Supporting Information

Enantioselective Ruthenium(II)-Catalyzed Access to Benzonorca-radienes by Coupling of Oxabenzonorbornadienes and Alkynes

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General Methods

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. THF, Et₂O and dichloromethane were purified by a Innovative Technology Solvent Delivery System. DMF was dried over 4A molecular sieves. Chemicals were used as obtained from the suppliers unless stated otherwise. Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or phosphate buffered silica (pH=7). Analytical thin-layer chromatography was performed with commercially available 0.25 mm silica gel coated on a glass plate (Merck, TLC Silicagel 60 F₂₅₄). Compounds were either visualised under UV-light at 254 nm or stained the plates with an aqueous potassium permanganate solution. Proton nuclear magnetic resonance (¹H NMR) data were acquired at 400 MHz on a Bruker AV400 spectrometer or at 600 MHz on a Bruker AV600 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm) or residual dichloromethane (s, 5.32 ppm). 1D NOE experiments were performed with a Bruker AV600. Proton decoupled Carbon-13 nuclear magnetic resonance (¹³C{¹H} NMR) data were acquired at 100 MHz on a Bruker AV400 or at 151 MHz on a Bruker AV600 spectrometer. Chemical shifts are reported in ppm relative to residual chloroform (77.16 ppm) or residual dichloromethane (53.84 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet. All NMR data were recorded at 298 K unless stated otherwise. Infrared (IR) data were recorded on a Bruker Alpha FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm⁻¹). HRMS measurements were performed on an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Enantiomeric excesses were measured on an Agilent HPLC. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter. X-ray analysis was performed by Dr. R. Scopelliti and Dr. F. F. Tirani at the EPF Lausanne.

Experimental sections

Preparation of phosphate buffered silica (pH = 7)

To 100 g of silica (Silicycle silica gel 60) was added 1 L of disodium hydrogen phosphate (aq, 0.2 M). The pH of the mixture was adjusted to 7 by adding phosphoric acid. The mixture was filtered and the resulting silica was dried in the oven.

Preparation of chiral Cp^xRu complexes

Fulvene-derived Cp^xRu(II) complex **Ru1**¹ and binaphthyl-derived Cp^xRu(II) complexes **Ru2** and **Ru3**² were prepared according to the reported procedures.

Preparation of oxabenzonorbornadienes and alkynes

But-2-yne-1,4-diol was purified by flash column chromatography and hept-2-yn-1-ol was distilled with a Hickman condenser prior to use.

The following compounds were prepared according to the published procedures.

6,7-Dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (**1b**)³, 5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (**1c**)¹, 6,7-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (**1d**)⁴, 6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalene (**1e**)⁵, but-2-yne-1,4-diyl dimethyl bis(carbonate) (**2a**)⁶, but-2-yne-1,4-diyl di-tert-butyl bis(carbonate) (**2b**)⁴, dibenzyl but-2-yne-1,4-diyl bis(carbonate) (**2c**)⁴, but-2-yne-1,4-diyl bis(phenylcarbamate) (**2d**)⁷, but-2-yne-1,4-diyl dibenzoate (**2e**)⁸, but-2-yne-1,4-diyl diacetate (**2f**)⁹, 2,2,3,3,10,10,11,11-octamethyl-4,9-dioxa-3,10-disiladodec-6-yne (**2g**)¹⁰, 1,4-bis(benzyloxy)but-2-yne (**2h**)⁴, hept-2-yn-1-yl methyl carbonate (**2k**)¹¹, 6-phenylhex-2-yn-1-ol (**2m**)¹², 4-hydroxybut-2-yn-1-yl methyl carbonate (**2n**)¹³.

6,7-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (**1b**)

White solid, 430 mg, 62% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.05 (s, 2H), 6.97 (s, 2H), 5.68 (s, 2H), 3.85 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.96, 143.47, 141.85, 106.89, 82.71, 56.60. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3086, 3008, 2962, 2944, 2916, 2836, 1599, 1485, 1467, 1455, 1412, 1325, 1285, 1206, 1190, 1180, 1062, 966, 871, 856, 787, 735, 694, 638; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3^+$ $[\text{M}]^+$: 204.0781, Found: 204.0780

5,8-dimethoxy-1,4-dihydro-1,4-epoxynaphthalene (**1c**)

White solid, 681 mg, 72% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.07 (s, 2H), 6.54 (s, 2H), 5.93 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.00, 143.02, 137.57, 111.75, 80.45, 56.49. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3016, 2999, 2942, 2906, 2835, 1615, 1493, 1462, 1278, 1253, 1076, 1002, 868, 835, 722, 711; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3^+$ $[\text{M}]^+$: 204.0781, Found: 204.0783.

6,7-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (**1d**)

White solid, 243 mg, 79% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.06 (s, 2H), 7.00 (s, 2H), 5.66 (s, 2H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.75, 143.24, 132.67, 122.27, 82.34, 19.91. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3081, 3014, 1572, 1430, 1348, 1315, 1279, 1229, 1195, 1159, 1082, 993, 892, 868, 846, 815, 753, 698, 645, 578; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{12}\text{H}_{13}\text{O}^+$ $[\text{M}+\text{H}]^+$: 173.0961, Found: 173.0963.

6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalene (**1e**)

White solid, 1.01 g, 66% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 2H), 7.00 (s, 2H), 5.67 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.34, 142.82, 125.61, 120.79, 81.93. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3081, 3014, 1572, 1431, 1279, 1082, 994, 868, 846, 698, 645, 578; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{10}\text{H}_6\text{OBr}_2^+ [\text{M}]^+$: 299.8780, Found: 299.8779.

White solid, 703 mg, 86% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 4.77 (s, 4H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.22, 81.01, 55.45, 55.31. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3009, 2961, 1751, 1445, 1376, 1252, 1156, 949, 902, 790; HRMS (ESI/QTOF) calcd for $\text{C}_8\text{H}_{10}\text{O}_6\text{Na}^+ [\text{M}+\text{Na}]^+$: 225.0370, Found: 225.0369.

Colorless oil, 1.09 g, 95% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) 4.70 (s, 4H), 1.49 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.85, 83.17, 81.03, 54.59, 27.84. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2981, 2938, 1745, 1479, 1457, 1436, 1370, 1271, 1251, 1148, 1086, 931, 856, 791; HRMS (APCI/QTOF) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_6\text{Na}^+ [\text{M}+\text{Na}]^+$: 309.1309, Found: 309.1300.

White solid, 0.69 g, 48% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.38 (ddd, J = 3.5, 2.4, 1.3 Hz, 7H), 7.36 – 7.33 (m, 3H), 5.19 (s, 4H), 4.78 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.60, 134.97, 128.79, 128.75, 128.50, 81.09, 70.25, 55.54. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3066, 3034,

2956, 1748, 1455, 1390, 1366, 1233, 1157, 938, 787, 754, 697; HRMS (ESI/QTOF) calcd for $C_{20}H_{18}O_6Na^+$ $[M+Na]^+$: 377.0996, Found: 377.0993.

White solid, 593 mg, 83% yield; Analytical data: 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 4H), 7.31 (dd, J = 8.6, 7.2 Hz, 4H), 7.09 (tt, J = 7.1, 1.3 Hz, 2H), 6.66 (s, 2H), 4.84 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.63, 137.53, 129.25, 123.96, 118.90, 81.25, 53.01. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 3331, 3053, 1702, 1604, 1542, 1502, 1447, 1316, 1301, 1233, 1060, 742, 691; HRMS (ESI/QTOF) calcd for $C_{18}H_{16}N_2O_4Na^+$ $[M+Na]^+$: 347.1002, Found: 347.1005.

White solid, 763 mg, 89% yield; Analytical data: 1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.4 Hz, 4H), 7.58 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 4H), 5.00 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93, 133.45, 129.94, 129.51, 128.55, 81.11, 52.75. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3064, 2944, 1721, 1601, 1452, 1371, 1315, 1260, 1177, 1156, 1093, 1069, 1026, 956, 708, 687; HRMS (ESI/QTOF) calcd for $C_{18}H_{14}O_4Na^+$ $[M+Na]^+$: 317.0784, Found: 317.0784.

Colorless oil, 470 mg, 91% yield; Analytical data: 1H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 4H), 2.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.09, 80.84, 52.10, 20.68. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2947, 1742, 1434, 1378, 1361, 1215, 1155, 1025, 966, 917, 831; HRMS (EXI/QTOF) calcd for $C_8H_{10}O_4Na^+$ $[M+Na]^+$: 193.0471, Found: 193.0472.

Colorless oil, 522 mg, 95% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 4.34 (s, 4H), 0.91 (s, 18H), 0.12 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 83.49, 51.95, 25.98, 18.45, -5.00. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 2930, 2887, 2858, 1472, 1463, 1363, 1254, 1135, 1095, 1069, 1005, 833, 815, 776; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{10}\text{H}_{34}\text{O}_2\text{Si}_2^+$ $[\text{M}]^+$: 314.2092, Found: 314.2092.

Colorless oil, 600 mg, 84% yield; Analytical data: ^1H NMR (400 MHz, CDCl_3) 7.40 – 7.27 (m, 10H), 4.62 (s, 4H), 4.25 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.49, 128.57, 128.18, 128.00, 82.64, 71.75, 57.56. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3029, 2942, 2854, 1496, 1454, 1386, 1348, 1260, 1207, 1138, 1118, 1068, 1027, 939, 905, 736, 696, 605; HRMS (APPI/LTQ-Orbitrap) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2^+$ $[\text{M}]^+$: 266.1301, Found: 266.1302.

Preparation of S,S'-(but-2-yne-1,4-diyl) diethanethioate (**2i**)

1,4-Dibromobut-2-yne (0.223 ml, 2.12 mmol) was added to 3 mL of DMF and cooled to 0 °C. Potassium thioacetate (0.534 g, 4.67 mmol) in 3 ml of DMF was added within 30 min. The ice bath was subsequently removed and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was added to 60 mL of 1 N HCl. Next, the aqueous layer was extracted with Et_2O (2×15 ml). The combined organic layers were washed with 1 N HCl (aq) (2×25 ml) and dried over MgSO_4 . After the solvent was removed under reduced pressure, the residue was

purified by silica gel column chromatography (*n*-pentane/ethyl acetate = 10/1) to afford the product **2i** (515 mg, 91% yield).

Pale yellow solid, 515 mg, 91% yield; Mp = 42-43 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 3.64 (s, 4H), 2.35 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 194.06, 77.54, 30.26, 18.08. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2962.09, 2918.61, 1688.04, 1398.93, 1353.16, 1241.64, 1128.33, 1101.60, 1003.66, 954.14, 708.66, 619.32, 528.56; HRMS (APPI/LTQ-Orbitrap) calcd for C₈H₁₀O₂S₂Na⁺ [M+Na]⁺: 225.0014, Found: 225.0017.

Colorless oil, 244 mg, 54% yield; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 4.72 (t, *J* = 2.2 Hz, 2H), 3.81 (s, 3H), 2.22 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.59 – 1.45 (m, 2H), 1.45 – 1.31 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) 155.46, 88.67, 73.44, 56.42, 55.13, 30.51, 22.03, 18.56, 13.69. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2958, 2935, 2873, 2235, 1750, 1444, 1375, 1251, 1150, 945, 901, 791; HRMS (APPI/LTQ-Orbitrap) calcd for C₁₀H₆OBr₂⁺ [M+H]⁺: 171.1016, Found: 171.1009.

Colorless oil, 3.03 g, 87% yield; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 4.27 (t, *J* = 2.1 Hz, 2H), 2.76 – 2.68 (m, 2H), 2.24 (tt, *J* = 7.0, 2.2 Hz, 2H), 1.84 (p, *J* = 7.2 Hz, 2H), 1.50 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.62, 128.62, 128.46, 126.02, 86.16, 78.97, 51.49, 34.91, 30.21, 18.30. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3330, 3026, 2936,

2861, 2289, 2224, 1603, 1496, 1454, 1430, 1133, 1009, 745, 699; HRMS (APPI/LTQ-Orbitrap) calcd for $C_{12}H_{14}O^+$ $[M]^+$: 174.1039, Found: 174.1037.

Colorless oil, 293 mg, 68% yield; Analytical data: 1H NMR (400 MHz, $CDCl_3$) 4.78 (t, $J = 1.8$ Hz, 1H), 4.31 (t, $J = 1.8$ Hz, 1H), 3.82 (s, 1H), 1.65 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.40, 85.98, 79.16, 55.75, 55.32, 51.01. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3405, 2960, 2863, 1746, 1445, 1376, 1253, 1138, 1017, 942, 902, 789; HRMS (APPI/LTQ-Orbitrap) calcd for $C_6H_8O_4^+$ $[M]^+$: 144.0417, Found: 144.0414.

General Procedure for the Ruthenium(II)-Catalyzed Enantioselective Synthesis of Benzonorcaradiene by Reconstitutive Coupling of an Oxabenzonorbornadiene and an Internal Alkyne

Ru1 (5.00 mol %, 5.20 μ mol, 3.26 mg) and tetrabutylammonium iodide (6.00 mol %, 6.24 μ mol, 2.30 mg) were dissolved in freshly distilled 2-butanone (0.45 ml) in a microwave tube under an N₂ atmosphere. A solution of an oxabenzonorbornadiene (0.104 mmol, 15.0 mg, 1.00 equiv.) and an alkyne (0.104 mmol, 1.00 equiv.) in 2-butanone (0.38 ml) was added in one portion. The reaction mixture was heated to 100 °C and stirred at that temperature. After completion of the reaction (TLC control), the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The reaction mixture was purified by silica gel column chromatography (*n*-pentane/ethyl acetate) to afford the desired benzonorcaradiene **3**.

For the compounds (**3ba** and **3ca**), phosphate buffered silica (pH=7) was used because of instability of the compounds on silica gel.

2-((1*S*,1*aR*,7*bR*)-1-(((methoxycarbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate (**3aa**)

Off-white solid, 25.5 mg, 76% yield, 95:5 *er*. $[\alpha]_{\text{D}}^{20}$ -94.7 ($c = 1.0$, CH_2Cl_2); Mp = 96-97 °C; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.39 (dd, $J = 6.9, 1.9$ Hz, 1H), 7.32 – 7.23 (m, 2H), 7.20 (m, 1H), 6.68 (d, $J = 9.6$ Hz, 1H), 6.19 (dd, $J = 9.5, 5.2$ Hz, 1H), 5.15 (s, 2H), 4.05 (d, $J = 13.2$ Hz, 1H), 3.85 (s, 3H), 3.82 (d, $J = 13.2$ Hz, 1H), 3.65 (s, 3H), 3.42 (d, $J = 8.7$ Hz, 1H), 3.02 (dd, $J = 8.7, 5.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.07, 155.55, 155.21, 132.43, 130.30, 130.11, 129.32, 128.42, 128.26, 127.98, 122.63, 70.02, 61.63, 55.45, 54.99, 38.52, 36.05, 24.26. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3024, 2958, 2857, 1751, 1704, 1488, 1444, 1421, 1378, 1265, 1191, 1166, 1108, 1066, 997, 964, 917, 842, 789; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_7\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 369.0945, Found: 369.0945. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 17.9 min, t_{R} (minor) = 21.9 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.905	BB	0.4411	4408.57129	149.02773	49.9908
2	21.874	BB	0.5404	4410.19629	117.35560	50.0092

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.784	MM	0.5564	1.17861e4	353.07254	94.5909
2	22.124	MM	0.7225	673.98114	15.54729	5.4091

2-((1*S*,1*aR*,7*bR*)-1-(((*tert*-butoxycarbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl *tert*-butyl carbonate (**3ab**)

White solid, 32.0 mg, 71% yield, 93.5:6.5 *er*. $[\alpha]_D^{20}$ -85.4 ($c = 1.0$, CH₂Cl₂); Mp = 112-113 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃)

δ 7.43 – 7.36 (m, 1H), 7.26 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 6.67 (d, $J = 9.6$ Hz, 1H), 6.18 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.11 (s, 2H), 3.99 (d, $J = 13.2$ Hz, 1H), 3.77 (d, $J = 13.3$ Hz, 1H), 3.39 (d, $J = 8.7$ Hz, 1H), 2.99 (dd, $J = 8.7, 5.2$ Hz, 1H), 1.52 (s, 9H), 1.36 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 203.63, 153.16, 153.02, 132.49, 130.30, 130.01, 129.64, 128.33, 128.19, 127.82, 122.73, 83.02, 82.54, 69.42, 60.40, 38.26, 36.03, 27.86, 27.78, 24.35. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2981, 2935, 1742, 1705, 1477, 1456, 1422, 1394, 1369, 1280, 1248, 1157, 1133, 1105, 1092, 1061, 1037, 980, 948, 913, 861, 791, 778, 732; HRMS (ESI) calcd for C₂₄H₃₀O₇Na⁺ [M+Na]⁺: 453.1884, Found: 453.1884. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 10.3 min, t_R (minor) = 16.1 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.357	BB	0.3961	2886.00635	113.72443	50.0178
2	16.178	BB	0.6034	2883.94678	70.18487	49.9822

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.341	BB	0.4669	1.00922e4	305.88452	93.2309
2	16.112	BB	0.6141	732.75281	14.53579	6.7691

benzyl (2-((1*S*,1*aR*,7*bR*)-1-(((benzyloxy)carbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl) carbonate (**3ac**)

Yellow oil, 33.5 mg, 65% yield, 94:6 *er*. $[\alpha]_D^{20}$ -69.3 ($c = 1.0$, CH₂Cl₂);

Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.21 (m, 8H), 7.22 – 7.17 (m, 2H), 7.17 – 7.07 (m, 3H), 6.55 (d, $J = 9.6$ Hz, 1H), 6.05 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.13 (s, 2H), 5.05 (s, 2H), 4.90 (s, 2H), 3.96 (d, $J = 13.1$ Hz, 1H), 3.77 (d, $J = 13.1$ Hz, 1H), 3.32 (d, $J = 8.7$ Hz, 1H), 2.92 (dd, $J = 8.7, 5.2$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 202.91, 154.92, 154.57, 135.11, 135.05, 132.43, 130.30, 130.14, 129.36, 128.72, 128.72, 128.69, 128.41, 128.37, 128.35, 128.25, 127.95, 122.60, 70.29, 70.09, 69.86, 61.70, 38.49, 36.12, 24.38. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3065, 3034, 2952, 1748, 1703, 1455, 1424, 1383, 1263, 1236, 1192, 1165, 1107, 1063, 952, 910, 842, 780, 737, 697; HRMS (ESI) calcd for C₃₀H₂₆O₇Na⁺ [M+Na]⁺: 521.1571, Found: 521.1565. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 25.5 min, t_R (minor) = 29.5 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.890	MM	0.9138	3228.29712	58.88136	49.5036
2	29.836	BB	0.7360	3293.04346	58.56320	50.4964

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.477	BB	0.8522	9669.59277	161.57611	94.4050
2	29.516	BB	0.7005	573.07703	9.68280	5.5950

2-oxo-2-((1S,1aR,7bR)-1-(((phenylcarbamoyl)oxy)methyl)-1a,7b-dihydro-1H-cyclopropa[a]naphthalen-1-yl)ethyl phenylcarbamate
(**3ad**)

Yellow solid, 30.8 mg, 63% yield, 7:93 *er.* $[\alpha]_D^{20}$ -65.2 ($c = 1.0$,

CH₂Cl₂), Mp = 103-104 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.35 (t, *J* = 9.6 Hz, 3H), 7.26 (s, 3H), 7.24 – 7.13 (m, 5H), 7.10 – 6.98 (m, 3H), 6.72 (s, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.12 (dd, *J* = 9.6, 5.2 Hz, 1H), 5.37 – 5.13 (m, 2H), 4.06 (d, *J* = 13.2 Hz, 1H), 3.90 (d, *J* = 13.3 Hz, 1H), 3.39 (d, *J* = 8.7 Hz, 1H), 3.00 (dd, *J* = 8.8, 5.2 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 205.02, 152.91, 137.62, 137.54, 132.45, 130.16, 130.14, 129.47, 129.17, 129.14, 128.35, 128.33, 127.97, 123.92, 123.68, 122.54, 118.94, 118.66, 77.37, 76.95, 68.05, 58.83, 38.53, 35.89, 24.59. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3317, 3057, 3043, 2936, 2252, 1698, 1600, 1529, 1501, 1444, 1376, 1314, 1214, 1191, 1165, 1117, 1102, 1083, 1058, 1027, 978, 908, 849, 788, 754, 730, 692, 649, 506; HRMS (ESI) calcd for C₂₈H₂₄N₂O₅Na⁺ [M+Na]⁺: 491.1577, Found: 491.1583. The enantiomeric excess was determined by Daicel Chiralpak IF (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t_R (major) = 19.8 min, t_R (minor) = 13.7 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.914	BB	0.5518	4348.52881	118.05169	50.4772
2	20.386	BB	0.7405	4266.31689	81.79529	49.5228

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.726	BB	0.5046	732.69067	21.02078	6.8124
2	19.803	BB	0.7564	1.00225e4	194.12154	93.1876

((1*S*,1*aR*,7*bR*)-1-(2-(benzyloxy)acetyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methyl benzoate (**3ae**)

Off-white solid, 28.0 mg, 61% yield, 5:95 *er*. $[\alpha]_D^{20}$ -38.5 ($c = 1.0$, CH₂Cl₂), Mp = 150 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, $J = 7.8$ Hz, 2H), 7.98 (d, $J = 7.7$ Hz, 2H), 7.62 (dd, $J = 9.7, 7.2$ Hz, 2H), 7.56 – 7.42 (m, 5H), 7.36 – 7.21 (m, 3H), 6.74 (d, $J = 9.6$ Hz, 1H), 6.26 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.63 – 5.41 (m, 2H), 4.40 – 4.16 (m, 2H), 3.56 (d, $J = 8.7$ Hz, 1H), 3.17 (dd, $J = 8.7, 5.2$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 203.60, 166.24, 166.08, 133.48, 133.33, 132.48, 130.25, 130.18, 130.06, 129.72, 129.70, 129.60, 129.51, 128.59, 128.41, 128.30, 127.92, 122.68, 68.01, 58.87, 38.43, 36.07, 24.58. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3063, 3035, 2936, 1719, 1704, 1601, 1451, 1418, 1375, 1315, 1271, 1192, 1177, 1108, 1064, 1026, 968, 791, 778, 708, 687; HRMS (ESI) calcd for C₂₈H₂₂O₅Na⁺ [M+Na]⁺:461.1359, Found: 461.1365. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 16.2 min, t_R (minor) = 19.9 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.172	BB	0.4893	3781.79053	118.83089	50.5939
2	19.713	BB	0.6268	3693.00366	91.13680	49.4061

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.177	BB	0.5288	1.26864e4	365.58609	94.3974
2	19.909	BB	0.7033	752.94751	16.28921	5.6026

((1*S*,1*aR*,7*bR*)-1-(2-acetoxyacetyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methyl acetate (**3af**)

Yellow oil, 19.3 mg, 63% yield, 95.5:4.5 *er.* $[\alpha]_D^{20}$ -97.5 ($c = 1.0$, CH₂Cl₂);

Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.37 (dd, $J = 6.4, 2.4$ Hz, 1H), 7.26 (m, 2H), 7.19 (dd, $J = 7.0, 2.1$ Hz, 1H), 6.67 (d, $J = 9.6$ Hz, 1H), 6.16 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.12 (d, $J = 3.6$ Hz, 2H), 3.96 (d, $J = 13.5$ Hz, 1H), 3.82 (d, $J = 13.6$ Hz, 1H), 3.38 (d, $J = 8.7$ Hz, 1H), 3.00 (dd, $J = 8.7, 5.2$ Hz, 1H), 2.21 (s, 3H), 1.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.66, 170.50, 170.41, 132.43, 130.16, 130.11, 129.65, 128.28, 127.89, 122.58, 67.42, 58.17, 38.23, 35.89, 24.33, 20.67, 20.65. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3035, 3024, 2936, 1745, 1702, 1488, 1421, 1374, 1229, 1188, 1166, 1092, 1055, 1030, 966, 840, 794, 780, 601, 494; HRMS (ESI) calcd for C₁₈H₁₈O₅Na⁺ [M+Na]⁺: 337.1046, Found: 337.1053. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 13.0 min, t_R (minor) = 16.2 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.615	BB	0.3172	3346.28931	161.83864	49.5821
2	15.277	BB	0.4012	3402.70337	130.09207	50.4179

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.960	BB	0.4100	6476.92383	246.90945	95.6517
2	16.159	BB	0.4630	294.44159	9.84381	4.3483

2-((*tert*-butyldimethylsilyl)oxy)-1-((1*S*,1*aR*,7*bR*)-1-(((*tert*-butyldimethylsilyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)ethan-1-one (**3ag**)

Colorless oil, 23.0 mg, 48% yield, 26:74 *er*. $[\alpha]_D^{20}$ -41.5 ($c = 1.0$, CH_2Cl_2); Analytical data ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 2.8$ Hz, 1H), 7.24 – 7.19 (m, 2H), 7.17 – 7.13 (m, 1H), 6.57 (d, $J = 9.6$ Hz, 1H), 6.12 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.02 – 4.87 (m, 2H), 3.36 (d, $J = 12.1$ Hz, 1H), 3.27 (d, $J = 12.8$ Hz, 1H), 3.23 (d, $J = 8.5$ Hz, 1H), 2.78 (dd, $J = 8.6, 5.2$ Hz, 1H), 0.94 (s, 9H), 0.77 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H), -0.22 (s, 3H), -0.33 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.00, 132.74, 130.83, 130.40, 128.93, 128.05, 127.65, 127.25, 123.87, 69.04, 56.10, 36.73, 34.59, 26.25, 26.03, 25.88, 18.73, 18.12, -5.17, -5.22, -5.85, -5.94. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952, 2928, 2885, 2856, 1702, 1471, 1463, 1389, 1361, 1253, 1150, 1121, 1079, 1052, 1023, 1006, 973, 835, 775, 745; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 481.2565, Found: 481.2581. The enantiomeric excess was determined by Daicel Chiralpak IF (25 cm), Hexane/IPA = 99.5/0.5, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 9.6 min, t_R (minor) = 8.3 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.091	BB	0.2360	1463.81738	100.45472	49.9431
2	9.432	BB	0.2077	1467.15088	107.18236	50.0569

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.281	BV	0.2412	1088.55225	72.49139	25.5972
2	9.627	BB	0.2092	3164.07275	234.80605	74.4028

2-(benzyloxy)-1-(((1*S*,1*aR*,7*bR*)-1-((benzyloxy)methyl)-1*a*,7*b*-

dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)ethan-1-one (**3ah**)

Pale yellow oil, 25.0 mg, 63% yield, 25:75 *er*. $[\alpha]_{\text{D}}^{20}$ -56.3 ($c = 1.0$, CH_2Cl_2); Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.31 (m, 6H), 7.26 (s, 5H), 7.16 – 7.11 (m, 1H), 7.05 – 6.97 (m, 2H), 6.53 (d, $J = 9.5$ Hz, 1H), 6.15 (dd, $J = 9.6, 5.2$ Hz, 1H), 4.72 (d, $J = 2.6$ Hz, 2H), 4.64 (d, $J = 2.1$ Hz, 2H), 4.11 (q, $J = 11.8$ Hz, 2H), 3.32 (d, $J = 8.6$ Hz, 1H), 3.19 (d, $J = 11.6$ Hz, 1H), 3.08 (d, $J = 11.7$ Hz, 1H), 2.91 (dd, $J = 8.6, 5.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) 208.44, 137.74, 137.68, 132.74, 130.63, 130.24, 129.00, 128.56, 128.40, 128.18, 128.06, 127.97, 127.82, 127.74, 127.37, 123.73, 74.15, 73.46, 73.40, 63.04, 37.41, 35.03, 25.21. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3062, 3030, 2924, 2856, 1697, 1495, 1488, 1454, 1362, 1270, 1187, 1164, 1121, 1099, 1075, 1058, 1028, 976, 950, 836, 780, 738, 698;

HRMS (ESI) calcd for $C_{28}H_{26}O_3Na^+$ $[M+Na]^+$: 433.1774, Found: 433.1778. The enantiomeric excess was determined by Daicel Chiralpak IG (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, λ = 254 nm, t_R (major) = 18.3 min, t_R (minor) = 16.8 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.673	BB	0.4594	3105.66479	104.90746	49.9072
2	18.212	BB	0.5203	3117.21533	95.13756	50.0928

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.811	BB	0.5178	2069.53662	62.58076	24.8852
2	18.333	BB	0.5378	6246.81152	179.59009	75.1148

S-(((1*R*,1*aR*,7*bR*)-1-(2-(acetylthio)acetyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methyl) ethanethioate (**3ai**)

Colorless oil, 18.2 mg, 51% yield, 2.5:97.5 *er*. $[\alpha]_{\text{D}}^{20}$ -175.0 ($c = 1.0$, CH_2Cl_2); Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 6.68 (d, $J = 9.5$ Hz, 1H), 6.14 (dd, $J = 9.6, 5.2$ Hz, 1H), 4.13 (s, 2H), 3.37 (d, $J = 8.8$ Hz, 1H), 3.03 (d, $J = 14.9$ Hz, 1H), 2.96 (dd, $J = 8.8, 5.3$ Hz, 1H), 2.87 (d, $J = 15.0$ Hz, 1H), 2.39 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 204.32, 195.28, 194.39, 132.69, 130.71, 130.04, 129.71, 128.36, 128.22, 127.84, 122.99, 39.64, 38.33, 36.91, 30.56, 30.30, 26.85, 24.01. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3036, 2991, 2965, 2919, 1684, 1488, 1433, 1354, 1304, 1283, 1132, 1099, 1055, 1022, 996, 958, 820, 779, 627; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 369.0590, Found: 369.0595. The enantiomeric excess was determined by Daicel Chiralpak IF (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 11.1 min, t_{R} (minor) = 9.8 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.826	BB	0.2673	4441.49072	254.94209	50.1375
2	11.241	BB	0.3159	4417.13428	214.77298	49.8625

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.788	BB	0.3196	314.64703	15.19195	2.6278
2	11.135	BB	0.3596	1.16591e4	500.78586	97.3722

Alternative Conditions for 2-hydroxy-1-((1*S*,1*aR*,7*bR*)-1-(hydroxymethyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)ethan-1-one (3aj)

Ru1 (5 mol %, 1.39 μ mol, 0.869 mg) and triphenylphosphine (10 mol %, 2.77 μ mol, 0.728 mg) were dissolved in freshly distilled 2-butanone (0.10 ml) in a microwave reaction vial under N₂ atmosphere. Iodomethane (35 mol %, 9.71 μ mol, 1.39 mg) was added followed by addition of a solution of an oxabenzonorbornadiene (1.00 equiv., 27.7 μ mol, 4 mg), but-2-yne-1,4-diol (1.00 equiv., 27.7 μ mol, 2.39 mg) and 2-methylpyridine (40 mol %, 11.1 μ mol, 1.03 mg) in 2-butanone (0.12 ml). The reaction mixture was heated to 80 °C for 90 min. After completion of the reaction (TLC control), the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The reaction mixture was purified by silica gel column chromatography (*n*-pentane/ethyl acetate) to afford benzonorcaradiene **3aj**.

2-hydroxy-1-((1*S*,1*aR*,7*bR*)-1-(hydroxymethyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)ethan-1-one (**3aj**)

White solid, 15.4 mg, 76% yield, 85:15 *er*. $[\alpha]_{\text{D}}^{20}$ -106.2 ($c = 1.0$, CH_2Cl_2); Mp = 145-146 °C; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.46 –

7.35 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 6.69 (d, $J = 9.6$ Hz, 1H), 6.22 (dd, $J = 9.6, 5.2$ Hz, 1H), 4.80 (d, $J = 4.6$ Hz, 2H), 3.48 – 3.31 (m, 4H), 2.96 (dd, $J = 8.7, 5.2$ Hz, 1H), 1.06 (t, $J = 6.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 211.90, 132.56, 129.84, 129.81, 129.76, 128.49, 128.07, 127.75, 122.74, 67.48, 55.70, 37.88, 35.69, 27.31. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3424, 3035, 2894, 1681, 1487, 1366, 1308, 1270, 1187, 1164, 1094, 1056, 1024, 960, 841, 778; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 253.0835, Found: 253.0834. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 16.7 min, t_{R} (minor) = 19.2 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.366	BB	0.4282	3891.32446	136.65958	49.9978
2	18.283	BB	0.4663	3891.66895	124.62547	50.0022

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.667	BB	0.4781	1.39498e4	419.35922	85.0501
2	19.178	BB	0.5076	2452.06348	71.59395	14.9499

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.354	BV	0.4710	3478.51978	107.63944	97.3773
2	18.756	BB	0.4034	93.68734	2.80709	2.6227

2-((1*S*,1*aR*,7*bR*)-5,6-dimethoxy-1-
 (((methoxycarbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-
 cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate
 (**3ba**)

Off-white solid, 25.9 mg, 65% yield, 8:92 *er*. $[\alpha]_D^{20}$ -123.3 ($c = 0.5$, CH_2Cl_2), $\text{Mp} = 97\text{-}101\text{ }^\circ\text{C}$; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 6.89 (s, 1H), 6.69 (s, 1H), 6.59 (d, $J = 9.5$ Hz, 1H), 6.09 (dd, $J = 9.5, 5.2$ Hz, 1H), 5.22 – 5.10 (m, 2H), 4.00 (d, $J = 13.1$ Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.83 (d, $J = 13.3$ Hz, 1H), 3.66 (s, 3H), 3.40 (d, $J = 8.9$ Hz, 1H), 3.02 (dd, $J = 8.9, 5.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 203.23, 155.63, 155.32, 149.30, 148.79, 129.76, 125.76, 122.32, 120.70, 112.60, 110.66, 70.09, 61.78, 56.21, 56.08, 55.45, 54.99, 39.00, 36.74, 24.07. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3004, 2958, 2837, 1751, 1700, 1514, 1445, 1352, 1264, 1194, 1171, 1130, 1060, 996, 967, 847, 789; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{O}_9\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 429.1156, Found: 429.1152. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 49.9 min, t_R (minor) = 42.9 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.860	MM	1.5299	3492.56934	38.04867	50.2220
2	49.858	MM	1.5958	3461.69580	36.15487	49.7780

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.675	MM	1.5203	679.84412	7.45286	8.0552
2	49.784	MM	1.6689	7760.00830	77.49805	91.9448

2-((1*S*,1*aR*,7*bR*)-4,7-dimethoxy-1-(((methoxycarbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate (**3ca**)

Brown solid, 24.8 mg, 62% yield, 88:12 *er*. $[\alpha]_D^{20}$ -90.2 ($c = 1.0$, CH₂Cl₂); Mp = 121-123 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, $J = 9.8$ Hz, 1H), 6.73 (s, 2H), 6.19 (ddd, $J = 9.8, 5.2, 0.7$ Hz, 1H), 5.29 – 5.04 (m, 2H), 4.10 (d, $J = 13.1$ Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.76 (dd, $J = 13.6, 4.4$ Hz, 1H), 3.67 (s, 3H), 3.59 (d, $J = 8.9$ Hz, 1H), 3.01 (dd, $J = 9.0, 5.2$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 203.00, 155.54, 155.33, 152.78, 149.89, 123.64, 122.99, 122.33, 119.39, 110.46, 109.97, 69.97, 61.90, 56.28, 56.21, 55.42, 54.96, 35.15, 33.89, 23.10. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3004, 2957, 2838, 1751, 1704, 1483, 1443, 1421, 1378, 1344, 1261, 1192, 1103, 1086, 963, 910, 843, 791, 731; HRMS (ESI) calcd for C₂₀H₂₂O₉Na⁺ [M+Na]⁺: 429.1156, Found: 429.1157. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 26.2 min, t_R (minor) = 35.6 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.461	BB	0.7768	2819.69873	53.51037	50.3652
2	35.985	BB	1.1353	2778.80273	30.60352	49.6348

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.194	BV	0.8901	7161.63281	123.93897	87.2968
2	35.620	BB	1.1431	1042.14478	10.76838	12.7032

2-((1*S*,1*aR*,7*bR*)-1-(((methoxycarbonyl)oxy)methyl)-5,6-dimethyl-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate (**3da**)

Off-white solid, 35.2 mg, 81% yield, 7.5:92.5 *er*. $[\alpha]_D^{20}$ -109.5 (*c* 1.0, CH₂Cl₂); Mp = 111 °C; Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.15 (s, 1H), 6.96 (s, 1H), 6.60 (d, *J* = 9.5 Hz, 1H), 6.11 (dd, *J* = 9.6, 5.2 Hz, 1H), 5.13 (s, 2H), 4.06 (d, *J* = 13.1 Hz, 1H), 3.85 (s, 3H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.67 (s, 3H), 3.35 (d, *J* = 8.8 Hz, 1H), 3.01 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.04, 155.57, 155.28, 137.24, 136.41, 131.27, 130.27, 129.91, 129.29, 126.70, 121.57, 70.02, 61.91, 55.42, 54.96, 38.60, 36.02, 24.68, 19.73, 19.58. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3009, 2957, 2860, 1748, 1701,

1501, 1443, 1421, 1376, 1253, 1190, 1143, 1106, 997, 949, 911, 884, 842, 786, 729, 648, 581, 543, 432; HRMS (ESI) calcd for $C_{20}H_{22}O_7Na^+$ $[M+Na]^+$: 397.1258, Found: 397.1262. The enantiomeric excess was determined by Daicel Chiralpak IF (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 11.9 min, t_R (minor) = 9.7 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.012	BB	0.3325	4263.61719	195.46851	50.3397
2	12.361	BB	0.5052	4206.06934	129.40663	49.6603

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.754	BB	0.3786	889.36096	33.62734	7.4910
2	11.929	BB	0.5292	1.09830e4	314.65701	92.5090

2-((1*S*,1*aR*,7*bR*)-5,6-dibromo-1-(((methoxycarbonyl)oxy)methyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate (**3ea**)

White solid, 24.0 mg, 48% yield, 4:96 *er*. $[\alpha]_{\text{D}}^{20}$ -106.8 ($c = 1.0$, CH_2Cl_2), $\text{Mp} = 136\text{--}137\text{ }^\circ\text{C}$; Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.65 (s, 1H), 7.46 (s, 1H), 6.58 (d, $J = 9.6$ Hz, 1H), 6.27 (dd, $J = 9.6, 5.2$ Hz, 1H), 5.14 (s, 2H), 4.04 (d, $J = 13.4$ Hz, 1H), 3.86 (d, $J = 13.4$ Hz, 1H) 3.85 (s, 3H), 3.68 (s, 3H), 3.29 (d, $J = 8.6$ Hz, 1H), 2.99 (dd, $J = 8.7, 5.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.34, 155.54, 155.16, 134.98, 132.97, 132.64, 130.02, 128.17, 124.65, 124.10, 123.98, 70.00, 61.24, 55.52, 55.20, 36.67, 35.30, 24.55. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2957, 2855, 2258, 1747, 1703, 1583, 1466, 1442, 1419, 1372, 1242, 1186, 1159, 1112, 1065, 997, 959, 907, 856, 836, 809, 787, 768, 727, 664, 649, 588, 524; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{O}_7\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 524.9155, Found: 524.9172. The enantiomeric excess was determined by Daicel Chiralpak IG (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 18.9 min, t_{R} (minor) = 16.0 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.738	BB	0.5164	5301.86621	158.44095	50.2908
2	18.655	BB	0.6017	5240.55078	130.16704	49.7092

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.005	BB	0.5982	686.46088	16.13927	4.4370
2	18.887	BB	0.6824	1.47849e4	332.74652	95.5630

methyl (((1*S*,1*aR*,7*bR*)-1-pentanoyl-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methyl) carbonate (**3ak**)

Pale yellow oil, 8.5 mg, 26% yield, 97:3 *er*. $[\alpha]_{\text{D}}^{20}$ -179.4 ($c = 0.3$, CH_2Cl_2); Analytical data: ^1H NMR (400 MHz, CDCl_3) 7.35 (dd, $J = 6.6, 2.2$ Hz, 1H), 7.27 – 7.18 (m, 2H), 7.20 – 7.16 (m, 1H), 6.63 (d, $J = 9.6$ Hz, 1H), 6.19 (dd, $J = 9.6, 5.2$ Hz, 1H), 4.15 (d, $J = 12.8$ Hz, 1H), 3.86 (d, $J = 12.7$ Hz, 1H), 3.65 (s, 3H), 3.27 (d, $J = 8.6$ Hz, 1H), 2.92 (dd, $J = 8.6, 5.2$ Hz, 1H), 2.76 (t, $J = 7.3$ Hz, 2H), 1.63 (p, $J = 7.4$ Hz, 2H), 1.45 – 1.30 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.64, 155.54, 132.57, 130.18, 130.16, 129.45, 128.20, 128.17, 127.63, 123.48, 63.03, 54.82, 40.21, 37.68, 34.90, 26.22, 25.15, 22.50, 14.06. IR (ATR): $\tilde{\nu}$ (cm^{-1}) 2958, 2932, 2873, 1749, 1686, 1443, 1382, 1265, 1182, 1058, 952, 781; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 337.1410, Found: 337.1410. The enantiomeric excess was determined by Daicel Chiralpak ID (25 cm), Hexane/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 7.8 min, t_{R} (minor) = 10.2 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.827	VB	0.1946	2712.95435	212.92879	49.3596
2	9.824	BV	0.2345	2783.35449	181.90279	50.6404

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.772	BV	0.2303	8013.73535	542.60797	96.9957
2	10.185	BB	0.2700	248.21368	13.79074	3.0043

1-((1S,1aR,7bR)-1-(hydroxymethyl)-1a,7b-dihydro-

1H-cyclopropa[a]naphthalen-1-yl)pentan-1-one (**3al**)

Yellow oil, 10.5 mg, 39% yield, 94:6 *er*. $[\alpha]_D^{20}$ -122.7 ($c = 1.0$, CH₂Cl₂);

Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.34 (m, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 6.63 (d, $J = 9.4$ Hz, 1H), 6.20 (dd, $J = 9.6, 5.2$ Hz, 1H), 3.51 (dd, $J = 13.3, 4.8$ Hz, 1H), 3.40 (dd, $J = 13.2, 5.6$ Hz, 1H), 3.23 (d, $J = 8.6$ Hz, 1H), 2.87 – 2.82 (m, 2H), 2.80 (dd, $J = 8.6, 5.2$ Hz, 1H), 1.65 (p, $J = 7.4$ Hz, 2H), 1.44 – 1.32 (m, 2H), 1.25 (t, $J = 5.2$ Hz, 1H), 0.94 (t, J

= 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 212.84, 132.74, 130.64, 129.80, 129.36, 128.36, 128.07, 127.51, 123.62, 57.01, 39.69, 36.43, 34.14, 28.86, 26.32, 22.55, 14.13. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3458, 3035, 2957, 2932, 2871, 1679, 1488, 1456, 1408, 1379, 1344, 1270, 1162, 1060, 1024, 965, 822, 777; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 279.1356, Found: 279.1354. The enantiomeric excess was determined by Daicel Chiralpak IG (25 cm), Hexane/IPA = 90/10, 1.0 mL/min, λ = 254 nm, t_{R} (major) = 12.8 min, t_{R} (minor) = 14.7 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.831	VB	0.3251	9726.29395	455.56976	50.2446
2	14.687	VV	0.4946	9631.58691	260.96353	49.7554

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.835	BB	0.3396	9057.16992	413.37427	94.7439
2	15.117	BB	0.3816	502.46075	15.60681	5.2561

1-((1*S*,1*aR*,7*bR*)-1-(hydroxymethyl)-1*a*,7*b*-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)-4-phenylbutan-1-one (**3am**)

Pale yellow oil, 11.2 mg, 34% yield, 95:5 *er.* $[\alpha]_{\text{D}}^{20}$ -146.5 ($c = 0.5$, CH_2Cl_2); Analytical data: ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.33 (m, 1H), 7.33 – 7.24 (m, 4H), 7.23 – 7.16 (m, 4H), 6.63 (d, $J = 9.6$ Hz, 1H), 6.19 (dd, $J = 9.6, 5.2$ Hz, 1H), 3.48 (d, $J = 13.2$ Hz, 1H), 3.37 (d, $J = 13.2$ Hz, 1H), 3.22 (d, $J = 8.5$ Hz, 1H), 2.91 – 2.84 (m, 2H), 2.78 (dd, $J = 8.6, 5.2$ Hz, 1H), 2.68 (dd, $J = 8.4, 6.9$ Hz, 2H), 2.01 (p, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 212.44, 141.97, 132.72, 130.58, 129.80, 129.39, 128.66, 128.52, 128.38, 128.09, 127.54, 126.05, 123.57, 56.92, 39.22, 36.56, 35.30, 34.35, 28.90, 25.63. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3466, 3059, 3025, 2930, 2857, 1677, 1495, 1488, 1454, 1407, 1372, 1270, 1160, 1104, 1071, 1052, 1027, 967, 777, 747, 700; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 341.1512, Found: 341.1509. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexane/IPA = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t_{R} (major) = 14.9 min, t_{R} (minor) = 17.2 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.939	BV	0.3447	2881.30591	127.96694	50.2151
2	17.166	BV	0.3948	2856.62280	109.35695	49.7849

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.966	MM	0.3715	4370.30127	196.05707	94.9112
2	17.241	MM	0.4264	234.32150	9.15981	5.0888

2-((1*S*,1*aR*,7*bR*)-1-(hydroxymethyl)-1*a*,7*b*-dihydro-

1*H*-cyclopropa[*a*]naphthalen-1-yl)-2-oxoethyl methyl carbonate (**3an**)

Colorless oil, 18.6 mg, 60% combined yield (**3an** and **3an'**), 14:86 *er*.

$[\alpha]_D^{20}$ -37.0 (*c* = 0.5, CH₂Cl₂); Analytical data: ¹H NMR (400 MHz, CDCl₃)

δ 7.42 – 7.35 (m, 1H), 7.31 – 7.21 (m, 3H), 7.22 – 7.15 (m, 1H), 6.65 (d, *J* = 9.5 Hz, 1H), 6.19 (dd, *J* = 9.5, 5.2 Hz, 1H), 5.31 (d, *J* = 3.6 Hz, 2H), 3.88 – 3.79 (m, 6H), 3.48 – 3.34 (m, 3H), 3.33 (d, *J* = 8.6 Hz, 1H), 2.90 (dd, *J* = 8.7, 5.2 Hz, 1H), 1.12 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 204.67, 155.76, 132.81, 130.14, 130.04, 129.94, 128.61, 128.18, 127.84, 123.02, 70.51, 56.06, 55.32, 37.52, 35.37, 27.64. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3501, 3022, 2957, 1754, 1697, 1446, 1419, 1377, 1269, 1182, 1164, 1066, 995, 956, 917, 841, 790, 778; HRMS (ESI) calcd for C₁₆H₁₆O₅Na⁺ [M+Na]⁺: 311.0890, Found: 311.0896. The enantiomeric excess was determined by Daicel Chiralpak IA (25 cm), Hexane/IPA = 95/5, 1.0 mL/min, λ = 254 nm, *t_R* (major) = 43.3 min, *t_R* (minor) = 30.9 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.894	BB	0.8860	3609.71460	55.55563	50.5176
2	43.282	BB	1.0258	3535.74390	41.09584	49.4824

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.038	BB	0.8142	1142.64392	17.91417	14.1311
2	43.262	BB	1.1911	6943.40137	79.17642	85.8689

((1*S*,1*aR*,7*bR*)-1-(2-hydroxyacetyl)-1*a*,7*b*-dihydro-

1*H*-cyclopropa[*a*]naphthalen-1-yl)methyl methyl carbonate (**3an'**)

Colorless oil, 18.6 mg, 60% combined yield (**3an** and **3an'**), 91.5:8.5 *er.* $[\alpha]_D^{20}$ -178.9 ($c = 0.15$, CH₂Cl₂); Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, $J = 6.9, 1.9$ Hz, 1H), 7.34 – 7.24 (m, 2H), 7.25 – 7.19 (m, 1H), 6.69 (d, $J = 9.5$ Hz, 1H), 6.20 (dd, $J = 9.6, 5.2$ Hz, 1H), 4.66 (d, $J = 4.6$ Hz, 2H), 4.04 (d, $J = 13.1$ Hz, 1H), 3.79 (d, $J = 13.1$ Hz, 1H), 3.65 (s, 3H), 3.46 (d, $J = 8.7$ Hz, 1H), 3.31 (t, $J = 4.7$ Hz, 1H), 3.08 (dd, $J = 8.7, 5.2$ Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 210.43, 155.28, 132.45, 130.25, 130.18, 129.25, 128.50, 128.35, 128.09, 122.57, 67.42, 61.44, 55.03, 39.08, 36.47, 24.06. IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3472, 3024, 2957, 2857, 1748, 1687, 1443, 1282, 1266, 1197, 1098, 1055, 950, 784; HRMS (ESI) calcd for C₁₆H₁₆O₅Na⁺ [M+Na]⁺: 311.0890, Found: 311.0895. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexane/IPA = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t_R (major) = 23.4 min, t_R (minor) = 28.0 min.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.450	BB	0.5329	1431.08960	40.63544	49.8484
2	27.883	BB	0.6223	1439.79211	34.82635	50.1516

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.391	BB	0.5410	1.13931e4	318.77936	91.2583
2	28.010	BB	0.5792	1091.34668	25.60997	8.7417

Preparation of *endo*-benzonorcaradiene 4aa

[CpRu(CH₃CN)₃]PF₆ (5.00 mol %, 10.4 μmol, 4.52 mg) and tetrabutylammonium iodide (6 mol %, 12.4 μmol, 4.60 mg) were dissolved in freshly distilled 2-butanone (0.55 ml) in a microwave reaction vial under N₂ atmosphere. The solution of an oxabenzonorbornadiene (0.208

mmol, 30 mg, 1.0 equiv.) and but-2-yne-1,4-diyl dimethyl dicarbonate (0.208 mmol, 42.1 mg, 1.0 equiv.) in 2-butanone (1.1 ml) was added into the microwave reaction vial. The reaction mixture was stirred at 40 °C for 45 min. The reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography with phosphate buffered silica gel (pH =7) (*n*-pentane/ethyl acetate = 5/1 (v/v')) to afford the *endo*-product (*rac*-**4aa**) (38 mg, 53% yield).

Ru1 (5 mol %, 10.4 μmol , 6.52 mg) and tetrabutylammonium iodide (6 mol %, 12.0 μmol , 4.60 mg) were dissolved with freshly distilled 2-butanone (0.55 ml) in a microwave reaction vial under N_2 atmosphere. The solution of an oxabenzonorbornadiene (208 μmol , 30.0 mg, 1.0 equiv.) and but-2-yne-1,4-diyl dimethyl dicarbonate (208 μmol , 42.1 mg, 1.00 equiv.) in 2-butanone (1.10 ml) was added in one portion. The reaction mixture was stirred at 40 °C for 25 min, then to room temperature. The solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography on phosphate buffered silica gel (pH =7) (*n*-pentane/ethyl acetate = 5/1 (v/v')) to afford the *endo*-product (**4aa**) (53 mg, 74% yield).

Colorless oil, 38 mg, 53% yield; Analytical data: ^1H NMR (600 MHz, CD_2Cl_2) δ 7.44 – 7.39 (m, 1H), 7.28 (td, $J = 7.5, 1.5$ Hz, 1H), 7.24 (td, $J = 7.5, 1.4$ Hz, 1H), 7.11 (dd, $J = 7.5, 1.4$ Hz, 1H), 6.48 (d, $J = 9.6$ Hz, 1H), 6.11 (dd, $J = 9.7, 5.1$ Hz, 1H), 4.56 (d, $J = 17.2$ Hz, 1H), 4.48 (d, $J = 11.9$ Hz, 1H), 4.32 (d, $J = 12.0$ Hz, 1H), 4.29 (d, $J = 17.2$ Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.97 (d, $J = 8.3$ Hz, 1H), 2.55 (dd, $J = 8.3, 5.1$ Hz, 1H). ^{13}C NMR (151

MHz, CD₂Cl₂) δ 196.75, 155.65, 155.08, 131.50, 129.98, 129.46, 128.35, 128.06, 127.81, 127.43, 122.15, 72.60, 69.66, 55.41, 55.36, 31.41, 29.09, 28.84.; IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3020, 2958, 1746, 1442, 1375, 1252, 1167, 1118, 1064, 951, 780, 741; HRMS (ESI) calcd for C₁₈H₁₈O₇Na⁺ [M+Na]⁺:369.0945, Found: 369.0942.

All NMR data for the *endo* product (**4aa**) were acquired at 0 °C because the *endo* product is slowly converted to *exo* product at room temperature.

Thermal isomerization from *endo*-benzonorcaradiene (**4aa**) to *exo*-benzonorcaradiene (**3aa**)

endo-benzonorcaradiene (**4aa**) (0.051 mmol, 17.7 mg) was dissolved in freshly distilled 2-butanone (0.56 ml) in a microwave reaction vial under N₂ atmosphere. The reaction mixture was stirred at 100 °C for 30 min. The reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography with silica gel (*n*-pentane/ethyl acetate = 5/1 (v/v')) to afford the *exo*-benzonorcaradiene (**3aa**) (17.0 mg, 96% yield).

1D NOE experiments on *exo*-benzonorcaradiene (**3aa**) and *endo*-benzonorcaradiene (**4aa**)

1D NOE experiments were performed with *exo*-benzonorcaradiene (**3aa**) and *endo*-benzonorcaradiene (**4aa**). Both samples were measured at 0 °C. Deuterated dichloromethane (CD₂Cl₂) and deuterated chloroform (CDCl₃) were used for *endo*-benzonorcaradiene and *exo*-benzonorcaradiene, respectively.

1D NOE results of the *endo* product (4aa)

1D NOE results of the *exo* product (3aa)

X-ray Structure of 3aj.

X-ray Structure of 3aj, CCDC 1947117

Computational Details

GAMESS¹⁴ was used for the quantum chemical calculation. The geometries of all species were optimized with B3LYP¹⁵/6-31G(d,p)¹⁶. The same method and basis sets are used for computing Gibbs free energy considering thermal and zero-point energy contribution, and scale factor for vibrational frequencies are adapted.¹⁷ All of transition states have only one imaginary vibrational mode and none of minima has an imaginary vibrational mode.

Energy Diagram

Summary of Computed Energies of Relevant Species

	B3LYP/6-31G(d,p) Electronic Energy (hartree)	B3LYP/6-31G(d,p) Gibbs Free Energy Correction (298.15 K, scale factor =1) (kcal/mol)	B3LYP/6-31G(d,p) Gibbs Free Energy Correction (373.15 K, scale factor =0.9627) (kcal/mol)	Total Gibbs Free Energy (373.15 K, scale factor = 0.9627) (kcal/mol)	Relative Gibbs Free Energy (373.15K) (kcal/mol)
D	-1222.627860	178.125	156.094	-767053.892	0.0
TS1	-1222.601644	177.246	155.484	-767038.051	15.8
4aa	-1222.641955	177.353	155.267	-767063.564	-9.7
TS2	-1222.617120	176.205	154.289	-767048.957	4.9
E	-1222.617415	176.180	154.046	-767049.386	4.5
TS3	-1222.597438	176.937	155.058	-767035.838	18.1
E'	-1222.609816	174.734	152.178	-767046.485	7.4
TS4	-1222.609669	175.209	152.985	-767045.586	8.3
3aa	-1222.652013	179.743	158.145	-767066.997	-13.1
5aa	-1222.653823	179.416	157.622	-767068.656	-14.8

Optimized Geometry

Allyl vinyl ether (D)

C	6.0	-2.4901476069	-1.9961422854	-0.1453761804
C	6.0	-1.3704001544	-2.6934888220	0.5890125912
C	6.0	-2.0952425638	-1.2219641996	-1.2475777115
C	6.0	-0.6023791816	-1.2103007028	-1.5332841531
C	6.0	-0.4103378433	-3.3502035736	-0.3736771147
C	6.0	-0.0280437174	-2.6152005580	-1.4219443797
C	6.0	-3.8326909857	-2.0685777359	0.2192224194
C	6.0	-4.7901837767	-1.3680023619	-0.5214339159
C	6.0	-4.3957454076	-0.5869073794	-1.6082842804
C	6.0	-3.0463714142	-0.5063040964	-1.9699970635
O	8.0	-0.6339167090	-1.7195757179	1.4184496122
C	6.0	0.1057781324	-0.3623917517	-0.4622445793
C	6.0	0.0320964987	-0.6684399836	0.8524644715
C	6.0	0.7229106964	0.1117622013	1.9424838383
C	6.0	0.9547186186	0.7634372998	-0.9604423207
O	8.0	2.1461985865	-0.1745108238	1.8760025799
C	6.0	2.9763323257	0.3519630313	2.7926205739
O	8.0	4.1663014766	0.1557973981	2.7783714746
O	8.0	2.3197392401	1.1100265004	3.6994768361
C	6.0	3.1621785053	1.7006851765	4.7049472135
O	8.0	0.0864900116	1.6856077189	-1.6885086737
C	6.0	0.6163044501	2.7472062107	-2.3149512420
O	8.0	-0.0460931684	3.5196958961	-2.9640265563
O	8.0	1.9527619921	2.8374060279	-2.1237016505
C	6.0	2.5753991907	3.9600765579	-2.7714150147
H	1.0	-1.7537664961	-3.3908690104	1.3354776142
H	1.0	-0.4118799395	-0.7717045798	-2.5152411452
H	1.0	-0.0090257205	-4.3350014224	-0.1561575534
H	1.0	0.7226470559	-2.9511370672	-2.1323400789
H	1.0	-4.1325840062	-2.6704059504	1.0738955966
H	1.0	-5.8395213096	-1.4305041972	-0.2480668038
H	1.0	-5.1391103570	-0.0392375749	-2.1807844321
H	1.0	-2.7385812662	0.1127684587	-2.8082830071
H	1.0	0.3261564224	-0.2033275373	2.9087514338
H	1.0	0.5664295686	1.1876689851	1.8336385153
H	1.0	1.7185204415	0.3954542959	-1.6553713464
H	1.0	1.4729967122	1.3014679552	-0.1668305570
H	1.0	2.4906080348	2.2643444855	5.3527312094
H	1.0	3.6829296639	0.9251336542	5.2709872460
H	1.0	3.8992399444	2.3633112768	4.2453647508
H	1.0	3.6390789134	3.8711579164	-2.5503051124
H	1.0	2.4010481816	3.9254999731	-3.8492838155
H	1.0	2.1777842671	4.8983490848	-2.3771181726

Transition state 1 (TS1)

C	6.0	-2.5773601175	-2.2756809836	-0.2569420986
C	6.0	-1.4458941877	-2.8894822252	0.4469068337
C	6.0	-2.2714977302	-1.2891752436	-1.2108527938
C	6.0	-0.8192099671	-0.9560438215	-1.4167668439
C	6.0	-0.2153036676	-3.0556144406	-0.2213437126
C	6.0	0.1143788740	-2.1031618937	-1.1577504186
C	6.0	-3.9073515662	-2.6234343919	-0.0074318326
C	6.0	-4.9343439662	-2.0004074378	-0.7193851804
C	6.0	-4.6303903775	-1.0246501134	-1.6696680147
C	6.0	-3.2993255130	-0.6688518215	-1.9149760248
O	8.0	-1.0791652024	-1.2396170437	1.5280286213
C	6.0	-0.0878381744	-0.1453070157	-0.3375638179
C	6.0	-0.2389497595	-0.4019601157	1.0261027943
C	6.0	0.6574880261	0.2757750785	2.0565511068
C	6.0	0.9179863360	0.8296467809	-0.8661747329
O	8.0	2.0365950389	-0.1202876588	1.8222997506
C	6.0	3.0103132401	0.3195586340	2.6379388934
O	8.0	4.1683521458	0.0156816572	2.4876837420
O	8.0	2.5341586891	1.1259152092	3.6117905029
C	6.0	3.5373016540	1.6300573375	4.5115949861
O	8.0	0.1728010855	1.8297613146	-1.6331229652
C	6.0	0.8248040349	2.8188370569	-2.2610643255
O	8.0	0.2609109855	3.6496503393	-2.9311490621
O	8.0	2.1602394108	2.7668014133	-2.0481907045
C	6.0	2.9088094546	3.8090460440	-2.6970112927
H	1.0	-1.6798740718	-3.5364043767	1.2869740874
H	1.0	-0.6643458770	-0.4826930745	-2.3871887504
H	1.0	0.5222674250	-3.7595692520	0.1497563892
H	1.0	1.0887097336	-2.0898183914	-1.6353008381
H	1.0	-4.1363586752	-3.3798045108	0.7388610737
H	1.0	-5.9683371031	-2.2721431540	-0.5282425723
H	1.0	-5.4285365099	-0.5340837589	-2.2194191198
H	1.0	-3.0652505558	0.0997372110	-2.6469156158
H	1.0	0.3383919222	-0.0559608870	3.0455132933
H	1.0	0.5795395981	1.3668151730	2.0070798844
H	1.0	1.6461510953	0.3646572896	-1.5399389164
H	1.0	1.4822285088	1.3264057905	-0.0786314433
H	1.0	3.0001040093	2.2513963844	5.2280417329
H	1.0	4.0441087831	0.8059060599	5.0186928893
H	1.0	4.2764784735	2.2213694310	3.9662879519
H	1.0	3.9516084346	3.6213513375	-2.4409686652
H	1.0	2.7643558109	3.7680087527	-3.7792254326
H	1.0	2.5933486550	4.7899709397	-2.3337763591

endo-benzonorcaradiene (**4aa**)

C	6.0	-2.6070697781	-2.5676890522	-0.4208828605
C	6.0	-1.4799579633	-3.3645002143	0.0504748008
C	6.0	-2.3687213092	-1.3994603881	-1.1814059300
C	6.0	-0.9735549065	-0.9965502014	-1.5132983445
C	6.0	-0.2011616013	-3.0676336973	-0.2481891621
C	6.0	0.1535761418	-1.8889271435	-1.0638622926
C	6.0	-3.9291944947	-2.9553634034	-0.1621171686
C	6.0	-5.0015664325	-2.2130539680	-0.6518532560
C	6.0	-4.7620636638	-1.0720843539	-1.4207222137
C	6.0	-3.4505177319	-0.6763079146	-1.6880677456
O	8.0	-1.3000605571	-0.6493933204	1.4421437450
C	6.0	0.0554515103	-0.4297080840	-0.5150306437
C	6.0	-0.2931838909	-0.2053367814	0.9211502031
C	6.0	0.6552873501	0.6272721191	1.7970164521
C	6.0	1.0514602592	0.5186470853	-1.1452583095
O	8.0	1.9756420698	0.0410326809	1.7214015906
C	6.0	2.9396043105	0.4394045356	2.5747708989
O	8.0	4.0533666183	-0.0211746161	2.5474623076
O	8.0	2.4999467369	1.3876100729	3.4260806407
C	6.0	3.4811953089	1.8416583107	4.3763461337
O	8.0	0.4155088313	1.8247993486	-1.2123157291
C	6.0	1.0482119293	2.8553073478	-1.7997696025
O	8.0	0.5645879620	3.9579579395	-1.8689877841
O	8.0	2.2574404825	2.4983091867	-2.2863064047
C	6.0	2.9789122303	3.5646246135	-2.9300088439
H	1.0	-1.7063394827	-4.2507712200	0.6385057729
H	1.0	-0.8786479658	-0.5253451122	-2.4893830672
H	1.0	0.6081750990	-3.7136580114	0.0802768530
H	1.0	1.0079083615	-2.0245763439	-1.7245650557
H	1.0	-4.1113880905	-3.8486501113	0.4303996975
H	1.0	-6.0201775008	-2.5242772884	-0.4385606781
H	1.0	-5.5927922970	-0.4895766350	-1.8085432490
H	1.0	-3.2625447860	0.2126811459	-2.2851728994
H	1.0	0.2715118221	0.5874928348	2.8162476193
H	1.0	0.6886315939	1.6686233540	1.4582173925
H	1.0	1.3045738759	0.1915044664	-2.1571716504
H	1.0	1.9749300211	0.5918767824	-0.5688659138
H	1.0	2.9750011096	2.5970897805	4.9769280992
H	1.0	3.8173641978	1.0122228408	5.0025882892
H	1.0	4.3420450326	2.2727068904	3.8600530326
H	1.0	3.9273611311	3.1275337994	-3.2421247889
H	1.0	2.4214324298	3.9338010106	-3.7938350926
H	1.0	3.1442106163	4.3885182963	-2.2324294945

Transition state 1 (TS2)

C	6.0	1.3417312015	0.3999490711	-0.7802151475
C	6.0	0.1554071036	0.1106031653	-0.1256286348
C	6.0	2.5562861929	-0.2656588929	-0.6066274476
C	6.0	2.6997611296	-1.6053519167	-0.1824809573
C	6.0	1.5597708682	-2.4377410637	0.1506665304
C	6.0	0.3230343075	-1.9327163384	0.5742626968
C	6.0	0.1114255245	-0.5938542090	1.1887767573
C	6.0	-1.2509115931	-0.4484353404	1.8907729855
C	6.0	1.1282787807	-0.0966606541	2.2504490355
O	8.0	-2.2799890309	-0.8988493573	0.9916715242
O	8.0	1.3146249689	1.0859656151	2.4246085840
C	6.0	1.7800027779	-1.1460382636	3.1558485199
O	8.0	2.1527335498	-0.5784969255	4.4086573725
C	6.0	-3.5304191601	-0.8476016474	1.4935776591
O	8.0	-4.3684827811	-1.2818059784	0.5440343446
C	6.0	-5.7549397293	-1.2847673201	0.9289206830
C	6.0	3.9737782587	-2.2475291079	-0.3296769528
C	6.0	1.7197726972	-3.8614836552	0.0559214139
C	6.0	4.1019238731	-3.6107189081	-0.2945226114
C	6.0	3.2518641805	0.1990191991	4.5031880422
O	8.0	3.5029321058	0.8307837197	5.4971684784
O	8.0	4.0254264759	0.1281633921	3.4006169060
C	6.0	5.1902367393	0.9685570356	3.4391483968
C	6.0	2.9499393601	-4.4322429049	-0.1335258793
O	8.0	-3.8312492634	-0.4757208219	2.6050276353
H	1.0	1.3084186969	1.1859396668	-1.5328594253
H	1.0	-0.7897448977	0.4585209456	-0.5321026816
H	1.0	3.4439733976	0.1947850592	-1.0353122682
H	1.0	-0.5454829302	-2.5832731797	0.5147673433
H	1.0	-1.4190605721	0.6005115310	2.1499045479
H	1.0	-1.2914953463	-1.0426772056	2.8098527760
H	1.0	2.6360701996	-1.5887681398	2.6398991252
H	1.0	1.0729646797	-1.9469400511	3.3902901056
H	1.0	-6.0878565765	-0.2732953569	1.1740468565
H	1.0	-5.9125770914	-1.9322914825	1.7947267078
H	1.0	-6.2938603283	-1.6656446399	0.0618764331
H	1.0	4.8413261964	-1.6211418131	-0.5209913733
H	1.0	0.8439724085	-4.4854789196	0.2149574703
H	1.0	5.0770074683	-4.0710885153	-0.4246516840
H	1.0	5.7277460511	0.7670707268	2.5123247113
H	1.0	5.8095261780	0.7265826161	4.3057981596
H	1.0	4.8964808928	2.0196837875	3.4901576990
H	1.0	3.0523553585	-5.5133179190	-0.1488547407

Cycloheptatriene (E)

C	6.0	1.3355792268	0.4169626056	-0.7501957560
C	6.0	0.1764099649	0.1987951657	-0.0574329768
C	6.0	2.5481561676	-0.2937854964	-0.6030298665
C	6.0	2.6862665701	-1.6260963123	-0.1999838323
C	6.0	1.5519112418	-2.4685412572	0.1742660414
C	6.0	0.3534631132	-1.9870497882	0.6734731866
C	6.0	0.1343977374	-0.6069431849	1.2083535043
C	6.0	-1.2268593151	-0.4668993004	1.9176858072
C	6.0	1.1472928879	-0.1134400797	2.2864966332
O	8.0	-2.2555769953	-0.9082090182	1.0128577816
O	8.0	1.3316862766	1.0679595424	2.4699365584
C	6.0	1.8011824258	-1.1659301247	3.1874536337
O	8.0	2.1774281620	-0.6012224982	4.4405248485
C	6.0	-3.5074033514	-0.8461552690	1.5091158223
O	8.0	-4.3459134320	-1.2699207169	0.5549758610
C	6.0	-5.7337775224	-1.2586764957	0.9337523378
C	6.0	3.9625331980	-2.2727823822	-0.3783141111
C	6.0	1.7160390323	-3.8991778835	0.0474271792
C	6.0	4.0895583926	-3.6312645913	-0.3637042075
C	6.0	3.2747926760	0.1786906331	4.5333539420
O	8.0	3.5276276808	0.8089808956	5.5278157155
O	8.0	4.0461695261	0.1112606813	3.4287722783
C	6.0	5.2095643417	0.9535564452	3.4663684070
C	6.0	2.9364277838	-4.4608089152	-0.1839869937
O	8.0	-3.8102653601	-0.4740089856	2.6201669966
H	1.0	1.3184535219	1.1916736311	-1.5153445353
H	1.0	-0.7548822403	0.6368043990	-0.4051843060
H	1.0	3.4379145895	0.1666200243	-1.0285616262
H	1.0	-0.4950912217	-2.6659110818	0.7053976445
H	1.0	-1.3957839835	0.5787900370	2.1887530496
H	1.0	-1.2673207101	-1.0710951058	2.8301942358
H	1.0	2.6562244965	-1.6070909965	2.6681372059
H	1.0	1.0959186299	-1.9680192928	3.4222487703
H	1.0	-6.0579930297	-0.2435307279	1.1758003410
H	1.0	-5.9021739660	-1.9027865941	1.8002221922
H	1.0	-6.2729189086	-1.6360002051	0.0651666846
H	1.0	4.8254506846	-1.6435641615	-0.5807581623
H	1.0	0.8449660230	-4.5257491860	0.2210123492
H	1.0	5.0602446571	-4.0912460131	-0.5242039502
H	1.0	5.7489950676	0.7501415444	2.5411540503
H	1.0	5.8277745122	0.7155858417	4.3347093236
H	1.0	4.9137476248	2.0043279149	3.5132167156
H	1.0	3.0421058236	-5.5410486971	-0.2214067735

Transition state 3 (TS3)

C	6.0	-4.0987172561	-0.7144984077	0.4534754179
C	6.0	-4.2795439148	-1.0751178258	-0.9340990566
C	6.0	-3.2060211806	-1.1775011097	-1.7529587017
C	6.0	-1.8433994549	-0.9386496731	-1.3052665305
C	6.0	-1.6479184516	-0.5577116080	0.1175645537
C	6.0	-2.8599503438	-0.4755521439	0.9407503650
C	6.0	-0.8479740251	-1.0939629905	-2.2324482590
C	6.0	0.5799443936	-0.9523625829	-2.1026867645
C	6.0	1.3472790310	-0.5888133601	-1.0570413360
C	6.0	0.9728361900	-0.1655449285	0.3529916018
C	6.0	-0.4807568256	-0.2784256650	0.7630061403
C	6.0	1.8909395434	-1.0308728330	1.2848817103
C	6.0	1.4447825593	1.3027926625	0.5271265517
O	8.0	3.0451120896	-0.7155314932	1.4890907042
C	6.0	1.3377543798	-2.3028222800	1.9277541692
O	8.0	0.6465059899	-3.0929096456	0.9493910044
C	6.0	-0.5395965445	-3.6789282634	1.2097333144
O	8.0	-1.1185245585	-4.3340349620	0.3812915802
O	8.0	-0.9680154793	-3.4516886037	2.4681903805
C	6.0	-2.2611196421	-4.0112415386	2.7670950061
O	8.0	1.2017844029	1.6762039989	1.9008112052
C	6.0	1.7912766675	2.7594928569	2.4338961426
O	8.0	1.6288347396	3.0815655329	3.5848500963
O	8.0	2.5548899670	3.4174149994	1.5362476724
C	6.0	3.2319631091	4.5727881639	2.0625392275
H	1.0	-4.9673858436	-0.6305590220	1.1003059447
H	1.0	-5.2798282141	-1.2663072963	-1.3109023970
H	1.0	-3.3383427019	-1.4568190746	-2.7946772873
H	1.0	-2.7275821392	-0.1948308854	1.9821092720
H	1.0	-1.1763556167	-1.3877313021	-3.2270173032
H	1.0	1.1287304159	-1.1882031567	-3.0132028622
H	1.0	2.4236015785	-0.5755620717	-1.2218572505
H	1.0	-0.6057951700	-0.0117244240	1.8110090789
H	1.0	0.8725286767	1.9560419643	-0.1377077133
H	1.0	2.5083343497	1.3816817303	0.3005934935
H	1.0	0.6767161257	-2.0291159517	2.7543052943
H	1.0	2.1840362607	-2.8744142612	2.3175636282
H	1.0	-2.2661212742	-5.0850404938	2.5697390039
H	1.0	-3.0282794319	-3.5257308910	2.1593995975
H	1.0	-2.4254237209	-3.8115303712	3.8260344568
H	1.0	3.8223625895	4.9658086448	1.2348606837
H	1.0	2.5082524727	5.3155908750	2.4064317211
H	1.0	3.8775043203	4.2888422488	2.8965874741

Cycloheptatriene (E')

C	6.0	-3.1235638096	-0.5512100160	-2.1739671989
C	6.0	-2.5221742130	0.0085893662	-3.3459823857
C	6.0	-1.1673218148	-0.0197839659	-3.5027841751
C	6.0	-0.2988651262	-0.5856089335	-2.5014159195
C	6.0	-0.8999054365	-0.9785492843	-1.2297345007
C	6.0	-2.3430670642	-1.0498704638	-1.1739712597
C	6.0	1.0057729380	-0.9343098742	-2.8642937548
C	6.0	1.9175448440	-1.6987759179	-2.0993654944
C	6.0	1.9539501231	-1.8399632235	-0.7366813956
C	6.0	1.2318456254	-0.9217686068	0.2115722209
C	6.0	-0.1936257856	-1.2889966914	-0.0799658648
C	6.0	1.6513832733	-1.2180747107	1.6725823546
C	6.0	1.6090789570	0.5565387649	-0.0424301407
O	8.0	2.7893598055	-1.5503509396	1.9298182110
C	6.0	0.6420055519	-1.0199590795	2.8120045051
O	8.0	-0.0914551103	-2.2648725972	2.9087984017
C	6.0	-1.0236438352	-2.4141695609	3.8736284070
O	8.0	-1.6818012606	-3.4177656609	3.9801308265
O	8.0	-1.1075351595	-1.3258575452	4.6625683399
C	6.0	-2.0832445574	-1.4224357046	5.7174475944
O	8.0	0.9009953041	1.3583701345	0.9320504413
C	6.0	0.9802767287	2.7005246624	0.8942338353
O	8.0	0.4273752378	3.4031350477	1.7033759828
O	8.0	1.7390835775	3.1315503468	-0.1342857009
C	6.0	1.8653683629	4.5621253308	-0.2268772166
H	1.0	-4.2054900079	-0.5649404006	-2.0806602217
H	1.0	-3.1542553131	0.4232738808	-4.1259668961
H	1.0	-0.7128977383	0.3447581629	-4.4205400234
H	1.0	-2.7956108112	-1.4445792253	-0.2681558376
H	1.0	1.2728169309	-0.7552880602	-3.9041024226
H	1.0	2.6454328003	-2.2785665820	-2.6658654241
H	1.0	2.5765051370	-2.6092176084	-0.2896004516
H	1.0	-0.7258187939	-1.8311515915	0.6964522890
H	1.0	1.3326903774	0.8647659383	-1.0483721502
H	1.0	2.6879554714	0.6786873425	0.0903290546
H	1.0	-0.0376652437	-0.1896052483	2.6126214954
H	1.0	1.1998201032	-0.8396962996	3.7328194689
H	1.0	-1.8273541265	-2.2387066761	6.3967634320
H	1.0	-3.0772392486	-1.6002378931	5.3012820473
H	1.0	-2.0462886958	-0.4641208222	6.2345856855
H	1.0	2.4923551491	4.7419965169	-1.1000284387
H	1.0	0.8844303351	5.0253654992	-0.3541489808
H	1.0	2.3365768658	4.9620697349	0.6739830593

Transition state 4 (TS4)

C	6.0	-3.0877086326	-0.5129191258	-2.1779148386
C	6.0	-2.4856237093	0.0663931908	-3.3323635191
C	6.0	-1.1266431021	0.0323150117	-3.4881344179
C	6.0	-0.2684649103	-0.5537303211	-2.4981052783
C	6.0	-0.8704653731	-0.9840553026	-1.2496657975
C	6.0	-2.3061460358	-1.0437044918	-1.1887567470
C	6.0	1.0453655837	-0.9124606804	-2.8615773799
C	6.0	1.9164405493	-1.7018944647	-2.1001061060
C	6.0	1.8893077908	-1.8903986751	-0.7290965790
C	6.0	1.2406607069	-0.9388170919	0.2280579369
C	6.0	-0.1518558479	-1.3608512121	-0.1113338687
C	6.0	1.6553046424	-1.2539999401	1.6849453059
C	6.0	1.6171487306	0.5339456155	-0.0283425028
O	8.0	2.7865944686	-1.6131401665	1.9356743801
C	6.0	0.6529385241	-1.0411886764	2.8270981087
O	8.0	-0.1558577885	-2.2411282411	2.8807011593
C	6.0	-1.0824791707	-2.3742918455	3.8533689041
O	8.0	-1.8099200294	-3.3325193429	3.9198078974
O	8.0	-1.0732056978	-1.3274163109	4.6999533333
C	6.0	-2.0350771083	-1.4095762539	5.7688515027
O	8.0	0.9014667475	1.3351970143	0.9409954043
C	6.0	0.9472024875	2.6781895154	0.8843198108
O	8.0	0.3801327426	3.3767553955	1.6872192575
O	8.0	1.6904610504	3.1148761800	-0.1527415161
C	6.0	1.7694159768	4.5472577300	-0.2702719743
H	1.0	-4.1693646901	-0.5202989093	-2.0807265546
H	1.0	-3.1133288208	0.5022577351	-4.1043225638
H	1.0	-0.6693542275	0.4122753923	-4.3982641827
H	1.0	-2.7615768849	-1.4568164140	-0.2925787050
H	1.0	1.3184586884	-0.7304056165	-3.8989844672
H	1.0	2.6571565271	-2.2798712202	-2.6512242987
H	1.0	2.4365614057	-2.7186605989	-0.2890965992
H	1.0	-0.6660768147	-1.9721588806	0.6245494360
H	1.0	1.3479767037	0.8417848390	-1.0358472628
H	1.0	2.6951264803	0.6583483832	0.1115726287
H	1.0	0.0250696322	-0.1658388706	2.6508809202
H	1.0	1.2161351917	-0.9245143851	3.7546244903
H	1.0	-1.8494566162	-2.2966864314	6.3783741536
H	1.0	-3.0490571265	-1.4559517428	5.3652960278
H	1.0	-1.8943089993	-0.5015412374	6.3543154678
H	1.0	2.3954466608	4.7326078804	-1.1429073755
H	1.0	0.7738835618	4.9739130039	-0.4122008766
H	1.0	2.2202464121	4.9793828590	0.6260556355

exo-benzonorcaradiene (**3aa**)

O	8.0	-1.0406798585	-1.1367420300	-0.4113061378
C	6.0	-2.1560886641	-1.2815987027	0.3242724751
O	8.0	1.4693888164	0.4705730901	-3.3306625271
O	8.0	-3.1052475624	-1.9206148408	-0.0701206472
O	8.0	-2.0713608609	-0.6517506993	1.5075336890
C	6.0	1.0107985360	-0.1070549242	-1.0761472195
C	6.0	2.1919570656	-1.1274177043	-1.1310312176
C	6.0	2.3347405486	-2.1740356462	-0.1023449857
C	6.0	2.6751185991	-1.8809556619	1.1686928056
C	6.0	2.9709512693	-0.5192879968	1.6087046312
C	6.0	3.3844691616	-0.2531601293	2.9249772995
C	6.0	3.7283289770	1.0363300363	3.3195138737
C	6.0	3.6745773360	2.0845960578	2.3958013754
C	6.0	3.2641314766	1.8367632603	1.0864630227
C	6.0	2.8911865960	0.5501846671	0.6829706575
C	6.0	2.4636506051	0.2914913724	-0.7172075718
C	6.0	-0.0133009159	-0.2017955265	0.0243552318
C	6.0	0.6253462428	0.3523819701	-2.4523734080
C	6.0	-0.8315347089	0.5822710651	-2.8614186545
C	6.0	-3.2960324901	-0.6164530710	2.2645456225
O	8.0	-1.5471659044	1.3310351087	-1.8647742818
C	6.0	-2.8558352632	1.0901943190	-1.6416817548
O	8.0	-3.4152414693	1.5069875458	-0.6546054577
O	8.0	-3.4182515850	0.3731980547	-2.6248497774
C	6.0	-4.7738259161	-0.0549837929	-2.3698399412
H	1.0	2.4458903791	-1.3988556146	-2.1516433776
H	1.0	2.1816180919	-3.2056611604	-0.4067978491
H	1.0	2.7785982540	-2.6768082315	1.9025191381
H	1.0	3.4404136153	-1.0735028727	3.6364687435
H	1.0	4.0443312704	1.2250101500	4.3414550937
H	1.0	3.9479851314	3.0919750126	2.6959090960
H	1.0	3.2207428181	2.6508333025	0.3671828393
H	1.0	2.8966497109	0.9404566790	-1.4740573553
H	1.0	0.4313930058	-0.5758276106	0.9450601330
H	1.0	-0.4738654852	0.7658419133	0.2240821160
H	1.0	-0.8194643553	1.1330461278	-3.8047052667
H	1.0	-1.3041879207	-0.3911292424	-3.0167103040
H	1.0	-3.0319745907	-0.1664878601	3.2214412085
H	1.0	-4.0305330563	0.0004610348	1.7418645129
H	1.0	-3.6887688529	-1.6254843928	2.4047590640
H	1.0	-5.0950595538	-0.5472077489	-3.2874647828
H	1.0	-4.7803489275	-0.7551091540	-1.5326405997
H	1.0	-5.4062335662	0.8072718457	-2.1504115118

Dihydrofuran (5aa)

C	6.0	1.0083860707	1.2660477169	4.6255888748
C	6.0	-0.2339028120	1.5275586947	5.2068383979
C	6.0	-1.3019411209	1.9282166251	4.4071959137
C	6.0	-1.1487777530	2.0745930760	3.0196695597
C	6.0	0.1099441461	1.8197377512	2.4401007441
C	6.0	1.1746799450	1.4172221345	3.2477129323
C	6.0	-2.2768293901	2.4689889544	2.1717547098
C	6.0	-2.1964256844	2.4950127184	0.8351626819
C	6.0	-0.9424109676	2.1310506496	0.0804328422
C	6.0	0.3369741889	2.0406963440	0.9540631935
C	6.0	-0.9597232003	0.7435845984	-0.5760513971
C	6.0	0.2416401846	0.1836537621	-0.3724715883
O	8.0	1.0968734373	0.9151575836	0.4058469318
C	6.0	0.8808767004	-1.0991829446	-0.8210237140
C	6.0	-2.0847468445	0.2377125556	-1.4041919593
O	8.0	0.1761117506	-1.7631009295	-1.8789162985
C	6.0	0.2587834704	-1.3060152181	-3.1499757938
O	8.0	-0.3930852416	-1.7947746457	-4.0385360956
O	8.0	1.1318933019	-0.2931009061	-3.2730838275
C	6.0	1.1615178429	0.3139366007	-4.5809704810
O	8.0	-1.9454108282	0.8180410740	-2.7447173331
C	6.0	-2.8981043675	0.4519792960	-3.6161730902
O	8.0	-3.8758968579	-0.2194458684	-3.3731331329
O	8.0	-2.5797862976	0.9741425091	-4.8153414188
C	6.0	-3.4859983691	0.6183411372	-5.8728749488
H	1.0	1.8456035008	0.9503043764	5.2413613606
H	1.0	-0.3698005390	1.4184685897	6.2790513168
H	1.0	-2.2736929341	2.1227184031	4.8545860465
H	1.0	2.1382403204	1.2128904153	2.7899338304
H	1.0	-3.2088169397	2.7270166057	2.6696971097
H	1.0	-3.0633196138	2.7735149969	0.2412622749
H	1.0	-0.7921447237	2.8837876031	-0.7081011914
H	1.0	0.9812931991	2.9150272449	0.8167385012
H	1.0	1.9157144152	-0.8914354315	-1.1065450441
H	1.0	0.8905807604	-1.8212431494	0.0015400625
H	1.0	-2.0793884699	-0.8480213396	-1.5006969649
H	1.0	-3.0556056655	0.5406830482	-1.0022515797
H	1.0	1.9320118984	1.0826281345	-4.5243007797
H	1.0	1.4128760627	-0.4311940524	-5.3387706076
H	1.0	0.1877214924	0.7539336995	-4.8059237447
H	1.0	-3.1088524612	1.1246553763	-6.7615118511
H	1.0	-3.4918367851	-0.4640632398	-6.0222831634
H	1.0	-4.5001208211	0.9536674499	-5.6420252789

5. NMR spectra

3af

3af

3aj

3aj

3da

3da

3al

3al

2D NMR of *endo*-product (4aa)

COSY spectra

HSQC spectra

HMBC spectra

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