**Highly Diastereoselective and Enantioselective C–H
Functionalization of 1,2-Dihydronaphthalenes:
A Combined C–H Activation-Cope Rearrangement
Followed by a Retro-Cope Rearrangement**

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Supporting Information

- A: General Procedure and Starting Materials (S2)
- B: Procedures and data of all new compounds (S3-S17)
- C: X-ray structure of compound **B** (S18-S19)

General Procedure:

¹H NMR spectra were run at either 400 or 500 MHz, and ¹³C NMR at either 75 or 125 MHz with the sample solvent being CDCl₃ unless otherwise noted. Mass spectral determinations were carried out in GC-MS (EI), LC-MS (ESI) or by Instrument Center, Department of Chemistry, University at Buffalo. IR spectra were obtained using a Nicolet Impact series 420 FT-IR. Optical rotations were measured using a Jasco DIP-370 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross GA. Enantiomeric excess was determined by HPLC using a Chiralcel OD-H or (*R,R*)-Whelk-O 1 chiral analytical column (UV detection at 254 nm). Analytical TLC was performed on 0.25 mm E. Merck silica gel (60F-254) plates using UV light.

Glassware was dried in oven overnight then flame or heat-gun dried prior to use. Reactions were conducted under argon atmosphere. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Solvent THF, Et₂O, CH₃CN, CH₂Cl₂ and toluene were dried by solvent purifier. 2,2-Dimethylbutane (DMB) was purified by passing through silica gel 60 (Merck, 230-400 mesh, activated by heating under argon), distilled from sodium then stored over MS (3Å), and degassed (by bubbling argon gas for 5-10 min) prior to use.

Starting Materials:

The following starting materials **1**,¹ **2**,² **4**,³ **11**,⁴ **14a**,⁵ **14b**,⁵ **17b**,⁶ **17c**,⁶ **19**⁷ and catalyst Rh₂(S-DOSP)₄⁸ were prepared according to the published procedure. Starting material **7** and **17a** were purchased from Aldrich®.

¹ Davies, H. M. L.; Clark, T. J. and Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817.

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³ Davies, H. M. L. and Jin, Q. *Prod. Natl. Acad. Sci. USA* **2004**, *101*, 5472.

⁴ Maekawa, H.; Itoh, K.; Goda, S. and Nishiguchi, I. *Chirality* **2003**, *15*, 95.

⁵ Harrowven, D. C. and Dainty, R. F. *Tetrahedron*, **1997**, *53*, 15771-15786.

⁶ Magnus, P.; Lacour, J.; Coldham, I.; Mugrage, B. and Bauta, W. B. *Tetrahedron* **1995**, *51*, 11087.

⁷ (a) Kirkiacharian, B. S.; Danan, A. and Koutsourakis, P. G. *Synthesis* **1991**, 879-881. (b)

Balasubramanian, T. and Balasubramanian, K. K. *Tetrahedron Lett.* **1991**, *32*, 6641-6644.

⁸ Davies, H. M. L.; Bruzinski, P.; Hutcheson, D. K.; Kong, N. and Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

3

To a solution of 4-methyl-1,2-dihydronaphthalene **2** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred overnight at rt (*ca.* 12 h). The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 to 10:1 pentane/ether eluent) to provide **3** (151 mg, 95% yield).

(*S*, 3*E*)-methyl 2-((*R*)-1,2-dihydro-4-methylnaphthalen-2-yl)-4-phenylbut-3-enoate (3**):**

white solid, mp 75-77 °C; R_f 0.35 (10:1 pentane/ether); $[\alpha]_D^{25}$ -30.4 (*c* 4.10, CHCl_3); FTIR (CH_2Cl_2): 3059, 3026, 2949, 1733, 1490, 1450, 1435, 1260, 1193, 1158, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.28 (m, 4H), 7.25-7.17 (m, 3H), 7.14 (td, J = 7.0, 1.8 Hz, 1H), 7.07 (br d, J = 7.0 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 9.8 Hz, 1H), 5.73 (br d, J = 3.0 Hz, 1H), 3.68 (s, 3H), 3.10 (*appt.* t, J = 9.3 Hz, 1H), 2.87 (dd, J = 14.2, 6.0 Hz, 1H), 2.86-2.79 (m, 1H), 2.71 (dd, J = 14.2, 6.5 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 136.6, 135.2, 134.3, 133.61, 133.56, 128.5, 127.8, 127.7, 127.1, 126.5, 126.3, 126.2, 126.0, 123.0, 53.1, 51.8, 36.0, 31.6, 19.4; LC-MS (ESI) m/z (relative intensity): 319.2 ($[\text{M}+\text{H}]^+$, 100), 341.1 ($[\text{M}+\text{Na}]^+$, 0.4); HPLC analysis: 99.5% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 9.2 min, major; t_R = 10.9 min, minor); Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2$: C, 82.99; H, 6.96. Found: C, 82.69; H, 6.87.

5

To a solution of 4-methyl-1,2-dihydronaphthalene **2** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (19 mg, 0.01 mmol) in 2,2-dimethylbutane (2 mL) was added a solution of (*E*)-methyl 2-diazo-3-hexanoate **4** (155 mg, 1.0 mmol) in DMB (5 mL) at rt over a 2 h period via syringe-pump. The mixture was stirred for an additional 5 min. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 to 10:1 pentane/ether eluent) to provide **5** (77 mg, 57% yield) as a colorless oil.

(*R*, 2*E*)-methyl 4-((*S*)-1,4-dihydro-1-methylnaphthalen-1-yl)hex-2-enoate (5**):**

colorless oil; R_f 0.31 (10:1 pentane/ether); $[\alpha]_D^{25} -2.8$ (c 2.75, CHCl_3); FTIR (film) 3028, 2964, 2874, 1724, 1654, 1493, 1436, 1350, 1268, 1243, 1174, 1138 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, $J = 7.9$ Hz, 1H), 7.20 (t, $J = 7.0$ Hz, 1H), 7.14 (td, $J = 7.3, 1.2$ Hz, 1H), 7.10 (d, $J = 7.3$ Hz, 1H), 6.84 (dd, $J = 15.6, 10.4$ Hz, 1H), 5.98 (dt, $J = 10.4, 3.7$ Hz, 1H), 5.92 (d, $J = 15.6$ Hz, 1H), 5.60 (dt, $J = 10.4, 2.1$ Hz, 1H), 3.76 (s, 3H), 3.42-3.30 (m, 2H), 2.30 (td, $J = 10.7, 3.1$ Hz, 1H), 1.32 (s, 3H), 1.22-1.05 (m, 2H), 0.60 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 150.0, 141.5, 134.4, 130.9, 128.1, 126.3, 125.8, 125.7, 124.6, 123.3, 58.0, 51.4, 41.9, 30.1, 29.4, 22.3, 12.4; GC-MS (EI) m/z (relative intensity): 128.0 (82), 143.1 (100); HPLC analysis: 98.4% ee (Chiralcel OD-H, 1.0% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 7.2$ min, major; $t_R = 9.1$ min, minor); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.93; H, 8.30.

6

A solution of **5** (74 mg, 98.4% ee) in toluene (5 mL) was refluxed for 6 h. Toluene was removed by rotavapor and the residue was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **6** (68 mg, 92% yield) as a colorless oil.

(*S*, 3*E*)-methyl 2-((*R*)-1,2-dihydro-4-methylnaphthalen-2-yl)hex-3-enoate (6**):**

colorless oil; R_f 0.38 (10:1 pentane/ether); $[\alpha]_D^{25} +141.1$ (c 3.40, CHCl_3); FTIR (film) 3024, 2963, 2874, 1736, 1488, 1451, 1434, 1378, 1336, 1250, 1225, 1191, 1157, 1026, 971 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.18 (m, 2H), 7.14 (td, $J = 7.0, 1.5$ Hz, 1H), 7.08 (br d, $J = 7.3$ Hz, 1H), 5.69-5.66 (m, 1H), 5.55 (dt, $J = 15.3, 6.2$ Hz, 1H), 5.36 (ddt, $J = 15.3, 9.5, 1.5$ Hz, 1H), 3.67 (s, 3H), 2.89 (t, $J = 9.5$ Hz, 1H), 2.84-2.78 (m, 1H), 2.72-2.63 (m, 2H), 2.08-2.01 (m, 2H), 2.04 (s, 3H), 0.99 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.2 (C), 136.7 (CH), 135.3 (C), 134.5 (C), 133.2 (C), 127.7 (CH), 127.0 (CH), 126.6 (CH), 126.4 (CH), 125.0 (CH), 122.9 (CH), 52.6 (CH), 51.6 (CH_3), 35.8 (CH), 31.5 (CH_2), 25.5 (CH_2), 19.3 (CH_3), 13.5 (CH_3); LC-MS (ESI) m/z (relative intensity): 271.1 ($[\text{M}+\text{H}]^+$, 100); HPLC analysis: 98.0% ee (Chiralcel OD-H, 1.0% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 7.5$ min, minor; $t_R = 9.4$ min, major); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.81; H, 8.24.

To a solution of 1,2-dihydronaphthalene **7** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was stirred for an additional 5 min. The solvent was then evaporated under reduced pressure and the residue (**8**:**9** = 5.5:1 based on crude ^1H NMR) was purified by flash chromatography on silica gel (20:1 to 10:1 pentane/ether eluent) to provide a mixture of **8** and **9** (121 mg, 79% yield).

(*R*, 2*E*)-methyl 4-((*S*)-1,4-dihydronaphthalen-4-yl)-4-phenylbut-2-enoate (8**):**

R_f 0.35 (5:1 pentane/ether); ¹H NMR (500 MHz, CDCl₃) δ 7.30 (dd, *J* = 15.8, 8.5 Hz, 1H), 7.18-7.11 (m, 5H), 7.07-7.04 (m, 1H), 6.97 (br d, *J* = 7.6 Hz, 1H), 6.94-6.90 (m, 2H), 6.00 (ddd, *J* = 9.8, 5.2, 1.8 Hz, 1H), 5.90 (ddd, *J* = 9.8, 4.9, 3.0 Hz, 1H), 5.82 (dd, *J* = 15.8, 0.6 Hz, 1H), 3.92-3.88 (m, 1H), 3.75-3.70 (m, 1H), 3.72 (s, 3H), 3.03 (ddd, *J* = 21.0, 5.2, 2.1 Hz, 1H), 2.67-2.58 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 166.8 (C), 149.4 (CH), 139.0 (C), 136.0 (C), 135.8 (C), 128.8 (CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 126.6 (CH), 126.1 (CH), 125.6 (CH), 121.9 (CH), 55.8 (CH), 51.4 (CH₃), 46.2 (CH), 29.9 (CH₂). Molecular analysis is not available due to its slow rearrangement to **10**.

(1R, 1αS, 7αS)-methyl 1α, 6,7,7α-tetrahydro-1-styryl-1H-cyclopropa[α]naphthalene-1-carboxylate (9):

colorless oil; R_f 0.35 (5:1 pentane/ether); FTIR (film) 3024, 2926, 2846, 1718, 1494, 1433, 1236 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.38 (br d, *J* = 7.3 Hz, 1H), 7.23-7.11 (m, 5H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.96 (br d, *J* = 7.3 Hz, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 5.97 (d, *J* = 16.2 Hz, 1H), 3.72 (s, 3H), 2.94 (d, *J* = 9.4 Hz, 1H), 2.61 (ddd, *J* = 16.5, 7.0, 4.0 Hz, 1H), 2.46 (m, 2H), 2.13-2.02 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 173.8, 137.3, 135.6, 135.5, 132.7, 130.2, 128.6, 128.4, 127.4, 126.5, 126.03, 126.01, 120.8, 52.4, 35.6, 30.3, 28.6, 26.6, 17.9; LRMS (EI) *m/z* (relative intensity): 115.0 (74), 128.1 (53), 129.1 (59), 245.1 (100), 304.2 (M⁺, 74); HRMS (EI) *m/z* Calcd for [C₂₁H₂₀O₂]⁺ (M⁺): 304.1458. Found: 304.1464.

10

A solution of **8** and **9** (6:1) in toluene was heated at 60 °C for 48 h. Toluene was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 to 10:1 pentane/ether eluent) to provide **10** (92 mg, 60% overall yield) and **9** (14 mg, 9% yield).

(S, 3E)-methyl 2-((R)-1,2-dihydronaphthalen-2-yl)-4-phenylbut-3-enoate (10):

white solid, mp 83-84 °C; R_f 0.23 (10:1 pentane/ether); $[\alpha]_D^{25} +9.5$ (c 3.00, CHCl_3); FTIR (CH_2Cl_2) 3028, 2949, 1734, 1451, 1434, 1258, 1193, 1162 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.28 (m, 4H), 7.26-7.22 (m, 1H), 7.18-7.11 (m, 2H), 7.07-7.02 (m, 2H), 6.52 (d, $J = 9.8$ Hz, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.14 (dd, $J = 15.9, 9.8$ Hz, 1H), 5.92 (dd, $J = 9.8, 4.3$ Hz, 1H), 3.69 (s, 3H), 3.14 (*appt.* t, $J = 9.5$ Hz, 1H), 2.94-2.86 (m, 2H), 2.82-2.74 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 136.5, 133.8, 133.4, 129.4, 128.8, 128.5, 127.9, 127.7, 127.4, 126.6, 126.4, 126.1, 125.7, 52.9, 51.8, 36.0, 30.8; LC-MS (ESI) m/z (relative intensity): 305.0 ($[\text{M}+\text{H}]^+$, 80), 322.0 ($[\text{M}+\text{Na}]^+$, 100); HPLC analysis: 99.3% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 9.7$ min, minor; $t_R = 11.6$ min, major); Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2$: C, 82.86; H, 6.62. Found: C, 82.64; H, 6.55.

13

To a solution of 3,4-dihydronaphthalen-1-yl acetate **11** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (2 mL) and PhCF_3 (0.4 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was stirred for an additional 5 min. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/ether eluent) to provide **13** (129 mg, 85% yield).

(*S, E*)-methyl 4-(naphthalen-4-yl)-4-phenylbut-2-enoate (13):

colorless oil; R_f 0.35 (5:1 pentane/ether); $[\alpha]_D^{25} +70.5$ (c 5.00, CHCl_3); FTIR (film) 3060, 3024, 2950, 1722, 1652, 1600, 1511, 1495, 1453, 1432, 1132, 1270, 1170 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.95-7.90 (m, 1H), 7.86-7.81 (m, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.56 (dd, $J = 15.6, 6.4$ Hz, 1H), 7.45-7.39 (m, 3H), 7.30-7.25 (m, 3H), 7.23-7.19 (m, 1H), 7.17 (br d, $J = 7.6$ Hz, 2H), 5.64 (d, $J = 15.6$ Hz, 1H), 5.62 (d, $J = 6.4$ Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.8, 150.4, 140.9, 137.0, 134.0, 131.4, 128.83, 128.76,

128.67, 127.9, 126.9, 126.5, 126.2, 125.6, 125.3, 123.7, 123.0, 51.5, 49.4; LC-MS (ESI) m/z (relative intensity): 271.4 (21), 303.2 ($[M+H]^+$, 100), 335.1 ($[M+Na]^+$, 79); HRMS (ESI) m/z Calcd for $[C_{21}H_{18}NaO_2]^+$ ($[M+Na]^+$): 325.1199. Found: 325.1210. HPLC analysis: 99.6% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 13.0 min, major; t_R = 39.4 min, minor).

15a

To a solution of 7-methoxy-4-methyl-1,2-dihydronaphthalene **14a** (0.5 mmol) and $Rh_2(S-DOSP)_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred overnight at rt (*ca* 12h). The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (5:1 pentane/ether eluent) to provide **15a** (157 mg, 90% yield).

(*S*,3*E*)-methyl 2-((*R*)-1,2-dihydro-7-methoxy-4-methylnaphthalen-2-yl)-4-phenylbut-3-enoate (15a**):**

white solid, mp 87-88 °C; R_f 0.30 (5:1 pentane/ether); $[\alpha]_D^{25}$ -15.1 (*c* 6.60, $CHCl_3$); FTIR ($CDCl_3$): 3027, 2998, 2949, 2836, 1733, 1607, 1570, 1499, 1449, 1433, 1309, 1251, 1191, 1159, 1143, 1071, 1032 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 4H), 7.27-7.22 (m, 1H), 7.16 (d, J = 8.5 Hz, 1H), 6.73 (dd, J = 8.5, 2.4 Hz, 1H), 6.65 (d, J = 2.4 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 9.8 Hz, 1H), 5.59 (br d, J = 2.7 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.10 (*appt.* t, J = 9.5 Hz, 1H), 2.88-2.78 (m, 2H), 2.68 (dd, J = 14.4, 6.4 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 158.7, 136.6, 136.2, 133.6, 133.2, 128.5, 128.4, 127.6, 126.3, 126.0, 124.1, 123.7, 113.9, 111.0, 55.1, 53.2, 51.8, 36.1, 32.1, 19.4; LC-MS (ESI) m/z (relative intensity): 349.1 ($[M+H]^+$, 100); HPLC analysis: 98.9% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8

mL/min, λ = 254 nm, t_R = 10.4 min, major; t_R = 14.9 min, minor); Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.09; H, 7.02.

15b

To a solution of 6-methoxy-4-methyl-3,4-dihydronaphthalene **14b** (0.5 mmol) and $Rh_2(S-DOSP)_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred overnight at rt (*ca.* 12 h). The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (5:1 pentane/ether eluent) to provide **15b** (134 mg, 77% yield).

(*S*,*3E*)-methyl 2-((*R*)-1,2-dihydro-6-methoxy-4-methylnaphthalen-2-yl)-4-phenylbut-3-enoate (15b**):**

colorless oil; R_f 0.30 (5:1 pentane/ether); $[\alpha]_D^{25}$ -54.3 (*c* 3.80, $CHCl_3$); FTIR (film): 3025, 2949, 2835, 1733, 1605, 1569, 1490, 1449, 1433, 1256, 1205, 1158 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.26-7.22 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.2, 2.4 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 9.6 Hz, 1H), 5.75 (br d, J = 3.1 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.10 (*appt.* t, J = 9.2 Hz, 1H), 2.84-2.76 (m, 2H), 2.64 (dd, J = 17.1, 9.8 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 158.4, 136.6, 136.3, 133.6, 133.5, 128.5, 128.4, 127.7, 126.9, 126.5, 126.4, 126.0, 111.4, 109.8, 55.3, 53.1, 51.8, 36.3, 30.7, 19.4; LRMS (ESI) m/z (relative intensity): 349.3 ($[M+H]^+$, 36); HRMS (ESI) m/z Calcd for $[C_{23}H_{24}NaO_3]^+$ ($[M+Na]^+$): 371.1618. Found: 376.1614. HPLC analysis: 99.3% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 11.4 min, major; t_R = 15.9 min, minor).

17a

To a solution of (3,4-dihydronaphthalen-1-yloxy)-trimethylsilane **16a** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred for another 2 h at rt. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **17a** (108 mg, 55% yield).

(*S*,3*E*)-methyl 2-((*R*)-1,2-dihydro-4-trimethylsiloxylnaphthalen-2-yl)-4-phenylbut-3-enoate (17a**):**

colorless oil; R_f 0.30 (10:1 pentane/ether); $[\alpha]_D^{25}$ -46.5 (c 3.00, CHCl_3); FTIR (film): 3061, 3027, 2952, 1734, 1636, 1488, 1450, 1435, 1363, 1341, 1254, 1159, 1089, 1064 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.42 (d, $J = 7.5$ Hz, 1H), 7.35-7.28 (m, 4H), 7.26-7.19 (m, 2H), 7.17 (td, $J = 7.3, 1.2$ Hz, 1H), 7.06 (d, $J = 7.3$ Hz, 1H), 6.39 (d, $J = 15.6$ Hz, 1H), 6.13 (dd, $J = 15.6, 9.7$ Hz, 1H), 5.14 (d, $J = 5.1$ Hz, 1H), 3.66 (s, 3H), 3.10 (*appt.* t, $J = 9.5$ Hz, 1H), 2.95-2.85 (m, 2H), 2.77 (d, $J = 14.7, 4.3$ Hz, 1H), 0.26 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 137.7, 149.0, 136.6, 134.9, 133.8, 132.8, 128.5, 127.8, 127.7, 127.5, 126.4, 126.3, 126.1, 122.1, 106.2, 53.3, 51.8, 35.5, 31.0, 0.1; LRMS (ESI) m/z (relative intensity): 343.4 (100), 415.3 ($[\text{M}+\text{Na}]^+$, 44); HRMS (ESI) m/z Calcd for $[\text{C}_{24}\text{H}_{28}\text{NaO}_3\text{Si}]^+$ ($[\text{M}+\text{Na}]^+$): 415.1700. Found: 415.1716. HPLC analysis: 97.5% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 7.3$ min, major; $t_R = 11.5$ min, minor).

17b

To a solution of *tert*-butyl-(3,4-dihydronaphthalen-1-yloxy)-dimethylsilane **16b** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred for another 2h at rt. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **17b** (171 mg, 78% yield).

(*S*,3*E*)-methyl 2-((*R*)-1,2-dihydro-4-*tert*-butyldimethylsiloxy)naphthalen-2-yl)-4-phenylbut-3-enoate (17b**):**

colorless oil; R_f 0.33 (10:1 pentane/ether); $[\alpha]_D^{25}$ -51.7 (c 4.00, CHCl_3); FTIR (film): 3061, 3026, 2953, 2930, 2885, 2858, 1735, 1636, 1601, 1572, 1488, 1472, 1450, 1434, 1363, 1340, 1259, 1158, 1088, 1064 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.48 (br d, J = 7.6 Hz, 1H), 7.35-7.28 (m, 4H), 7.25-7.18 (m, 2H), 7.16 (td, J = 7.3, 1.2 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 6.13 (dd, J = 15.6, 9.6 Hz, 1H), 5.12 (d, J = 4.9 Hz, 1H), 3.66 (s, 3H), 3.10 (*appt.* t, J = 9.5 Hz, 1H), 2.93-2.84 (m, 2H), 2.79-2.72 (m, 1H), 1.01 (s, 9H), 0.21 (s, 3H), 0.20 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.7 (C), 149.2 (C), 136.6 (C), 134.9 (C), 133.8 (CH), 133.0 (C), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.4 (CH), 126.3 (CH), 126.1 (CH), 122.1 (CH), 105.7 (CH), 53.4 (CH), 51.8 (CH_3), 35.6 (CH), 31.0 (CH_2), 25.8 (CH_3), 18.3 (C), -4.4 (CH_3), -4.8 (CH_3); LRMS (ESI) m/z (relative intensity): 435.5 ($[\text{M}+\text{H}]^+$, 15), 457.3 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) m/z Calcd for $[\text{C}_{27}\text{H}_{34}\text{NaO}_3\text{Si}]^+$ ($[\text{M}+\text{Na}]^+$): 457.2169. Found: 457.2185. HPLC analysis: 95.2% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 6.2 min, major; t_R = 8.8 min, minor).

17c

To a solution of 1-(3,4-dihydronaphthalenyloxy)-triisopropylsilane **16c** (0.5 mmol) and $\text{Rh}_2(\text{S-DOSP})_4$ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinyl diazoacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred for another 2 h at rt. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **17c** (127 mg, 53% yield).

(*S*,3*E*)-methyl 2-((*R*)-1,2-dihydro-4-triisopropylsiloxylnaphthalen-2-yl)-4-phenylbut-3-enoate (17c**):**

colorless oil; R_f 0.38 (10:1 pentane/ether); $[\alpha]_D^{25}$ -51.9 (c 4.60, CHCl_3); FTIR (film): 3061, 3026, 2946, 2892, 2867, 1735, 1636, 1600, 1574, 1487, 1464, 1434, 1362, 1340, 1260, 1158, 1089, 1066 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, J = 7.3 Hz, 1H), 7.36-7.28 (m, 4H), 7.25-7.19 (m, 2H), 7.17 (td, J = 7.3, 1.2 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.14 (dd, J = 15.9, 9.8 Hz, 1H), 5.11 (d, J = 4.9 Hz, 1H), 3.65 (s, 3H), 3.11 (*appt.* t, J = 9.8 Hz, 1H), 2.93-2.86 (m, 2H), 2.75 (dd, J = 17.5, 8.0 Hz, 1H), 1.28 (hept, J = 7.6 Hz, 3H), 1.12 (d, J = 7.6 Hz, 9H), 1.11 (d, J = 7.6 Hz, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.7 (C), 149.3 (C), 136.6 (C), 134.9 (C), 133.8 (CH), 133.0 (C), 128.5 (CH), 127.72 (CH), 127.68 (CH), 127.5 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 122.2 (CH), 104.7 (CH), 53.4 (CH), 51.7 (CH_3), 35.6 (CH), 31.1 (CH_2), 18.07 (CH_3), 18.05 (CH_3), 12.7 (CH); LRMS (ESI) m/z (relative intensity): 477.5 ($[\text{M}+\text{H}]^+$, 6), 499.3 ($[\text{M}+\text{Na}]^+$, 100); HRMS (ESI) m/z Calcd for $[\text{C}_{30}\text{H}_{40}\text{NaO}_3\text{Si}]^+$ ($[\text{M}+\text{Na}]^+$): 457.2169. Found: 457.2185. HPLC analysis: 91.3% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 6.0 min, major; t_R = 8.9 min, minor).

18

To a stirring solution of **17b** (91 mg) in CH₃CN (2 mL) was added 3 drops of HF solution (48%). The resulting solution was stirred for 1.5h at rt. Ethyl acetate (30 mL) was added. The mixture was washed with saturated NaHCO₃ (5 mL) and brine (5 mL), then dried over MgSO₄. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (1:1 pentane/ether) to afford **18** (56 mg, 84% yield).

(*R, E*)-methyl 2-((*R*)-1,2,3,4-tetrahydro-1-oxonaphthalen-3-yl)-4-phenylbut-3-enoate (18**):**

colorless oil; R_f 0.40 (1:1 pentane/ether); [α]_D²⁵ −66.1 (*c* 3.20, CHCl₃); FTIR (film): 3060, 3027, 2951, 2843, 1734, 1683, 1601, 1496, 1456, 1435, 1359, 1295, 1261, 1226, 1194, 1160, 1118, 1023 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.48 (td, *J* = 7.3, 1.2 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.36-7.30 (m, 3H), 7.29-7.25 (m, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 9.8 Hz, 1H), 3.74 (s, 3H), 3.19 (*appt.* t, *J* = 8.8 Hz, 1H), 3.07 (br d, *J* = 14.9 Hz, 1H), 2.82-2.67 (m, 3H), 2.49 (dd, *J* = 16.4, 11.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 197.0, 172.8, 142.6, 136.2, 134.5, 133.8, 132.1, 129.0, 128.6, 128.0, 127.1, 127.0, 126.4, 124.6, 54.7, 52.1, 43.4, 37.5, 33.2; LC-MS (ESI) *m/z* (relative intensity): 319.2 ([M+H]⁺, 100), 341.1 ([M+Na]⁺, 0.4); HPLC analysis: 96.2% ee (*R,R*-Whelk O1, 20.0% *i*-PrOH in hexane, 1.0 mL/min, λ = 254 nm, t_R = 22.2 min, major; t_R = 30.6 min, minor); Anal. Calcd for C₂₁H₂₀O₃: C, 78.73; H, 6.29. Found: C, 78.65; H, 6.34.

20

To a solution of 4-methyl-2*H*-chromene **19** (0.5 mmol) and Rh₂(*S*-DOSP)₄ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl phenylvinylidiazooacetate **1** (111 mg, 0.55 mmol) in DMB (5 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling). The resulting mixture was then stirred for another 5 min. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (10:1 pentane/ether eluent) to provide **20** (120 mg, 75% yield).

(*S*,3*E*)-methyl 2-((*R*)-4-methyl-2*H*-chromen-2-yl)-4-phenylbut-3-enoate (20**):**

colorless oil; R_f 0.35 (5:1 pentane/ether); [α]_D²⁵ +25.1 (*c* 3.38, CHCl₃); FTIR (film): 3028, 2950, 1734, 1654, 1605, 1576, 1488, 1450, 1435, 1380, 1356, 1226, 1164, 1128, 1041, 1010 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.25 (m, 4H), 7.24-7.19 (m, 1H), 7.15-7.10 (m, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 9.1 Hz, 1H), 5.53 (br d, *J* = 2.4 Hz, 1H), 5.19 (m, 1H), 3.70 (s, 3H), 3.52 (dd, *J* = 9.1, 7.2 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.6, 152.6, 136.6, 134.1 (2C), 131.2, 129.3, 128.4, 127.6, 126.4, 123.5, 123.2, 121.1, 119.1, 116.2, 75.1, 54.8, 52.1, 18.0; LC-MS (ESI) *m/z* (relative intensity): 241.7 (82), 268.2 (30), 294.2 (37), 321 ([M+H]⁺, 100); HPLC analysis: 95.1% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t_R = 11.9 min, minor; t_R = 39.2 min, major); Anal. Calcd for C₂₁H₂₀O₃: C, 78.73; H, 6.29. Found: C, 78.63; H, 6.29.

A

To a solution of *tert*-butyl-(3,4-dihydronaphthalen-1-yloxy)-dimethylsilane **16b** (0.5 mmol) and Rh₂(*S*-DOSP)₄ (4.8 mg, 0.0025 mmol) in 2,2-dimethylbutane (1 mL) was added a solution of (*E*)-methyl *p*-bromophenylvinylidiazooacetate (155 mg, 0.55 mmol) in DMB (9 mL) over a 45 min period via syringe-pump at 0 °C (with crashed-ice cooling).

The resulting mixture was then stirred for another 4 h at rt. The solvent was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **A** (173 mg, 67% yield).

(*S*,3*E*)-methyl 4-(4-bromophenyl)-2-((*R*)-1,2-dihydro-4-*tert*-butyldimethylsiloxynaphthalen-2-yl)but-3-enoate (A**):**

colorless oil; R_f 0.33 (10:1 pentane/ether); $[\alpha]_D^{25} -75.5$ (c 2.69, CHCl_3); FTIR (film): 3024, 2952, 2930, 2885, 2857, 1734, 1635, 1487, 1471, 1434, 1363, 1341, 1257, 1158, 1072, 1009 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 7.3$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.23-7.15 (m, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 7.05 (d, $J = 7.0$ Hz, 1H), 6.32 (d, $J = 15.9$ Hz, 1H), 6.13 (dd, $J = 15.9, 9.6$ Hz, 1H), 5.09 (d, $J = 5.2$ Hz, 1H), 3.68 (s, 3H), 3.09 (*appt.* t, $J = 9.6$ Hz, 1H), 2.94-2.85 (m, 2H), 2.77-2.70 (m, 1H), 1.01 (s, 9H), 0.21 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.5, 149.3, 135.5, 134.9, 133.0, 132.5, 131.6, 127.9, 127.8, 127.5, 126.9, 126.4, 122.2, 121.4, 105.5, 53.4, 51.8, 35.6, 31.0, 25.8, 18.3, -4.4, -4.8; LRMS (ESI) m/z (relative intensity): 398.9 (52), 513.0 ($[\text{M}+\text{Na}]^+$, 98); HRMS (ESI) m/z Calcd for $[\text{C}_{27}\text{H}_{33}\text{BrNaO}_3\text{Si}]^+$ ($[\text{M}+\text{Na}]^+$): 535.1275. Found: 535.1288. HPLC analysis: 95.2% ee (Chiralcel OD-H, 0.5% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 11.1$ min, minor; $t_R = 13.6$ min, major).

B

To a stirring solution of **A** (102 mg) in CH_3CN (5 mL) was added 4 drops of HF solution (48%). The resulting solution was stirred for 1 h at rt. The mixture was diluted with Ethyl acetate (30 mL), washed with saturated NaHCO_3 (5 mL) and brine (5 mL), then dried over MgSO_4 . The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (1:1 pentane/ether) to afford **B** (67 mg, 83% yield) as a white solid which can be recrystallized from ether/pentane to give a colorless crystal (98.6 % ee) suitable for X-ray crystallography.

(*R, E*)-methyl 4-(4-bromophenyl)-2-((*R*)-1,2,3,4-tetrahydro-1-oxonaphthalen-3-yl)but-3-enoate (B**):**

white solid, mp 103-112 °C; R_f 0.35 (1:1 pentane/ether); $[\alpha]_D^{25}$ -65.9 (c 3.35, CHCl_3); FTIR (CH_2Cl_2): 3027, 2949, 1733, 1684, 1603, 1487, 1455, 1434, 1295, 1259, 1227, 1194, 1160, 1118, 1073, 1008 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (dd, $J = 7.6, 0.9$ Hz, 1H), 7.48 (td, $J = 7.6, 0.9$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 7.6$ Hz, 1H), 6.45 (d, $J = 15.9$ Hz, 1H), 6.23 (dd, $J = 15.9, 9.7$ Hz, 1H), 3.74 (s, 3H), 3.18 (appt. t, $J = 9.5$ Hz, 1H), 3.04 (br d, $J = 15.0$ Hz, 1H), 2.82-2.67 (m, 3H), 2.48 (dd, $J = 16.4, 11.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 196.9, 172.6, 142.4, 135.1, 133.8, 133.3, 132.1, 131.7, 129.0, 128.0, 127.1, 127.0, 125.4, 121.8, 54.6, 52.2, 43.3, 37.5, 33.2; LRMS (ESI) m/z (relative intensity): 399.1 ($[\text{M}+\text{H}]^+$, 9), 421.0 ($[\text{M}+\text{Na}]^+$, 95); HRMS (ESI) m/z Calcd for $[\text{C}_{21}\text{H}_{19}\text{BrNaO}_3]^+$ ($[\text{M}+\text{Na}]^+$): 421.0410. Found: 421.0402. HPLC analysis: 98.6% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 35.6$ min, minor; $t_R = 37.7$ min, major). Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{BrO}_3$: C, 63.17; H, 4.80; Br, 20.01. Found: C, 63.23; H, 4.79; Br, 19.77.

In order to prove the stereochemistry, **10** was converted to **18** by the following procedure (conditions have not been optimized):

To a solution of **10** (50 mg) in THF-H₂O (4:1, 2.25 mL) was added NBS (32.5 mg, 1.1 eq.) at rt. The resulting mixture was stirred for 0.5 h, then diluted with EtOAc (20 mL), washed with brine (10 mL) and dried over MgSO_4 . The crude product was purified by flash chromatography on silica gel (1:1 pentane/ether eluent) to give **C** (54 mg, 81% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.43-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.30-7.22 (m, 3H), 7.11-7.07 (m, 1H), 6.66 (d, $J = 15.9$ Hz, 1H), 6.21 (dd, $J = 15.9, 9.8$ Hz, 1H), 4.98 (d, $J = 2.7$ Hz, 1H), 4.44 (s, 1H), 3.76 (s, 3H), 3.43 (appt. t, $J = 9.9$ Hz, 1H), 2.86-

2.76 (m, 2H), 2.72-2.62 (m, 1H), 2.53 (br s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 136.2, 134.8, 134.6, 133.6, 130.5, 129.0, 128.65, 128.57, 128.0, 126.8, 126.5, 124.7, 72.9, 55.8, 53.8, 52.3, 35.0, 29.4.

Pyridinium chlorochromate (54 mg, 2 eq.) was added to a stirring suspension of **C** (45 mg), NaOAc (20 mg, 2 eq.) and celite in DCM (5 mL) at rt. The mixture was stirred for 3h at rt and then filtrated through a pad of silica gel. The cake was washed with DCM and ether. The solvent was removed and the crude product was purified by flash chromatography on silica gel (2:1 pentane/ether eluent) to afford the ketone (33.5 mg, 74% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.43 (d, J = 7.6 Hz, 2H), 7.38-7.33 (m, 3H), 7.32-7.27 (m, 1H), 7.23 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 15.9 Hz, 1H), 6.16 (dd, J = 15.9, 9.8 Hz, 1H), 4.24 (br d, J = 2.1 Hz, 1H), 3.77 (s, 3H), 3.52 (*appt.* t, J = 9.8 Hz, 1H), 2.96-2.86 (m, 2H), 2.67-2.61 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 190.0, 172.1, 141.7, 135.9, 135.5, 134.3, 129.1, 128.9, 128.7, 128.2, 127.3, 126.5, 123.7, 54.1, 53.1, 52.4, 40.7, 29.3.

To a stirring solution of the ketone obtained the above step (14 mg) in HOAc (2 mL) was added zinc dust (12 mg, 5 eq.) at rt. The mixture was stirred overnight, diluted with EtOAc (20 mL), washed with NaHCO_3 and brine, and then dried over MgSO_4 . The crude product was purified by flash chromatography (2:1 petroleum ether/ether eluent) to give **18** (6.5 mg, 56% yield). The ^1H NMR data, HPLC trace (>99% ee) and optical rotation sign ($[\alpha]_{\text{D}}^{22}$ -56.0 (c 0.65, CHCl_3)) of **18** were consistent with the data of **18** obtained from **16**.

X-ray Structure of compound **B**:⁹

Torsion angle C3-C11-C20-O2 = 17.8(4)°

⁹ The X-ray crystallographic data have been submitted to the Cambridge Structure Database: Gerlits, O. O. and Coppens, P. *Private Communication* (1078), **2004**, CCDC 237040.

Torsion angle C24-C32-C41-O5 = 40.8(4)°