 0.03 (*s*, 3H, one dias.), 0.02 (*s*, 3H, one dias.), $\square$ 0.02 (*s*, 3H, one dias.), $\square$ 0.05 (*s*, 3H, one dias.). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 173.6 (one dias.), 173.5

(one dias.), 157.5 (one dias.), 157.5 (one dias.), 149.4 (two dias.), 136.06 (one dias.), 136.01 (one dias.), 122.3 (one dias.), 122.1 (one dias.), 119.8 (one dias.), 119.7 (one dias.), 66.8 (one dias.), 66.7 (one dias.), 52.4 (one dias.), 52.4 (one dias.), 44.2 (one dias.), 44.0 (one dias.), 40.1 (one dias.), 40.0 (one dias.), 39.0 (one dias.), 38.5 (one dias.), 33.7 (two dias.), 32.3 (one dias.), 32.2 (one dias.), 29.5 (two dias.), 25.8 (one dias.), 25.7 (one dias.), 19.9 (one dias.), 19.8 (one dias.), 18.1 (one dias.), 18.0 (one dias.), $\square$ 4.9 (one dias.), $\square$ 5.0 (one dias.).

4 (mixture of two diastereomers, more polar): ^1H NMR (500 MHz, CDCl_3) $\square$ 8.41 $\square$ 8.38 (*m*, 2H, two dias.), 7.50 $\square$ 7.46 (*m*, 2H, two dias.), 7.20 $\square$ 7.17 (*m*, 2H, two dias.), 7.00 (*dt*, $J = 1.1, 7.4$, 1H, one dias.), 6.99 (*dt*, $J = 1.1, 7.4$, 1H, one dias.), 4.71 (*t*, $J = 7.9$, 1H, one dias.), 4.65 (*dd*, $J = 7.5, 8.3$, 1H, one dias.), 3.72 (*s*, 3H, one dias.), 3.718 (*s*, 3H, one dias.), 3.57 $\square$ 3.45 (*m*, 2H, two dias.), 2.00 $\square$ 1.68 (*m*, 12H, two dias.), 1.56 $\square$ 1.47 (*m*, 2H, two dias.), 1.29 $\square$ 1.13 (*m*, 4H, two dias.), 1.04 $\square$ 0.92 (*m*, 2H, two dias.), 0.90 $\square$ 0.83 (*m*, 2H, two dias.), 0.88 (*s*, 9H, one dias.), 0.85 (*s*, 9H, one dias.), 0.06 (*s*, 3H, one dias.), 0.05 (*s*, 3H, one dias.), 0.01 (*s*, 3H, one dias.), 0.005 (*s*, 3H, one dias.). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 173.5 (one dias.), 173.4 (one dias.), 157.3 (one dias.), 157.2 (one dias.), 149.5 (one dias.), 149.4 (one dias.), 136.1 (one dias.), 136.1 (one dias.), 122.2 (two dias.), 119.9 (two dias.), 71.2 (one dias.), 71.2 (one dias.), 52.4 (two dias.), 44.3 (one dias.), 43.9 (one dias.), 42.7 (one dias.), 42.4 (one dias.), 38.8 (one dias.), 38.7 (one dias.), 35.9 (two dias.), 34.4 (one dias.), 34.3 (one dias.), 31.9 (one dias.), 31.6 (one dias.), 25.93 (one dias.), 25.90 (one dias.), 23.9 (one dias.), 23.8 (one dias.), 18.2 (one dias.), 18.1 (one dias.), $\square$ 4.6 (two dias.). Mixture of four diastereomers: IR (neat) $\square$ 2930, 2860, 1740, 1580, 1450, 1410, 1250, 1120, 1070, 840, 760 cm^{-1} . MS (ESI) m/z 432.21 ($[\text{M}+\text{Na}]^+$), 410.23 (MH^+). Anal. Calcd for $\text{C}_{21}\text{H}_{35}\text{NO}_3\text{SSi}$ (409.66): C 61.57; H 8.61. Found: C 61.69; H 8.53.

1-*tert*-Butyldimethylsilyloxy-3-(2-pyridylsulfanyl)cyclohexane. Mixture of two diastereomers: ^1H NMR (500 MHz, CDCl_3) $\square$ 8.42 $\square$ 8.40 (*m*, 2H, two dias.), 7.47 $\square$ 7.43 (*m*, 2H, two dias.), 7.15 (*dt*, $J = 1.0, 8.0$, 1H, one dias.), 7.14 (*dt*, $J = 1.0, 8.1$, 1H, one dias.), 6.96 (*ddd*, $J = 1.2, 4.8, 7.4$, 1H, one dias.), 6.95 (*ddd*, $J = 1.2, 4.9, 7.4$, 1H, one dias.), 4.24 $\square$ 4.18 (*m*, 1H, one dias.), 4.07 $\square$ 4.03 (*m*, 1H, one dias.), 3.74 (*tt*, $J = 3.7, 12.3$, 1H, one dias.), 3.68 (*tt*, $J = 4.2, 10.6$, 1H, one dias.), 2.32 $\square$ 2.27 (*m*, 1H, one dias.), 2.06 $\square$ 1.93 (*m*, 3H, two dias. + one dias.), 1.91 $\square$ 1.78 (*m*, 2H, one dias.), 1.76 $\square$ 1.69 (*m*, 2H, one dias.), 1.65 $\square$ 1.23 (*m*, 8H, two dias.), 0.91 (*s*, 9H, one dias.), 0.88 (*s*, 9H, one dias.), 0.05 (*s*, 6H, one dias.), 0.04 (*s*, 6H, one dias.).

Methyl 3-[3-(*tert*-Butyldimethylsilyloxy)cyclohexyl]propanoate (5). Prepared according to the general procedure C from **4** (225 mg, 0.55 mmol). FC (hexane/EtOAc 98:2) gave **5** (149 mg, 90%) as a 1:1 mixture of two diastereomers. GC: 100 $^\circ\text{C}$ 10 min, 5 $^\circ\text{C}/\text{min}$, column OPTIMA 1701, retention times: 38 min (49.5%) and 40 min (50.5%). Colorless oil

Diastereomer 1 (less polar): ^1H NMR (500 MHz, CDCl_3) $\square$ 4.03 $\square$ 4.00 (*m*, 1H), 3.66 (*s*, 3H), 2.30 (*t*, $J = 7.9$, 2H), 1.77 $\square$ 1.61 (*m*, 4H), 1.60 $\square$ 1.39 (*m*, 4H), 1.35 (*ddd*, $J = 2.6, 3.9, 12.5$, 1H), 1.09 (*ddd*, $J = 2.3, 11.1, 13.3$, 1H), 0.95 $\square$ 0.88 (*m*, 1H), 0.88 (*s*, 9H), 0.02 (*s*, 6H). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 174.6, 66.9, 51.5, 40.1, 33.7, 32.3, 31.8, 31.1, 25.8, 20.0, 18.1, $\square$ 4.8.

Diastereomer 2 (more polar): ^1H NMR (500 MHz, CDCl_3) $\square$ 3.67 (*s*, 3H), 3.55 $\square$ 3.47 (*m*, 1H), 2.34 $\square$ 2.31 (*m*, 2H), 1.88 $\square$ 1.81 (*m*, 2H), 1.76 $\square$ 1.68 (*m*, 1H), 1.64 $\square$ 1.59 (*m*, 1H), 1.59 $\square$ 1.54 (*m*, 1H), 1.33 $\square$ 1.24 (*m*, 2H), 1.23 $\square$ 1.12 (*m*, 2H), 1.00 $\square$ 0.89 (*m*, 1H), 0.88 (*s*, 9H), 0.82 $\square$ 0.73 (*m*, 1H), 0.05 (*s*, 6H). ^{13}C NMR (500 MHz, CDCl_3) $\square$ 174.4, 71.3, 51.5, 42.6, 36.06, 36.04, 31.9, 31.66, 31.63, 25.9, 24.0, 18.2, $\square$ 4.6.

Mixture of two diastereomers: IR (neat) $\bar{\nu}$ 2930, 2860, 1740, 1460, 1360, 1250, 1100, 1070, 880, 840, 770 cm^{-1} . MS (CI, CH_4) m/z 301 (MH^+ , 10), 285 (22), 244 (11), 243 (66), 171 (10), 170 (100), 168 (10), 138 (15). HRMS (CI, isobutane) for $\text{C}_{16}\text{H}_{33}\text{O}_3\text{Si}$ (MH^+) (300.5): calcd 301.2199; found: 301.2194.

Methyl 5-(4-methyl-cyclohex-3-enyl)-2-(2-pyridylsulfanyl)-hexanoate (7). Prepared according to the general procedure B from (*S*)-($\square$)-limonene **6**. Hydroboration with $[\text{Rh}(\text{COD})\text{Cl}]_2$, PPh_3 and catecholborane (0.35 mL, 3.3 mmol, or 0.64 mL, 6 mmol) at rt overnight. FC (hexane/EtOAc 95:5) gave **7** (441 mg, 44% or 479 mg, 48% respectively) as a 1:1:1:1 mixture of four diastereomers (colorless oil) and 1-methyl-4-(1-methyl-2-(2-pyridylsulfanyl)-ethyl)cyclohex-1-ene (direct trapping) (80 mg, 11% or 109 mg, 15% respectively) as a 1:1 mixture of two diastereomers.

Prepared according to the general procedure B from (*S*)-($\square$)-limonene **6**. Hydroboration with the Wilkinson catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ (56 mg, 0.06 mmol) and catecholborane (0.35 mL, 3.3 mmol) at rt overnight. FC (hexane/EtOAc 95:5) gave **7** (431 mg, 43%) as a 1:1:1:1 mixture of four diastereomers (colorless oil) and 1-methyl-4-(1-methyl-2-(2-pyridylsulfanyl)-ethyl)cyclohex-1-ene (direct trapping) (73 mg, 10%) as a 1:1 mixture of two diastereomers.

Mixture of four diastereomers: IR (neat) $\bar{\nu}$ 2920, 1740, 1580, 1560, 1450, 1410, 1260, 1160, 1120, 760, 730 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.41–8.38 (*m*, 4H, four dias.), 7.48 (*dt*, $J = 1.8, 7.9$, 4H, four dias.), 7.21–7.18 (*m*, 4H, four dias.), 7.01–7.97 (*m*, 4H, four dias.), 5.38–5.34 (*m*, 4H, four dias.), 4.58–4.53 (*m*, 4H, four dias.), 3.73 (*s*, 12H, four dias.), 2.10–1.47 (*m*, 32H, four dias.), 1.63 (*s*, 12H, four dias.), 1.45–1.14 (*m*, 16H, four dias.), 0.86 (*d*, $J = 6.4$, 6H, two dias.), 0.84 (*d*, $J = 6.5$, 6H, two dias.). ^{13}C NMR (500 MHz, CDCl_3) δ 173.6 (two dias.), 173.5 (two dias.), 157.7 (four dias.), 149.75 (two dias.), 149.74 (two dias.), 136.4 (four dias.), 134.3 (four dias.), 122.6 (four dias.), 121.3 (two dias.), 121.28 (two dias.), 120.21 (four dias.), 52.7 (two dias.), 52.7 (two dias.), 47.1 (one dias.), 47.04 (one dias.), 47.01 (two dias.), 38.6 (one dias.), 38.5 (one dias.), 38.25 (one dias.), 38.23 (one dias.), 37.31 (one dias.), 37.2 (one dias.), 37.1 (one dias.), 37.0 (one dias.), 32.0 (one dias.), 31.9 (one dias.), 31.76 (one dias.), 31.71 (one dias.), 31.2 (two dias.), 31.1 (two dias.), 30.22 (one dias.), 30.19 (one dias.), 30.1 (one dias.), 30.0 (one dias.), 29.77 (one dias.), 29.75 (one dias.), 27.8 (one dias.), 27.7 (one dias.), 27.4 (two dias.), 25.73 (one dias.), 25.68 (one dias.), 23.7 (four dias.), 16.5 (two dias.), 16.09 (one dias.), 16.07 (one dias.). MS (CI, CH_4) m/z 334 (MH^+ , 97), 332 (22), 185 (16), 156 (21), 126 (15), 112 (100), 111 (48). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{S}$ (333.49): C 68.43; H 8.16. Found: C 68.49; H 8.16.

1-Methyl-4-[1-methyl-2-(2-pyridylsulfanyl)ethyl]cyclohex-1-ene. Mixture of two diastereomers: ^1H NMR (360 MHz, CDCl_3) δ 8.40 (*d*, $J = 6.4$, 2H), 7.45 (*t*, $J = 10.7$, 2H), 7.16 (*d*, $J = 10.8$, 2H), 6.98–6.90 (*m*, 2H), 5.38 (*s*, 2H), 3.38 (*dt*, $J = 7.0, 17.0$, 2H), 3.06–2.96 (*m*, 2H), 2.10–1.55 (*m*, 14H), 1.64 (*s*, 6H), 1.42–1.21 (*m*, 2H), 1.04–0.98 (*m*, 6H).

Methyl 5-(4-methyl-cyclohex-3-enyl)hexanoate (8). Prepared according to the general procedure C from **7** (189 mg, 0.57 mmol). FC (hexane/EtOAc 98:2) gave **8** (116 mg, 91 %, dr 1:1). The diastereomeric ratio was determined by inverse-gated decoupling ^{13}C NMR. Colorless oil.

IR (neat) $\bar{\nu}$ 2920, 1740, 1440, 1380, 1250, 1170, 1020, 790 cm^{-1} . Mixture of two diastereomers: ^1H NMR (500 MHz, CDCl_3) δ 5.39–5.35 (*m*, 2H, two dias.), 3.67 (*s*, 6H, two dias.), 2.34–2.24

(*m*, 4H, two dias.), 2.04–1.86 (*m*, 6H, two dias.), 1.81–1.62 (*m*, 6H, two dias.), 1.63 (*s*, 6H, two dias.), 1.61 (*m*, 2H, two dias.), 1.45–1.10 (*m*, 10H, two dias.), 0.86 (*d*, $J = 6.9$, 3H, one dias.), 0.84 (*d*, $J = 6.6$, 3H, one dias.). ^{13}C NMR (500 MHz, CDCl_3) δ 174.6 (two dias.), 134.3 (two dias.), 121.3 (one dias.), 121.2 (one dias.), 51.7 (two dias.), 38.6 (one dias.), 38.3 (one dias.), 37.3 (one dias.), 37.1 (one dias.), 34.7 (two dias.), 34.0 (one dias.), 33.7 (one dias.), 31.3 (one dias.), 31.1 (one dias.), 29.8 (one dias.), 27.8 (one dias.), 27.4 (one dias.), 25.7 (one dias.), 23.8 (two dias.), 23.16 (one dias.), 23.14 (one dias.), 16.5 (one dias.), 16.1 (one dias.). MS (CI, CH_4) m/z 225 (MH^+ , 97), 224 (M^+ , 43), 223 ($[\text{M}-\text{H}]^+$, 48), 193 (100), 175 (31), 129 (49), 95 (52), 82 (40). Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2$ (224.34): C 74.95; H 10.78. Found: C 74.99; H 10.80.

Methyl 3-[(1*R*,2*R*,4*R*)-2-norbornyl]-2-(2-pyridylsulfanyl)propanoate (10). Prepared according to the general procedure B from norbornene **9** (283 mg, 3.0 mmol) and (*R,R*)-DIOP. FC (hexane/AcOEt 85:15) gave **10** (667 mg, 76%) as a 1:1 mixture of two diastereomers and the direct trapping S-pyridyl derivative (78 mg, 13%). Yellow oil.

Prepared according to the general procedure B from **9** and (*S,S*)-BDPP. Hydroboration at -25°C , overnight. FC (hexane/EtOAc 95:5) gave **10** (596 mg, 68%) a mixture of two diastereomers (dr 1:1) and the direct trapping product (93 mg, 15%).

Prepared according to the general procedure A from **9** (283 mg, 3.0 mmol). FC (hexane/AcOEt 85:15) gave **10** (624 mg, 72%) as a mixture of two diastereomers (dr 1:1) and the direct trapping product (99 mg, 16%).

IR (neat) δ 2949, 2870, 1738, 1580, 1556, 1454, 1416, 1344, 1311, 1263, 1159, 1122, 1043, 987, 760, 725 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.40 (*d*, $J = 5.0$ Hz, 2H, two dias.), 7.48 (*td*, $J = 7.7$, 1.3 Hz, 2H, two dias.), 7.19 (*d*, $J = 8.2$ Hz, 2H, two dias.), 6.98 (*td*, $J = 6.8$, 5.4 Hz, 2H, two dias.), 4.56 (*t*, $J = 7.3$ Hz, 1H, one dias.), 4.53 (*t*, $J = 7.3$ Hz, 1H, one dias.), 3.73 (*s*, 3H, one dias.), 3.72 (*s*, 3H, one dias.), 2.20 (*br. s*, 2H, one dias.), 2.10–1.93 (*m*, 3H, two dias.), 1.87–1.73 (*m*, 2H, two dias.), 1.67–1.40 (*m*, 9H, two dias.), 1.32–1.02 (*m*, 10H, two dias.). ^{13}C NMR (125 MHz, CDCl_3) δ 173.5 (one dias.), 173.4 (one dias.), 157.4 (two dias.), 149.4 (two dias.), 136.0 (two dias.), 122.1 (two dias.), 119.8 (two dias.), 52.4 (one dias.), 52.3 (one dias.), 45.0 (one dias.), 44.9 (one dias.), 41.1 (one dias.), 40.9 (one dias.), 39.9 (one dias.), 39.8 (one dias.), 38.9 (one dias.), 38.6 (one dias.), 37.9 (one dias.), 37.8 (one dias.), 36.6 (one dias.), 36.5 (one dias.), 35.4 (one dias.), 35.3 (one dias.), 29.9 (one dias.), 29.8 (one dias.), 28.5 (two dias.). MS (CI, CH_4) m/z 292 (MH^+ , 100), 260 (9), 196 (12), 156 (8), 126 (13), 112 (31), 83 (7), 62 (5). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{S}$ (291.41): C, 65.95; H, 7.26. Found: C, 65.92; H, 7.21.

exo-5-(2-Pyridylsulfanyl)norbonane (direct trapping): ^1H NMR (360 MHz, CDCl_3) δ 8.42 (*d*, $J = 4.5$ Hz, 1H), 7.47 (*td*, $J = 7.7$, 1.8 Hz, 1H), 7.13 (*d*, $J = 8.2$ Hz, 1H), 6.96 (*dd*, $J = 7.3$, 5.0 Hz, 1H), 3.63–3.58 (*m*, 1H), 2.32 (*s*, 2H), 1.92–1.85 (*m*, 1H), 1.69–1.36 (*m*, 5H), 1.25–1.20 (*m*, 2H).

Methyl 3-[(1*R*,2*R*,4*R*)-2-norbornyl]propanoate (11). Prepared according to the general procedure C from **10** (311 mg, 1.06 mmol). FC (hexane/EtOAc 95:5) gave **11** (176 mg, 91%, 53% ee). GC (85 $^\circ\text{C}$): retention times: 123 min (76.4%) and 127 min (23.6%). The absolute configuration of C2 was assigned as 2*R* in accordance with the absolute configuration of the alcohol resulting from the oxidation of the corresponding *B*-alkylcatecholborane.² $[\alpha]_{\text{D}}^{22} = -13.8$ ($c = 0.81$, CHCl_3).

Prepared according to the general procedure C from **10** (172 mg, 0.59 mmol). FC (hexane/EtOAc 98:2) gave **11** (97 mg, 90%, 85% ee). GC (isotherm 85 $^\circ\text{C}$, β -cyclodextrine 25% acetoxy),

retention times: 123 min (92.4%) and 127 min (7.6%). $[\alpha]_D^{27} = +20.3$ ($c = 0.88$, CHCl_3).

Colorless oil. IR (neat) $\bar{\nu}$ 2949, 2870, 1741, 1437, 1354, 1311, 1248, 1172, 1012 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 3.66 (s, 3H), 2.27 (t, $J = 7.7$ Hz, 2H), 2.19 (s, 1H), 1.95 (s, 1H), 1.66–1.27 (m, 7H), 1.17–0.97 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 51.4, 41.7, 40.8, 37.8, 36.5, 35.2, 32.6, 31.8, 29.9, 28.7. MS (CI, CH_4) m/z 183 (MH^+ , 100), 151 (55), 149 (6), 133 (18), 109 (43), 95 (7), 81 (5), 67 (7). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2$ (182.26): C, 72.49; H, 9.95. Found: C, 72.44; H, 9.94.

Norborn-5-en-2,3-diol.³ To a solution of norbornadiene (10.0 g, 108 mmol) and NMO (6.36 g, 54.0 mmol, 0.5 equiv) in a mixture of acetone (65 mL) and water (10 mL) was added a solution of OsO_4 (25 mg, 0.1 mmol, 0.009 equiv) in t -BuOH (8 mL). The solution was stirred at rt during 2 days. The dark-brown solution was treated with sat. aq. NaHSO_3 and sat. aq. NaHCO_3 and extracted with CH_2Cl_2 (3 $\times$). The organic extract was washed with 1 M HCl, dried over MgSO_4 , filtered and concentrated in vacuo to give a 9:1 mixture of *exo/endo* diol as a brown paste (6.4 g) that was used without further purification for the acetalization step. Physical and spectral data were in accordance with literature data.⁴

exo-Isomer: ^1H NMR (200 MHz, CDCl_3) δ 6.04 (t, $J = 1.8$, 2H), 3.73 (d, $J = 1.6$, 2H), 2.71 (t, $J = 1.7$, 2H), 1.91 (d, $J = 9.4$, 1H), 1.66 (dt, $J = 9.3$, 1.6, 1H).

5,6-Isopropylidenedioxy-2-norbornene (12).³ To a solution of crude diol (6.4 g) in CHCl_3 (10 mL) was added at rt dimethoxypropane (6.0 g, 58.0 mmol, 1.5 equiv) and p -TsOH (50 mg). The mixture was heated at reflux during 3 h. The mixture was treated with Na_2CO_3 solid, filtered and concentrated in vacuo to give a brown oil (8.09 g) which was purified by FC (hexane/ AcOEt 99:1). A mixture of *exo*-12/*endo*-12 (6.14 g, 34% (over 2 steps)) was isolated. Pure 12-*exo* (3.26 g, 18% (over 2 steps)) can be isolated from the mixture. Physical and spectral data were in accordance with literature data.³

exo-12: ^1H NMR (200 MHz, CDCl_3) δ 6.07 (t, $J = 1.7$, 2H), 4.21 (d, $J = 1.4$, 2H), 2.79 (t, $J = 1.6$, 2H), 2.00 (d, $J = 9.1$, 1H), 1.70 (dt, $J = 9.1$, 1.6, 1H), 1.49 (s, 3H), 1.35 (s, 3H).

endo-12: ^1H NMR (200 MHz, CDCl_3) δ 6.15 (s, 2H), 4.71 (d, $J = 1.4$, 2H), 2.96 (d, $J = 1.5$, 2H), 1.68–1.56 (m, 2H), 1.31 (s, 3H), 1.28 (s, 3H).

Methyl-3-[(1*R*,2*R*,4*R*,5*S*,6*R*)-5,6-isopropylidenedioxy-2-norbornyl]-2-(2-pyridylsulfanyl)propanoate. Prepared according to the general procedure B from 12⁶ and (*S,S*)-BDPP. FC (hexane/ EtOAc 95:5) gave methyl 3-(5,6-isopropylidenedioxy-2-norbornyl)-2-(2-pyridylsulfanyl)propanoate (720 mg, 66%) as a 1:1 mixture of two diastereomers and *exo*-2,3-isopropylidenedioxy-*exo*-5-(2-pyridylsulfanyl)norbonane (direct trapping) (140 mg, 17%).

Colorless oil. IR (neat) $\bar{\nu}$ 2960, 1730, 1580, 1450, 1420, 1270, 1160, 1120, 1050, 760, 730 cm^{-1} . Mixture of two diastereomers: ^1H NMR (500 MHz, CDCl_3) δ 8.41 (ddd, $J = 1.0$, 1.9, 5.0, 1H, one dias.), 8.40 (ddd, $J = 1.0$, 1.5, 4.9, 1H, one dias.), 7.49 (ddd, $J = 1.9$, 7.3, 8.1, 1H, one dias.), 7.48 (ddd, $J = 1.9$, 7.2, 8.1, 1H, one dias.), 7.20–7.16 (m, 2H, two dias.), 7.00 (ddd, $J = 1.0$, 5.0, 7.4, 1H, one dias.), 6.99 (ddd, $J = 1.0$, 5.0, 7.3, 1H, one dias.), 4.62 (t, $J = 7.7$, 1H, one dias.), 4.61 (t, $J = 7.6$, 1H, one dias.), 3.99–3.93 (m, 3H, two dias. + one dias.), 3.91–3.88 (m, 1H, one dias.), 3.73 (s, 3H, one dias.), 3.72 (s, 3H, one dias.), 2.26–2.22 (m, 1H, one dias.), 2.18–2.16 (m, 1H, one dias.), 2.09 (s, 1H, one dias.), 2.08–2.02 (m, 1H, one dias.), 1.97–1.85 (m, 4H, two dias.), 1.76 (dt, $J = 7.5$, 13.8, 1H, one dias.), 1.67–1.56 (m, 4H, two dias.), 1.44 (s, 3H, one dias.), 1.43

(*s*, 3H, one dias.), 1.42–1.28 (*m*, 4H, two dias.), 1.27 (*s*, 3H, one dias.), 1.25 (*s*, 3H, one dias.), 1.19–1.13 (*m*, 1H, one dias.), 1.07 (*dt*, $J = 4.8, 12.9$, 1H, one dias.). ^{13}C NMR (500 MHz, CDCl_3) δ 173.5 (one dias.), 173.4 (one dias.), 157.35 (one dias.), 157.31 (one dias.), 149.8 (one dias.), 149.7 (one dias.), 136.4 (two dias.), 122.5 (two dias.), 120.3 (one dias.), 120.2 (one dias.), 109.2 (one dias.), 109.1 (one dias.), 82.37 (one dias.), 82.32 (one dias.), 82.04 (one dias.), 82.02 (one dias.), 52.8 (two dias.), 45.12 (two dias.), 45.09 (one dias.), 44.98 (one dias.), 40.6 (one dias.), 40.5 (one dias.), 38.4 (one dias.), 38.2 (one dias.), 34.3 (one dias.), 34.1 (one dias.), 31.6 (one dias.), 31.4 (one dias.), 29.3 (one dias.), 29.1 (one dias.), 25.8 (two dias.), 24.4 (one dias.), 24.3 (one dias.). MS (CI, CH_4) m/z 365 ($[\text{M}+2]^+$, 7), 364 (MH^+ , 30), 306 (10), 170 (100), 139 (28), 126 (41), 112 (20). Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_4\text{S}$ (363.47): C 62.78; H 6.93. Found: C 62.86; H 6.99.

***exo*-2,3-Isopropylidenedioxy-*exo*-5-(2-pyridylsulfanyl)norbornane.** ^1H NMR (500 MHz, CDCl_3) δ 8.40 (*ddd*, $J = 1.0, 1.9, 5.0$, 1H), 7.45 (*ddd*, $J = 1.9, 7.4, 8.0$, 1H), 7.12 (*dt*, $J = 1.0, 8.0$, 1H), 6.96 (*ddd*, $J = 1.1, 5.0, 7.4$, 1H), 4.19 (*d*, $J = 5.4$, 1H), 4.07 (*d*, $J = 5.4$, 1H), 3.47 (*ddd*, $J = 1.8, 4.8, 8.5$, 1H), 2.41 (*s*, 1H), 2.33 (*d*, $J = 4.8$, 1H), 1.75–1.71 (*m*, 1H), 1.69 (*ddd*, $J = 2.3, 8.6, 13.8$, 1H), 1.50–1.47 (*m*, 1H), 1.47–1.42 (*m*, 1H), 1.44 (*s*, 3H), 1.31 (*s*, 3H). ^{13}C NMR (500 MHz, CDCl_3) δ 159.4, 149.6, 135.8, 122.1, 119.4, 109.2, 81.5, 81.0, 46.5, 40.0, 39.5, 31.8, 29.5, 25.4, 24.1.

Methyl 3-[(1*R*,2*R*,4*R*,5*S*,6*R*)-5,6-isopropylidenedioxy-2-norbornyl]propanoate (13**).** Prepared according to the general procedure C from methyl methyl 3-[(1*R*,2*R*,4*R*,5*S*,6*R*)-5,6-isopropylidenedioxy-2-norbornyl]-2-(2-pyridylsulfanyl)propanoate (206 mg, 0.57 mmol). FC (hexane/ EtOAc 98:2) gave **13** (132 mg, 91%, 76% ee). GC (isotherm 115 °C, β -cyclodextrine 25% acetoxy), retention times: 224 min (11.9%) and 229 min (88.1). The absolute configuration of **13** was not proved but tentitatively assigned by assumed that the stereochemical outcome of the hydroboration of **12** was running similarly to **9**. $[\alpha]_{\text{D}}^{27} = +5.5$ ($c = 0.86$, CHCl_3).

White solid. Mp 48 °C. IR (neat) ν 2980, 1740, 1440, 1370, 1270, 1200, 1170, 1060, 860, 760 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 3.96 (*s*, 2H), 3.67 (*s*, 3H), 2.30 (*t*, $J = 7.7$, 2H), 2.23 (*d*, $J = 4.5$, 1H), 2.02 (*s*, 1H), 1.67 (*dq*, $J = 7.6, 13.6$, 1H), 1.62–1.59 (*m*, 1H), 1.55 (*dq*, $J = 7.7, 13.6$, 1H), 1.43 (*s*, 3H), 1.28 (*s*, 3H), 1.24 (*ddd*, $J = 2.4, 8.4, 12.3$, 1H), 1.20–1.14 (*m*, 2H), 1.01 (*dt*, $J = 4.6, 17.1$, 1H). ^{13}C NMR (500 MHz, CDCl_3) δ 173.9, 108.8, 82.1, 81.8, 51.5, 44.5, 40.1, 35.5, 32.5, 31.1, 30.7, 28.7, 25.5, 24.0. MS (CI, CH_4) m/z 256 ($[\text{M}+2]^+$, 15), 256 (MH^+ , 100), 239 (58), 197 (71), 179 (73), 165 (35), 148 (22), 120 (12), 60 (10). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4$ (254.32): C 66.12, H 8.72. Found: C 66.18, H 8.62.

Methyl (5*S*)-5,6,6-trimethyl-2-(2-pyridylsulfanyl)heptanoate. Prepared according to the general procedure B from **14** and (*R,R*)-DIOP. Hydroboration at rt overnight. FC (hexane/EtOAc 95:5) gave methyl (5*S*)-5,6,6-trimethyl-2-(2-pyridylsulfanyl)heptanoate (486 mg, 55%) as a 1:1 mixture of two diastereomers and (3*R*)-2,2,3-trimethyl-4-(2-pyridylsulfanyl)butane (direct reduction) (100 mg, 16%). Colorless oil. IR (neat) ν 2960, 2870, 1840, 1580, 1450, 1420, 1260, 1160, 1120, 760, 730 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.41 (*ddd*, $J = 1.0, 1.9, 4.9$, 1H, one dias.), 8.40 (*ddd*, $J = 1.0, 1.9, 3.7$, 1H, one dias.), 7.49 (*dt*, $J = 1.9, 7.4$, 1H, one dias.), 7.47 (*dt*, $J = 1.9, 7.4$, 1H, one dias.), 7.21–7.20 (*m*, 1H, one dias.), 7.20–7.19 (*m*, 1H, one dias.), 6.99 (*ddd*, $J = 1.1, 5.0, 7.5$, 1H, one dias.), 6.98 (*ddd*, $J = 1.1, 5.0, 7.5$, 1H, one dias.), 4.58–4.53 (*m*, 2H,

two dias.), 3.73 (*s*, 6H, two dias.), 2.15–2.07 (*m*, 1H, one dias.), 2.05–1.95 (*m*, 1H, one dias.), 1.92–1.84 (*m*, 1H, one dias.), 1.80–1.63 (*m*, 3H, two dias + one dias.), 1.23–1.06 (*m*, 3H, two dias + one dias.), 1.05–0.91 (*m*, 1H, one dias.), 0.84 (*d*, *J* = 6.8, 3H, one dias.), 0.83 (*s*, 9H, one dias.), 0.82 (*d*, *J* = 6.3, 3H, one dias.), 0.81 (*s*, 9H, one dias.). ¹³C NMR (500 MHz, CDCl₃) δ 173.4 (one dias.), 173.2 (one dias.), 157.5 (one dias.), 157.4 (one dias.), 149.4 (one dias.), 149.4 (one dias.), 136.1 (one dias.), 136.0 (one dias.), 122.3 (one dias.), 122.3 (one dias.), 119.8 (one dias.), 119.8 (one dias.), 52.4 (one dias.), 52.3 (one dias.), 46.8 (one dias.), 46.6 (one dias.), 42.7 (one dias.), 42.7 (one dias.), 33.1 (two dias.), 31.3 (one dias.), 31.0 (one dias.), 29.4 (one dias.), 29.2 (one dias.), 27.2 (two dias.), 14.1 (two dias.). MS (CI, CH₄) *m/z* 296 (MH⁺, 100), 294 (13), 280 (21), 261 (12), 113 (22), 111 (53), 58 (21), 56 (11). Anal. Calcd for C₁₆H₂₅NO₂S (295.44): C 65.05; H 8.53. Found: C 65.10, H 8.50.

(3*R*)-2,2,3-Trimethyl-4-(2-pyridylsulfanyl)butane. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (*ddd*, *J* = 1.0, 1.8, 4.9, 1H), 7.45 (*ddd*, *J* = 1.9, 7.4, 8.2, 1H), 7.17 (*dt*, *J* = 1.0, 8.2, 1H), 6.94 (*ddd*, *J* = 1.1, 4.9, 7.4, 1H), 3.63–3.59 (*m*, 1H), 2.65 (*dd*, *J* = 11.0, 12.6, 1H), 1.53 (*ddq*, *J* = 2.7, 6.9, 11.0, 1H), 1.01 (*dd*, *J* = 0.8, 6.8, 3H), 0.95 (*s*, 9H).

Methyl (5*S*)-5,6,6-trimethylheptanoate (15). Prepared according to the general procedure C from methyl (5*S*)-5,6,6-trimethyl-2-(2-pyridylsulfanyl)heptanoate (152 mg, 0.51 mmol). FC (hexane/ EtOAc 98:2) gave **15** (87 mg, 92%, ee 41% (5*S*)). GC (isotherm 55 °C, β -cyclodextrine 25% diacetoxy), retention times: 271 min (70.3%) and 282 min (29.7%). The absolute configuration was assigned as 5*S* in accordance with the absolute configuration of the alcohol resulting from the oxidation of the corresponding *B*-alkylcatecholborane.² [α]_D²⁷ = –17.6 (*c* = 0.96, CHCl₃). Colorless oil. IR (neat) ν 2960, 2870, 1740, 1470, 1440, 1370, 1240, 1170, 1020, 860 cm^{–1}. ¹H NMR (500 MHz, CDCl₃) δ 3.67 (*s*, 3H), 2.36–2.24 (*m*, 2H), 1.81–1.72 (*m*, 2H), 1.52–1.43 (*m*, 1H), 1.15–1.07 (*m*, 1H), 0.96–0.87 (*m*, 1H), 0.84 (*s*, 3H), 0.83 (*s*, 9H). ¹³C NMR (500 MHz, CDCl₃) δ 174.3, 51.4, 42.8, 34.4, 32.9, 31.2, 27.2, 24.0, 14.1. MS (CI, CH₄) *m/z* 189 (13), 187 (MH⁺, 100), 171 (19), 156 (7), 131 (16), 130 (16), 88 (8), 58 (13). HRMS (CI, isobutane) for C₁₁H₂₃O₂ MH⁺ (186.29): calcd: 187.1692; found: 187.1691.

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