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

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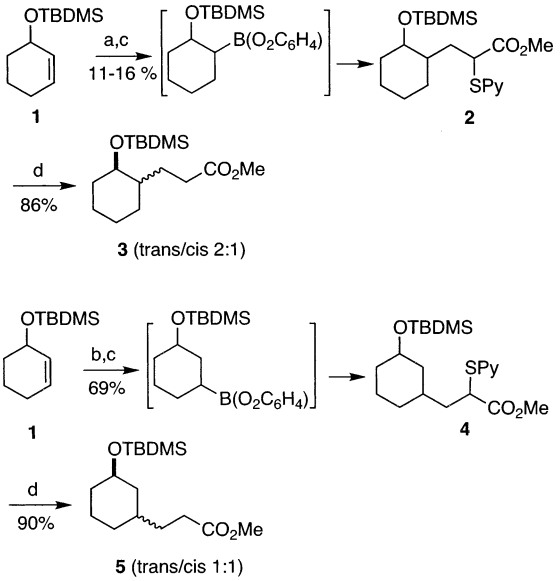
Abstract: *B*-Alkylcatecholboranes, prepared by rhodium(I)-catalyzed hydroboration of alkenes, are suitable radical precursors for conjugate addition to activated olefins. This procedure proved to be particularly useful for the control of the regio- and chemoselectivity of such tandem processes. Enantioselective hydroboration has also been successfully coupled with radical chain reaction in a one-pot process.

In 1967, organoboranes were recognized to participate in free-radical processes.[1] A few years ago, we started to examine the possibility of using organoboranes, easily available through hydroboration of alkenes, as radical precursors in chain reactions. For instance, we have shown that *B*-alkylcatecholboranes very easily undergo radical substitution at boron and therefore are particularly good precursors for radical chain reactions.[2] A general and efficient method for intermolecular conjugate addition to various activated olefins using a Barton carbonate (*N*-methoxycarbonyloxypyridine-2-thione = PTOC-OMe) as chain transfer reagent has been developed.[3] The starting organoboranes were prepared in situ by hydroboration of olefins with commercially available catecholborane catalyzed by the *N*,*N*-dimethylacetamide (10 mol %).[4] This environmentally friendly method is very efficient for simple systems. However, this approach is not satisfactory for the control of regio- and chemoselectivity. We report here that rhodium(I)-catalyzed hydroboration can be combined with radical reactions in one-pot processes. This approach allows an enhanced control of the regioselectivity and chemoselectivity of the reactions. Successful enantioselective carbon−carbon bond formation using this approach is also described.

The control of the regioselectivity of the hydroboration was examined with silylated cyclohexen-3-ol **1**. Hydroboration catalyzed by *N*,*N*-dimethylacetamide followed by radical conjugate addition to methyl acrylate afforded 2-*S*-pyridylthio-substituted ester **2** in low yield (Scheme 1). This product results from selective hydroboration at position 2. Desulfurization with zinc in acetic acid[5] gave ester **3** in 86% yield as a trans/cis 2:1 mixture of isomers. The low yield of the radical process is presumably caused by fragmentation of the unstable 2-siloxycyclohexylborane. Interestingly, by catalyzing the hydroboration step with $[Rh(COD)Cl]_2$ and PPh_3, the regioisomeric product **4** was isolated in 69% yield.[6] Desulfurization gave **5** in 90% yield as a trans/cis 1:1 mixture of stereoisomers. This first reaction proved that radical conjugate addition of organoboranes can be performed in the presence of a rhodium(I) catalyst and a phosphine without a detrimental effect on yield.

SCHEME 1. Regioselective Generation of Radicals from TBDMS-Protected Cyclohexen-3-ol[a]



[a] Key: (a) catecholborane, *N*,*N*-dimethylacetamide (10 mol %); (b) catecholborane, $[Rh(COD)Cl]_2$ (1 mol %) and PPh_3 (4 mol %); (c) CH_2=CHCOOMe (5 equiv), PTOC-OMe (3 equiv) in benzene, 150 W lamp, 10 °C; (d) Zn, AcOH.

The chemoselectivity of hydroboration of a diene was investigated next with commercially available (*S*)-(−)-limonene **6** (Scheme 2). Under *N*,*N*-dimethylacetamide catalysis, a nonseparable mixture of products resulting from hydroboration of both double bonds was obtained. Switching to rhodium(I)-catalyzed hydroboration changed dramatically the course of the reaction, and only the product **7** (as a 1:1:1:1 mixture of four diastereomers) resulting from the hydroboration of the *gem*-disubstituted alkene at the terminal position was isolated in 48−44% and 43% yield using $[Rh(COD)Cl]_2$ and Wilkinson catalyst $Rh(PPh_3)_3Cl$, respectively.[6] Small amounts (10−15% yield) of the *S*-pyridyl derivative resulting from the direct trapping of the radical with the PTOC-OMe chain-

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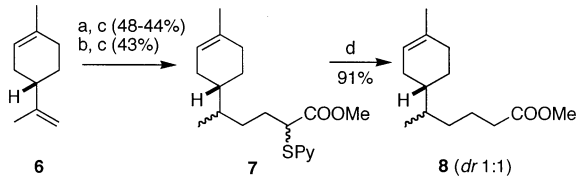
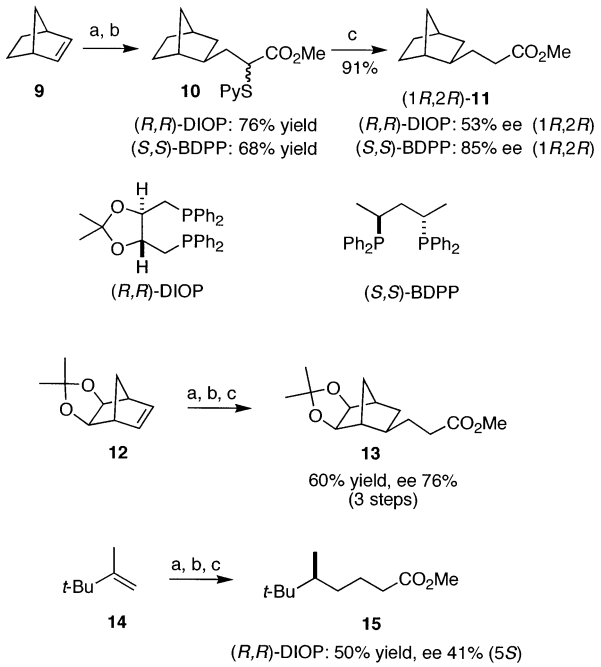
SCHEME 2. Chemoselective Generation of Radical from (*S*)-(−)-Limonene[a]



[a] Key: (a) catecholborane, $[Rh(COD)Cl]_2$ (1 mol %) and PPh_3 (4 mol %); (b) catecholborane, $Rh(PPh_3)_3Cl$ (2 mol %); (c) CH_2=CHCOOMe (5 equiv), PTOC-OMe (3 equiv) in benzene, 150 W lamp, 10 °C; (d) Zn, AcOH.

SCHEME 3. Enantioselective Hydroboration−Radical Conjugate Addition[a]



[a] Key: (a) catecholborane, $[Rh(COD)Cl]_2$ (1 mol %), diphopshine (2 mol %); (b) CH_2=CHCOOMe (5 equiv), PTOC-OMe (3 equiv) in benzene, 150 W lamp, 10 °C; (c) Zn, AcOH.

transfer reagent were also isolated since the reaction was performed under one-pot conditions without slow addition of the PTOC-OMe. Desulfurization of **7** afforded **8** as a 1:1 mixture of diastereomers in 91% yield.

It was also of interest to examine if the enantioselective hydroboration of alkenes can be coupled with radical reaction in a one-pot procedure without variation of yield and enantiomeric excess. The first experiment was run with norbornene **9** (Scheme 3) and methyl acrylate as radical trap. As catalysts for the hydroboration, $[Rh(COD)Cl]_2$ and the chiral diphosphines (*R*,*R*)-DIOP and (*S*,*S*)-BDPP were tested. The reaction product **10** was obtained in 76% and 68% yield, respectively. After desulfurization with zinc in acetic acid, ester **11** was analyzed by gas chromatography on a chiral column, and ee's of 53% with (*R*,*R*)-DIOP and 85% with (*S*,*S*)-BDPP were measured. These values fit well with the observed value after oxidative treatment of the organoborane reported by Burgess (ee 54-60% and 80%, respectively).[7] The reaction was further tested with substrates **12** and **14**, respectively, with (*S*,*S*)-BDPP and (*R*,*R*)-DIOP. After desulfurization, esters **13** and **15** were obtained in 68% and 55% yield from the corresponding alkenes. In case of the bicyclic system **13**, an enantiomeric excess of 76% was measured. The acyclic derivative **15** was obtained with an ee of 41% by using (*R*,*R*)-DIOP. The corresponding oxidative hydroboration was reported with an ee of 53%.[7b]

In conclusion, we have shown that rhodium(I)-catalyzed hydroboration is perfectly compatible with our recently developed tin free conjugate addition method. This enhances considerably the scope of this reaction and opens the way to cyclization reactions starting from polyenes. The coupling of enantioselective hydroborations with radical reactions offers also some promising opportunities for the synthesis of enantiomerically enriched products.

Experimental Section

Procedure A: *N*,*N*-Dimethylacetamide-Catalyzed Hydroboration−Intermolecular Conjugate Addition.[3a] Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at 0 °C to a solution of the olefin (3.0 mmol) and *N*,*N*-dimethylacetamide (28.0 μL, 0.3 mmol) in CH_2Cl_2 (2 mL).[4] The reaction mixture was heated at reflux for 3 h. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C, and the solution was stirred for 15 min at rt. A yellow solution of PTOC-OMe (9.0 mmol, 3 equiv), freshly prepared by stirring a solution of *N*-hydroxypyridine-2-thione sodium salt (1.41 g, 9.45 mmol) and methyl chloroformate (0.7 mL, 9.0 mmol) in benzene (15 mL) in the dark, was added to the *B*-alkylcatecholborane in benzene (15 mL) followed by the activated alkene, methyl acrylate (1.35 mL, 15 mmol), and DMPU (0.36 mL, 3.0 mmol). The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp overnight and treated with 1 N NaOH. The aqueous layer was extracted with CH_2Cl_2 (3×), and the combined organic phases were washed with aq satd NaCl, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by FC (hexane/EtOAc).

Procedure B: Rhodium(I)-Catalyzed Hydroboration−Intermolecular Conjugate Addition. Catecholborane (0.64 mL, 6.0 mmol) was added dropwise at −78 °C to a solution of the olefin (3.0 mmol) and rhodium catalyst (2 mol %), prepared according to the procedure reported by Burgess et al.[7b] from $[Rh(COD)Cl]_2$ (15 mg, 0.03 mmol) and PPh_3 (32 mg, 0.12 mmol) or (*R*,*R*)-DIOP (30 mg, 0.06 mmol) or (*S*,*S*)-BDPP (27 mg, 0.06 mmol), in THF (12 mL). The reaction mixture was stirred for 30 min at −78 °C and stored overnight at −25 °C. Methanol (0.15 mL, 3.6 mmol) was added at 0 °C, and the solution was stirred for 15 min at at 0 °C. The solvent was removed under vacuum. A yellow solution of PTOC-OMe (9.0 mmol), freshly prepared by stirring a solution of *N*-hydroxypyridine-2-thione sodium salt (1.41 g, 9.45 mmol) and methyl chloroformate (0.7 mL, 9.0 mmol) in benzene (15 mL) for 1 h in the dark, was added at rt to the *B*-alkylcatecholborane in benzene (15 mL) followed by the activated alkene, methyl acrylate (1.35 mL, 15 mmol), and DMPU (0.36 mL, 3.0 mmol, 1 equiv). The reaction mixture was irradiated at 10 °C with a 150 W tungsten lamp overnight and treated with 1 N NaOH. The aqueous layer was extracted with CH_2Cl_2 (3×), and the combined organic phases were washed with satd NaCl, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by FC (hexane/EtOAc).

Procedure C.[5] To a solution of α-thiopyridyl ester (1.0 mmol) in acetic acid (4 mL) was added at rt zinc in powder (654 mg, 10.0 mmol), and the disappearance of starting material was monitored by TLC. The reaction mixture was filtered through Celite and washed with Et_2O. The filtrate was washed with

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water (4×) and satd $NaHCO_3$ (4×) and dried ($MgSO_4$). After concentration in vacuo, the crude product was purified by FC (hexane/AcOEt).

Methyl 3-[3-(*tert*-Butyldimethylsilyloxy)cyclohexyl]-2-(2-pyridylsulfanyl)propanoate (4). Compound **4** was prepared according to general procedure B from **1** (640 mg, 3.0 mmol). Hydroboration was achieved with $[Rh(COD)Cl]_2$ 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 four diastereomers: IR (neat) ν 1740 cm^{-1}; MS (ESI) *m*/*z* 432.21 ($[M + Na]^+$), 410.23 (MH^+). Anal. Calcd for $C_{21}H_{35}NO_3SSi$ (409.66): C, 61.57; H, 8.61. Found: C, 61.69; H, 8.53.

Methyl 3-[3-(*tert*-Butyldimethylsilyloxy)cyclohexyl]propanoate (5). Compound **5** was prepared according to 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: colorless oil; GC (100 °C 10 min, 5 °C/min), column OPTIMA 1701, retention times: 38 min (49.5%) and 40 min (50.5%).

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

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

Mixture of two diastereomers: IR (neat) ν 1740 cm^{-1}; MS (CI, CH_4) *m*/*z* 301 (MH^+, 10), 285 (22), 244 (11), 243 (66), 170 (100); HRMS (CI, isobutane) for $C_{16}H_{33}O_3Si$ (MH^+) (300.5) calcd 301.2199, found 301.2194.

Methyl 5-(4-Methylcyclohex-3-enyl)-2-(2-pyridylsulfanyl)-hexanoate (7). Compound **7** was prepared according to general procedure B from (*S*)-(−)-limonene **6**. Hydroboration was achieved with $[Rh(COD)Cl]_2$, 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.

Compound **7** was prepared according to general procedure B from (*S*)-(−)-limonene **6**. Hydroboration was achieved with the Wilkinson catalyst $[RhCl(PPh_3)_3]$ (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.

7 (Mixture of four diastereomers): IR (neat) ν 1740 cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_2S$ (333.49): C, 68.43; H, 8.16. Found: C, 68.49; H, 8.16.

Methyl 5-(4-Methyl-cyclohex-3-enyl)hexanoate (8). Compound **8** was 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) ν 1740, 1440 cm^{-1}; ^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), 193 (100). Anal. Calcd for $C_{14}H_{24}O_2$ (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). Compound **10** was prepared according to 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.

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

Compound **10** was prepared according to 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) ν 1738 cm^{-1}; MS (CI, CH_4) *m*/*z* 292 (MH^+, 100), 260 (9). Anal. Calcd for $C_{16}H_{21}NO_2S$ (291.41): C, 65.95; H, 7.26. Found: C, 65.92; H, 7.21.

Methyl 3-[(1*R*,2*R*,4*R*)-2-Norbornyl]propanoate (11). Compound **11** was prepared according to general procedure C from **10** (311 mg, 1.06 mmol). FC (hexane/EtOAc 95:5) gave **11** (176 mg, 91%, 53% ee): GC (85 °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:[7b] $[\alpha]^{22}_D$ = −13.8 (*c* = 0.81, $CHCl_3$).

Compound **11** was prepared according to 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 °C, β-cyclodextrine 25% acetoxy), retention times: 123 min (92.4%) and 127 min (7.6%); $[\alpha]^{27}_D$ = −20.3 (*c* = 0.88, $CHCl_3$); colorless oil; ^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; IR (neat) ν 1741 cm^{-1}; MS (CI, CH_4) *m*/*z* 183 (MH^+, 100), 151 (55). Anal. Calcd for $C_{11}H_{18}O_2$ (182.26): C, 72.49; H, 9.95. Found: C, 72.44; H, 9.94.

Methyl 3-(5,6-Isopropylidenedioxy-2-norbornyl)-2-(2-pyridylsulfanyl)propanoate. The compound was prepared according to general procedure B from **12**[8] 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) ν 1730 cm^{-1}; MS (CI, CH_4) *m*/*z* 365 ($[M + 2]^+$, 7), 364 (MH^+, 30), 306 (10), 170 (100). Anal. Calcd for $C_{19}H_{25}NO_4S$ (363.47): C, 62.78; H, 6.93. Found: C, 62.86; H, 6.99.

Methyl 3-(5,6-Isopropylidenedioxy-2-norbornyl)propanoate (13). Compound **13** was prepared according to 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 tentitavely assigned by assumed that the stereochemical outcome of the hydroboration of **12** was running similarly to **9**: $[\alpha]^{27}_D$ = −5.5 (*c* = 0.86, $CHCl_3$); white solid; mp 48 °C; IR (neat) ν 1740 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* 255 (MH^+, 100), 239

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(58), 197 (71). Anal. Calcd for $C_{14}H_{22}O_4$ (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. The compound was prepared according to 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. Mixture of two diastereomers: IR (neat) ν 1840 cm^{-1}; MS (CI, CH_4) *m*/*z* 296 (MH^+, 100), 280 (21), 261 (12). Anal. Calcd for $C_{16}H_{25}NO_2S$ (295.44): C, 65.05; H, 8.53. Found: C, 65.10, H, 8.50.

Methyl (5*S*)-5,6,6-trimethyl-heptanoate (15). Compound **15** was 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% ee (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:[7b] $[\alpha]^{27}_D = -17.6$ ($c = 0.96$, $CHCl_3$); colorless oil; IR (neat) ν 1740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (500 MHz, $CDCl_3$) δ 174.3, 51.4, 42.8, 34.4, 32.9, 31.2, 27.2, 24.0, 14.1; MS (CI, CH_4) *m*/*z* 187 (MH^+, 100), 171 (19); HRMS (CI, isobutane) for $C_{11}H_{23}O_2$ MH^+ (186.29) calcd 187.1692, found 187.1691.

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Supporting Information Available: Detailed experimental procedures and full characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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