Highly Stereoselective Radical Carbonylations of *gem*-Dihalocyclopropane Derivatives with CO

Yoshinori Nishii,* Takao Nagano, Hideki Gotoh,[†] Ryohei Nagase,[†] Jiro Motoyoshiya, Hiromu Aoyama, Yoo Tanabe^{†*}

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan. [†]*Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan.*

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Supporting Information

General: All reactions were carried out in oven-dried glassware and stainless steel autoclave. Benzene was distilled from sodium. Column chromatography was performed with silica gel Merck 60 (70-230 mesh ASTM). TLC analysis was performed on 0.25 mm Silica gel Merck 60 F₂₅₄ plates. NMR spectra were recorded on 400 MHz spectrometer, operating at 400 or 300 MHz for ¹H NMR and 100 or 75 MHz for ¹³C NMR. Chemical shifts (ppm) in CDCl₃ were reported downfield from TMS (= 0) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to CDCl₃ (77.00 ppm) as an internal reference. Mass spectra were obtained by electron ionization (EI).

Preparation of *gem*-dihalocyclopropanes. *gem*-Dihalocyclopropanes **1a–1j** were prepared by phase transfer methods as previously described.^{1–10}

1,1-Dichloro-2-phenylcyclopropane (1a)²

1,1-Dichloro-2-hexylcyclopropane (1b)³

(2,2-Dichlorocyclopropyl)methanol (1c)⁴

(2,2-Dichloro-1-methylcyclopropyl)methanol (1d)⁵

[(1*S*^{*},3*S*^{*})-2,2-Dichloro-3-phenylcyclopropyl]methanol (1e)⁶

[(1*S*^{*},3*R*^{*})-2,2-Dichloro-1-methyl-3-phenylcyclopropyl]methanol (1f)⁷

7,7-Dichlorobicyclo[4.1.0]heptane (1g)^{1,2}

9,9-Dichlorobicyclo[6.1.0]nonane (1h)⁸

7,7-Dibromobicyclo[4.1.0]heptane (1i)⁹

***cis*- and *trans*-1-Bromo-1-chloro-2-phenylcyclopropane (1j)**¹⁰ (*cis/trans* = 1/1)

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cis- and trans-1-Bromo-1-chloro-2-hexylcyclopropane (1k) (*cis/trans* = 1/1)

Chlorodibromomethane (1.15 ml, 13.4 mmol) was added to a stirred suspension of potassium *t*-butoxide (1.50 g, 13.4 mmol) and 1-octene (1.00 g, 8.91 mmol) in hexane (18 ml) at 0-5 °C. After being stirred at the same temperature for 6 h, the mixture was diluted with water (50 mL) and extracted with Et₂O (40 mL x 2). The organic phase was washed with water and brine, dried (Na₂SO₄), and concentrated. The obtained crude oil was purified by SiO₂-column chromatography (hexane) to give the product **1k** (1/1 mixture of diastereoisomers, 1.44 g, 67%). **1k**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.04-1.17 (m, 1H), 1.25-1.39 (m, 6H), 1.41-1.52 (m, 3H), 1.55-1.71 (m, 3H); ¹³C NMR (400 MHz, CDCl₃) δ 14.1, 22.6, 27.6, 27.9, 28.4, 28.5, 28.9, 30.3, 30.9, 31.6, 31.7, 32.6, 45.4, 48.1; IR (neat) 2957, 2927, 1466, 1113 cm⁻¹; HRMS (EI) calcd for C₉H₁₆BrCl (M⁺) 238.0124, found 238.0128.

exo- and endo-1-Bromo-1-chlorobicyclo[4.1.0]heptane (1l)¹¹ (*exo/endo* = 1/1)

exo- and endo-1-Bromo-1-chlorobicyclo[6.1.0]nonane (1m)¹¹ (*exo/endo* = 1/1)

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[(1S^{*},2S^{*})- and (1S^{*},2R^{*})-2-Bromo-2-chloro-1-methylcyclopropyl]methanol (1n) (*cis/trans* = 1/1)

A mixture of 2-methyl-2-propen-1-ol (700 mg, 9.70 mmol), 3,4-dihydro-2*H*-pyran (980 mg, 11.7 mmol), and a little amount of *p*-toluenesulfonic acid in Et₂O (20 mL) was stored at rt for 12 h. sat. NaHCO₃ aqueous solution was added to mixture, which was extracted with Et₂O (30 mL x 2). The organic phase was washed with water and brine, dried (Na₂SO₄) and concentrated to give 1.50 g of the crude tetrahydropyranyl (THP) ether. Chlorodibromomethane (4.00 g, 19.2 mmol) was added to a vigorously stirred mixture of crude THP ether and potassium *t*-butoxide (1.62 g, 19.2 mmol) in hexane (20 mL) at 0-5 °C. After being stirred for 18 h at the same temperature, the mixture was diluted with water (30 mL) and extracted with Et₂O (20 mL x 2). The combined extracts were washed with water, brine, dried (Na₂SO₄), and concentrated. MeOH (20 mL) and a little *p*-toluenesulfonic acid were added to the residue which, after being stored over night, was treated with sat. NaHCO₃ aqueous solution, and then evaporated to give a residue. This was extracted with Et₂O (20 mL x 2). The extract was washed with water and brine, and concentrated to give a crude oil. The obtained crude oil was purified by SiO₂-column chromatography (hexane/AcOEt = 5/1) to give the product **1n** (1/1 mixture of diastereoisomers, 1.13 g, 59%). **1n**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.36 (t, *J* = 7.6 Hz, 1H), 1.48 (s, 3H x 1/2), 1.50 (s, 3H x 1/2), 1.51 (t, *J* = 7.6 Hz, 1H), 2.10 (brs, 1H), 3.66 (d, *J* = 11.9 Hz, 1H x 1/2), 3.71 (d, *J* = 11.9 Hz, 1H x 1/2), 3.83 (d, *J* = 11.9 Hz, 1H x 1/2), 3.85 (d, *J* = 11.9 Hz, 1H x 1/2); ¹³C NMR

(400 MHz, CDCl₃) δ 17.7, 20.9, 31.6, 31.7, 31.9, 31.9, 51.8, 52.1, 67.5, 70.1; IR (neat) 3356, 1037, 729, 486 cm⁻¹; HRMS (EI) calcd for C₅H₈⁸¹BrClO (M⁺) 199.9447, found 199.9456.

[(1*S*^{*},2*S*^{*},3*R*^{*})- and (1*S*^{*},2*R*^{*},3*R*^{*})-2-Bromo-2-chloro-1-methyl-3-phenylcyclopropyl]methanol (1o)

(mixture of diastereoisomers: *cis/trans* = 1/1)

Following the procedure for the preparation of **1n**, the reaction of (E)-2-methyl-3-phenylprop-2-en-3-ol (1.00 g, 6.70 mmol) gave the product **1o** (1/1 mixture of diastereoisomers, 818 mg, 44%). **1o**: ¹H NMR (400 MHz, CDCl₃) δ 1.30 (s, 3H x 1/2), 1.34 (s, 3H x 1/2), 1.55 (brs, 1H), 2.63 (s, 1H x 1/2), 2.69 (s, 1H x 1/2), 3.89 (d, *J* = 5.2 Hz, 1H), 4.03 (d, *J* = 5.2 Hz, 1H), 7.27-7.37 (m, 5H); ¹³C NMR (400 MHz, CDCl₃) δ 15.0, 17.9, 29.7, 36.1, 39.8, 40.3, 57.9, 69.2, 69.4, 127.4, 128.2, 128.3, 130.1, 130.2, 133.7; IR (CHCl₃) 3421, 3018, 1215, 756 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₂⁷⁹BrClO (M⁺) 273.9760, found 273.9757.

1,1-Dibromo-2-phenylcyclopropane (1p)¹²

1,1-Dibromo-2-butylcyclopropane (1q)¹³

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(1*R*^{*},2*R*^{*})-1-Chloro-2-phenylcyclopropanecarbaldehyde (2a)¹⁴

(1*R*^{*},2*S*^{*})-1-Chloro-2-phenylcyclopropanecarbaldehyde (3a)

(Method I) A typical procedure: 1,1-Dichloro-2-phenylcyclopropane

(1a) (187 mg, 1.00 mmol), AIBN (33 mg, 0.20 mmol), Bu₃SnH (349 mg, 1.20 mmol), and benzene (50 mL) were placed in a 100-mL stainless steel autoclave with a insert glass tube. The reaction mixture

was stirred under CO pressure (80 atm) at 80 °C for 3 h. AIBN (33 mg, 0.20 mmol) was added to the reaction mixture after temporary release of CO pressure. Then, the reaction mixture was stirred under CO pressure (80 atm) at 80 °C for 3 h. After evacuation of excess CO at rt, benzene was removed under reduced pressure. The residue was stirred for 1 h with Et₂O (10 ml) and aqueous sat. KF solution (10 ml). After Celite filtration, the separated organic phase was washed with water, brine, dried (Na₂SO₄), and concentrated. The obtained crude product was purified by SiO₂-column chromatography (hexane) to give an inseparable mixture of diastereoisomers **2a** and **3a** (**2a/3a** = 3/1, 92 mg, 51%). **(Method II)** A typical procedure: Following the procedure of method I, the reaction of 1-Bromo-1-chloro-2-phenylcyclopropane (**1j**) (230 mg, 1.00 mmol) with 0.2 equiv of AIBN (33 mg, 0.20 mmol, added once) in the place of 0.4 equiv of that (0.2 equiv added twice in method I) gave an inseparable mixture of diastereoisomers **2a** and **3a** (**2a/3a** = 3/1, 108 mg, 60%). Relative configuration of minor product **3a** was determined as *cis*-adduct based on known spectra data of

trans-adduct **2a**¹⁴. Additionally, due to the shielding effect¹⁵ (up field shift) of phenyl group, the chemical shift (CHO 8.88 ppm) of aldehyde **3a** was assigned to that of *cis*-adduct. Ratio was analyzed by ¹H NMR. **2a** and **3a**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (dd, *J* = 6.3 Hz, *J* = 8.6 Hz, 1H x 3/4), 2.00 (dd, *J* = 6.8 Hz, *J* = 9.9 Hz, 1H x 1/4), 2.18 (dd, *J* = 6.3 Hz, *J* = 10.4 Hz, 1H x 3/4), 2.38 (dd, *J* = 6.8 Hz, *J* = 8.6 Hz, 1H x 1/4), 3.00 (dd, *J* = 8.6 Hz, *J* = 10.4 Hz, 1H x 3/4), 3.25 (dd, *J* = 8.6 Hz, *J* = 10.4 Hz, 1H x 1/4), 7.21-7.38 (m, 5H), 8.88 (s, 1H x 1/4), 9.61 (s, 1H x 3/4); ¹³C NMR (100 MHz, CDCl₃) δ 22.1, 23.4, 34.9, 38.4, 52.9, 53.1, 127.8, 128.3, 128.6, 128.7, 129.2, 129.4, 133.2, 133.5, 193.8, 197.1; IR (neat) 2843, 1716, 1497 cm⁻¹; HRMS (EI) calcd for C₁₀H₉ClO (M⁺) 180.0342, found 180.0334.

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(1*S**,2*R**)-1-Chloro-2-hexylcyclopropanecarbaldehyde (**2b**)

(1*R**,2*R**)-1-Chloro-2-hexylcyclopropanecarbaldehyde (**3b**)

Following the procedure of method I, the reaction of **1b** (181 mg, 1.00 mmol) gave the products **2b** and **3b** (**2b**/**3b** = 3/1, 84 mg, 48%). Following the procedure of method II, the reaction of **1k** (232 mg, 1.00 mmol) gave the separable products **2b** (110 mg, 47%) and **3b** (36 mg, 16%). Purification was carried out by SiO₂-column chromatography (hexane/AcOEt = 30/1). Based on the the deshielding effect of alkyl group, the chemical shift (CHO 9.56 ppm, down field shift) of aldehyde **3b** was assigned to that of *cis*-adduct. **2b**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.13-1.16 (m, 1H), 1.23-1.37 (m, 7H), 1.41-1.50 (m, 2H), 1.58-1.68 (m, 3H), 1.79-1.82 (m, 1H), 9.39 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 25.3, 27.1, 28.7, 29.3, 31.6, 37.1, 50.0, 196.5; IR (neat) 2923, 2855, 1717 cm⁻¹; HRMS (EI) calcd for C₁₀H₁₇ClO (M⁺) 188.0968, found 188.0977. **3b**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.24-1.43 (m, 8H), 1.47-1.57 (m, 2H), 1.60-1.68 (m, 2H), 1.85-1.93 (m, 1H), 9.56 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 25.3, 28.7, 28.9, 29.1, 29.8, 31.6, 52.7, 197.4; IR (neat) 2856, 1697, 1440, 1290 cm⁻¹; HRMS (EI) calcd for C₁₀H₁₇ClO (M⁺) 188.0968, found 188.0972.

(1*S**,2*S**)-1-Chloro-2-hydroxymethylcyclopropanecarbaldehyde (**2c**)

(1*R**,2*R**,5*S**)- and (1*R**,2*S**,5*S**)-1-Chloro-3-oxabicyclo[3.1.0]hexan-2-ol (**3c**)

Following the procedure of method I, the reaction of **1c** (141 mg, 1.00 mmol) gave the products **2c** (14 mg, 10%) and **3c** (a couple of diastereoisomeric lactols, inseparable mixture, ratio = 5/1 in CDCl₃, 56 mg, 38%). Aldehyde **2c** and lactol **3c** was separated by SiO₂ column chromatography (hexane/AcOEt = 5/1). **2c**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.36 (dd, *J* = 5.8, 8.1 Hz, 1H), (m, 1H), 1.86 (dd, *J* = 5.8 Hz, *J* = 10.1 Hz, 1H), 2.02-2.10 (m, 1H) 3.75 (dd, *J* = 8.8 Hz, *J* = 12.0 Hz, 1H), 4.06 (dd, *J* = 4.4, 12.0 Hz, 1H), 9.42 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 22.7, 30.7, 51.4, 61.7, 196.4; IR (neat) 3487, 2954, 2863, 1725 cm⁻¹; HRMS (EI) calcd for C₅H₇ClO₂ (M⁺) 134.0135, found 134.0130. **3c**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.99 (dd, *J* = 4.0 Hz, *J* = 6.0 Hz, 1H), 1.23 (dd, *J* = 6.0 Hz, *J* = 8.4 Hz, 1H), 1.96-1.99 (m, 1H), 3.47 (dd, *J* = 7.1 Hz, *J* = 11.6 Hz, 1H), 3.59 (dd, *J* = 7.1 Hz, *J* = 11.6 Hz, 1H), 5.27 (d, *J* = 4.0 Hz, 1H x 5/6), 5.43 (d, *J* = 7.1 Hz, 1H x 1/6); ¹³C NMR (100 MHz, CDCl₃) δ 15.0, 22.4, 62.8, 67.7, 98.6; IR (neat) 3489, 2944, 2867 cm⁻¹; HRMS (EI) calcd for C₅H₇ClO₂ (M⁺) 134.0135, found 134.0139.

(1*S*^{*},2*S*^{*})-1-Chloro-2-hydroxymethyl-2-methylcyclopropanecarbaldehyde (2d)

(1*R*^{*},2*R*^{*},5*S*^{*})- and (1*R*^{*},2*S*^{*},5*S*^{*})-1-Chloro-5-methyl-3-oxabicyclo[3.1.0]hexan-2-ol (3d)

Following the procedure of method I, the reaction of **1d** (155 mg, 1.00 mmol) gave the products **2d** (15 mg, 15%) and **3d** (a couple of diastereoisomeric lactols, ratio = 1/4, 74 mg, 45%). Following the procedure of method II, the reaction of **1n** (199 mg, 1.00 mmol) gave the products **2d** (18 mg, 16 %) and **3d** (a couple of diastereoisomeric lactols, ratio = 4/1 in CDCl₃, 74 mg, 46 %). Aldehyde **2d** and lactol **3d** was separated by SiO₂-column chromatography (hexane/AcOEt = 5/1). **2d**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.34 (s, 3H), 1.42 (d, *J* = 6.3 Hz, 1H), 1.83 (d, *J* = 6.3 Hz, 1H), 3.77 (d, *J* = 12.1 Hz, 1H), 3.90 (d, *J* = 12.1 Hz, 1H), 9.60 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.0, 27.8, 36.7, 55.9, 68.0, 195.9; IR (neat) 3410, 2936, 2874, 1717 cm⁻¹; HRMS (EI) calcd for C₆H₉ClO₂ (M⁺) 148.0291, found 148.0289. **3d**: colorless oil; ¹H-NMR (400 MHz, CDCl₃) δ 0.83 (d, *J* = 5.8 Hz, 1H x 1/5), 0.91 (d, *J* = 5.8 Hz, 1H x 4/5), 1.12 (d, *J* = 5.8 Hz, 1H), 1.28 (s, 3H x 1/5), 1.35 (s, 3H x 4/5), 1.73 (brs, 1H), 2.97 (dd, *J* = 4.0 Hz, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 8.4 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H x 1/5, OH), 3.94 (d, *J* = 8.4 Hz, 1H 4/5, OH), 5.32 (d, *J* = 4.0 Hz, 1H x 4/5), 5.38 (d, *J* = 7.1 Hz, 1H x 1/5); ¹³C NMR (100 MHz, CDCl₃) δ 13.3, 22.6, 27.1, 52.0, 71.5, 98.3; IR (neat) 3462, 2842, 1476 cm⁻¹; HRMS (EI) calcd for C₆H₉ClO₂ (M⁺) 148.0291, found 148.0298.

D-H exchange of lactol **3d** using D₂O gave deuterated lactol. The spectrum of OH disappeared and coupling pattern of the anomeric proton [5.32 (d, *J* = 4.0 Hz, 1H x 4/5), 5.38 (d, *J* = 7.1 Hz, 1H x 1/5)] changed into singlet.

(1*S*^{*},2*S*^{*},3*S*^{*})-1-Chloro-2-hydroxymethyl-3-phenylcyclopropanecarbaldehyde (2e)

(1*R*^{*},2*R*^{*},5*S*^{*},6*S*^{*})- and (1*R*^{*},2*S*^{*},5*S*^{*},6*S*^{*})-(1-Chloro-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-ol (3e)

Following the procedure of method I, the reaction of **1e** (232 mg, 1.00 mmol) gave the products **2e** (20 mg, 9%) and **3e** (a couple of diastereoisomeric lactols, ratio = 5/1 in CDCl₃, 81 mg, 37%).

Aldehyde **2e** and lactol **3e** separated by SiO₂-column chromatography (hexane/AcOEt = 4/1). **2e**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.97 (brs, 1H), 2.81 (dt, *J* = 5.3, 8.6 Hz, 1H), 3.08 (d, *J* = 8.6 Hz, 1H), 3.96 (dd, *J* = 8.6 Hz, *J* = 12.1 Hz, 1H), 4.20 (dd, *J* = 5.3 Hz, *J* = 12.1 Hz, 1H), 7.20-7.26 (m, 1H), (m, 1H), 7.28-7.34 (m, 4H), 8.95 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 32.0, 33.3, 55.6, 62.0, 128.4, 129.0, 129.1, 133.1, 193.8; IR (neat) 3402, 2873, 1717, 1497 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₁ClO₂ (M⁺) 210.0448, found 210.0483. **3e**: colorless crystals; mp 79-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.78-1.85 (m, 1H), 2.28 (d, *J* = 4.8 Hz, 1H x 5/6), 2.65 (d, *J* = 4.8 Hz, 1H x 1/6), 3.83 (d, *J* = 8.6 Hz, 1H x 5/6), 3.96 (d, *J* = 9.1 Hz, 1H x 1/6), 4.00 (dd, *J* = 3.0 Hz, *J* = 9.1 Hz, 1H x 1/6), 4.28 (dd, *J* = 2.5 Hz, *J* = 8.6 Hz, 1H x 5/6), 5.34 (s, 1H x 5/6), 5.54 (s, 1H x 1/6), 7.14-7.20 (m, 3H), 7.26-7.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 30.5, 37.5, 54.3, 67.5, 98.1, 127.1, 128.1, 128.8, 134.6; IR (CHCl₃) 3453, 2876, 1489 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₁ClO₂ (M⁺) 210.0448, found 210.0445.

(1*R*^{*},2*R*^{*},5*S*^{*},6*R*^{*})- and (1*R*^{*},2*S*^{*},5*S*^{*},6*R*^{*})-1-Chloro-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-ol (3f)

Following the procedure of method I, the reaction of **1f** (231 mg, 1.00 mmol) gave the lactol **3f** (94 mg, 42%). Following the procedure of method II, the reaction of **1o** (100 mg, 0.36 mmol) gave the lactol **3f** (34 mg, 41%). A couple of diastereoisomeric lactols apparently existed (ratio = 4/1 in CDCl₃). **3f**: colorless

crystals; mp 88-91 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.18 (s, 3H x 1/5), 1.25 (s, 3H x 4/5), 2.36 (s, 1H x 4/5), 2.63 (s, 1H x 1/5), 3.85 (d, *J* = 8.3 Hz, 1H x 1/5), 3.96 (d, *J* = 8.3 Hz, 1H x 4/5), 4.07 (d, *J* = 8.3 Hz, 1H), 5.49 (s, 1H x 4/5), 5.53 (s, 1H x 1/5), 7.28-7.35 (m, 5H); ¹³C NMR (400 MHz, CDCl₃) δ 10.6, 29.5, 31.0, 56.2, 72.9, 99.0, 126.8, 128.1, 130.7, 133.8; IR (CHCl₃) 3387, 1501 cm⁻¹; HRMS (EI) calcd for C₁₂H₁₃ClO₂ (M⁺) 224.0604, found 224.0595.

endo-7-Chlorobicyclo[4.1.0]heptane-7-carbaldehyde (2g) (trans-adduct)

Following the procedure of method I, the reaction of **1g** (165 mg, 1.00 mmol) gave the products **2g** (87 mg, 55 %). Following the procedure of method II, The reaction of **1l** (210 mg, 1.00 mmol) gave the product **2g** (116 mg, 73 %). Based on our previous report¹⁶, the relative configuration was determined by a NOESY

measurement of **2g-2**, which was derived from **2g**. The stereochemical assignment is also possible by a comparison of chemical shift (CHO) of **2g** with that of **14l**. Due to a deshielding effect of alkyl substituent, chemical shift of aldehyde-proton of *cis*-adduct appears at lower field. The chemical

shift (CHO 9.72 ppm) of aldehyde **14i** was assigned to that of *cis*-adduct, hence, that (CHO 9.43 ppm) of **2g** was assigned to that of *trans*-adduct.

2g: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.24-1.35 (m, 2H), 1.39-1.47 (m, 2H), 1.62-1.69 (m, 2H), 1.90-1.94 (m, 2H), 1.97-2.06 (m, 2H), 9.43 (s, 1H, CHO); ^{13}C NMR (100 MHz, CDCl_3) δ 18.7, 20.8, 25.9, 58.7, 198.5; IR (neat) 2939, 2858, 1709, 1447 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{11}\text{ClO}$ (M^+) 158.0498, found 158.0498.

deshielding effect

2g-2: ^1H NMR (400 MHz, CDCl_3) δ 1.09-1.15 (m, 2H), 1.19-1.28 (m, 2H), 1.32-1.41 (m, 2H), 1.57-1.65 (m, 2H), 1.90-1.99 (m, 2H), 3.61 (d, $J = 6.1$ Hz, 2H).

16) Tanabe, Y.; Wakimura, K.; Nishii Y. *Tetrahedron Lett.* **1996**, 37, 1837

endo-9-Chlorobicyclo[6.1.0]nonane-9-carbaldehyde (2h) (*trans*-adduct)

Following the procedure of method I, the reaction of **1h** (193 mg, 1.00 mmol) gave the products **2h** (88 mg, 47 %). Following the procedure of method II, the reaction of **1m** (238 mg, 0.36 mmol) gave the product **2h** (125 mg, 67 %). Based on the analogy of spectra data of **2g**, the relative configuration of **2h** was

determined as *trans*-adduct. **2h**: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.39-1.52, (m, 6H), 1.59-1.74 (m, 6H), 1.82-1.93 (m, 2H), 9.43 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.4, 26.3, 28.1, 31.9, 57.4, 198.5; IR (neat) 2923, 2854, 1713 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{15}\text{ClO}$ (M^+) 186.0811, found 186.0814.

endo-7-Bromobicyclo[4.1.0]heptane-7-carbaldehyde (2i) (*trans*-adduct)

Following the procedure of method II, the reaction of **1i** (253 mg, 1.00 mmol) gave the product **2i** (28 mg, 14 %). **2i**: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.18-1.27 (m, 2H), 1.31-1.40 (m, 2H), 1.54-1.61 (m, 2H), 1.80-1.86 (m, 2H), 1.89-1.98 (m, 2H), 9.36 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 21.0, 32.9, 44.2, 195.8;

IR (neat) 2939, 2858, 1709, 1447; HRMS (EI) calcd for $\text{C}_8\text{H}_{11}\text{BrO}$ (M^+) 201.9993, found 201.9997.

The relative configuration of aldehyde **2i** was determined as *trans*-adduct by the comparison of chemical shift (CHO) of **14i** (another stereoisomer) with that of **2i**. Based on a deshielding effect of the alkyl substituent, the chemical shift (CHO: 9.55 ppm) of aldehyde **14i** was assigned to that of *cis*-adduct, hence, that (CHO: 9.36 ppm) of **2i** was assigned to that of *trans*-adduct.

(1*S, 2*S**)-1-(1-Chloro-2-phenylcyclopropyl)-3-buten-1-one (4a)**

1,1-Dichloro-2-phenylcyclopropane (**1a**) (187 mg, 1.00 mmol), AIBN (33 mg, 0.20 mmol), $\text{Bu}_3\text{Sn}(\text{CH}_2\text{CH}=\text{CH}_2)$ (662 mg, 2.00 mmol), and benzene (30 mL)

were placed in a 100-mL stainless steel autoclave with a insert glass tube. The reaction mixture was stirred under CO pressure (40 atm) at 80 °C for 12 h. AIBN (33 mg, 0.20 mmol) was added to the reaction mixture after temporary release of CO pressure. Then, the reaction mixture was stirred under CO pressure (40 atm) at 80 °C for 12 h. After evacuation of excess CO at room temperature, benzene was removed under reduced pressure. The residue was stirred for 1 h with Et₂O (10 ml) and aqueous sat. KF solution (10 ml). The residue was stirred for 1 h with Et₂O (10 ml) and aqueous sat. KF solution (10 ml). After Celite filtration, the separated organic phase was washed with water, brine, dried (Na₂SO₄), and concentrated. The obtained crude product was purified by SiO₂-column chromatography (hexane/EtOAc = 3/1) to give the desired product **4a** (113 mg, 51%). (b) (**Method IV**). Following the procedure of method III, the reaction of 1-Bromo-1-chloro-2-phenylcyclopropane (**1j**) (210 mg, 1.00 mmol) with 0.2 equiv of AIBN (33 mg, 0.20 mmol, added once) in the place of 0.4 equiv of that (0.2 equiv added twice in method III) gave the desired product product **4a** (126 mg, 58%). **4a**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.73 (dd, *J* = 7.0 Hz, *J* = 10.1 Hz, 1H), 2.21 (dd, *J* = 7.0 Hz, *J* = 10.1 Hz 1H), 3.01 (dd, *J* = 7.0 Hz, *J* = 10.1 Hz, 1H) 3.68 (m, 2H), 5.16-5.26 (m, 2H), 5.94-6.04 (m, 1H), 7.20-7.24 (m, 2H), 7.29-7.37 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 25.0, 36.3, 44.8, 52.5, 119.0, 127.6, 128.1, 129.3, 130.2, 134.6, 204.5; IR (neat) 2843, 1716, 1640, 1497 cm⁻¹; HRMS (EI) calcd for C₁₃H₁₃ClO (M⁺) 220.0655, found 220.0656.

In order to determine the relative configuration, aldehyde **2a** (*trans*-adduct) which was stereoselectively prepared by known method¹⁴ converted into ketone **4a** in two steps [(1) (CH₂=CHCH₂)MgBr, (2) Jones' oxidation]. Thus, the relative configuration of **4a** was assigned as *trans*-adduct.

(1*S**,2*R**)-1-(1-Chloro-2-pentylcyclopropyl)-3-buten-1-one (**4b**)

Following the procedure of method III, the reaction of **1b** (181 mg, 1.00 mmol) gave the product **4b** (108 mg, 47%). Following the procedure of method IV, the reaction of **1k** (232 mg, 1.00 mmol) gave the product **4b** (122 mg, 53%). Based on the analogy of spectra data of **2b**, the relative configuration of **4b** was determined as *trans*-adduct. **4b**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.89

(m, 3H), 0.95-0.98 (m, 1H), 1.23-1.36 (m, 6H), 1.39-1.49 (m, 2H), 1.53-1.69 (m, 3H), 1.82-1.85 (m, 1H), 3.62-3.65 (m, 2H), 5.13-5.21 (m, 2H), 5.90-6.00 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.6, 28.8, 29.0, 29.6, 31.7, 31.9, 44.7, 52.4, 118.7, 205.4; IR (neat) 2927, 1701, 1620 cm⁻¹; HRMS (EI) calcd for C₁₃H₂₁ClO (M⁺) 228.1281, found 228.1286.

(1*R,2*R**,5*S**)- and (1*R**,2*S**,5*S**)-2-Allyl-1-chloro-5-methyl-3-oxabicyclo[3.1.0]hexan-2-ol (5d)**

Following the procedure of method III, the reaction of **1d** (155 mg, 1.00 mmol) gave the products **5d** (72 mg, 38%). Following the procedure of method IV, the reaction of **1n** (199 mg, 1.00 mmol) gave the lactol **5d** (129 mg, 68%). A couple of diastereoisomeric lactols apparently existed (ratio = 2/1 in CDCl₃). Based on the analogy of spectra data of lactol **3d**, the relative configuration of **4b** was

tentatively determined as *cis*-adduct (lactol). **5d**: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (d, *J* = 5.8 Hz, 1H x 1/3), 0.91 (d, *J* = 4.8 Hz, 1H x 2/3), 1.01 (d, *J* = 4.8 Hz, 1H x 2/3), 1.13 (d, *J* = 5.8 Hz, 1H x 1/3), 1.34 (s, 3H), 1.55 (brs, 1H x 2/3), 1.60 (brs, 1H x 1/3), 2.15-2.21 (m, 1H x 2/3), 2.49-2.55 (m, 1H x 1/3), 2.58-2.64 (m, 1H x 1/3), 2.66-2.72 (m, 1H x 1/3), 3.70 (d, *J* = 8.4 Hz, 1H x 1/3), 3.88 (d, *J* = 8.4 Hz, 1H x 1/3), 4.00 (d, *J* = 9.1 Hz, 1H x 2/3), 4.19 (d, *J* = 9.1 Hz, 1H x 2/3), 5.04-5.07 (m, 1H x 2/3), 5.09-5.10 (m, 1H x 2/3), 5.23-5.24 (m, 1H x 1/3), 5.26-5.29 (m, 1H x 1/3), 5.83-6.00 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.5, 14.6, 22.7, 23.0, 27.5, 28.2, 30.4, 40.0, 54.4, 54.6, 71.2, 72.9, 103.9, 116.8, 120.1, 121.3, 131.7, 134.3; IR (neat) 3468, 1763, 1634 cm⁻¹; HRMS (EI) calcd for C₉H₁₃ClO₂ (M⁺) 188.0604, found 188.0599.

endo-1-(7-Chlorobicyclo[4.1.0]hept-7-yl)-3-buten-1-one (4g) (*trans*-adduct)

Following the procedure of method III, the reaction of **1g** (165 mg, 1.00 mmol) gave the product **4g** (73 mg, 55%). Following the procedure of method IV, the reaction of **1l** (210 mg, 1.00 mmol) gave the product **4g** (126 mg, 64%).

4g: colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.21-1.30 (m, 2H), 1.35-1.44 (m, 2H), 1.58-1.64 (m, 2H), 1.90-2.00 (m, 4H), 3.62-3.64 (m, 2H), 5.10-5.20 (m, 2H), 5.88-5.98 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.8, 20.8, 27.4, 44.9, 58.5, 118.5, 130.8, 205.6; IR (neat) 2931, 1693, 1639 cm⁻¹; HRMS (EI) calcd for C₁₁H₁₅ClO (M⁺) 198.0811, found 198.0818.

In order to determine the relative configuration, aldehyde **2g** (*trans*-adduct) which was stereoselectively prepared by the formylation converted into ketone **4a** in two steps [(1) (CH₂=CHCH₂)MgBr, (2) Jones' oxidation]. Thus, the relative configuration of **4a** was assigned as *trans*-adduct.

endo-1-(9-Chlorobicyclo[6.1.0]non-9-yl)-3-buten-1-one (4h) (*trans*-adduct)

Following the procedure of method III, the reaction of **1h** (193 mg, 1.00 mmol) gave the product **4g** (109 mg, 48%). Following the procedure of method IV, the reaction of **1m** (238 mg, 1.00 mmol) gave the product **4h** (123 mg, 54%). Based on the analogy of spectra data of **4g**, the relative

configuration of **4h** was determined as *trans*-adduct. **4h**: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.32-1.51, (m, 6H), 1.58-1.72 (m, 6H), 1.80-1.85 (m, 2H), 3.62 (dt, $J = 1.5, 6.8$ Hz, 2H), 5.10-5.20 (m, 2H), 5.89-6.00 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.7, 26.4, 28.2, 33.5, 45.0, 56.9, 118.5, 130.7, 205.7; IR (neat) 2923, 1697, 1643 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{ClO}$ (M^+) 226.1124, found 226.1128.

endo-1-(7-Bromobicyclo[4.1.0]hept-7-yl)-3-buten-1-one (4i) (*trans*-adduct)

Following the procedure of method IV, the reaction of **1i** (253 mg, 1.00 mmol) gave the product **4i** (42 mg, 17%). Based on the analogy of spectra data of **4g**, the relative configuration of **4i** was determined as *trans*-adduct. **4i**: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.32-1.50 (m, 4H), 1.58-1.72 (m, 4H), 1.80-1.85 (m, 2H), 3.61-3.62 (m, 1H), 3.63-3.64 (m, 1H), 5.11-5.20 (m, 2H), 5.90-6.00 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 20.8, 27.4, 44.9, 52.8, 118.5, 130.8, 203; IR (neat) 2931, 1693, 1639 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{15}\text{BrO}$ 242.0306, found 242.0312.

(1*R,2*R**,5*S**,6*R**)- and (1*R**,2*S**,5*S**,6*R**)-2-Allyl-1-chloro-5-methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-ol (5o)**

Following the procedure of method IV, the reaction of **1o** (100 mg, 0.36 mmol) gave the product **5o** (34 mg, 35%). A couple of diastereoisomeric lactols apparently existed (ratio = 2/1 in CDCl_3). Based on the analogy of spectra data of lactol **3f**, the relative configuration of **5o** was tentatively determined as *cis*-adduct (lactol). **5o**: colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.33 (s, 3H x 2/3), 1.54 (s, 3H x 1/3), 2.13-2.20 (m, 1H x 2/3), 2.35 (s, 1H), 2.49-2.53 (m, 1H x 1/3), 2.57-2.62 (m, 1H x 1/3), 2.65-2.71 (m, 1H x 2/3), 2.81 (s, 1H x 1/3), 3.02 (s, 1H x 2/3), 3.69 (d, $J = 8.4$ Hz, 1H x 1/3), 3.87 (d, $J = 8.4$ Hz, 1H x 1/3), 3.99 (d, $J = 8.8$ Hz, 1H x 2/3), 4.18 (d, $J = 8.8$ Hz, 1H x 1/3), 5.03-5.10 (m, 2H x 2/3), 5.22-5.28 (m, 2H x 1/3), 5.82-5.99 (m, 1H) 7.23-7.39 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.5, 14.7, 23.4, 26.5, 30.5, 35.4, 36.0, 40.0, 53.8, 71.4, 72.9, 116.9, 120.4, 127.6, 127.6, 128.3, 128.3, 128.8, 128.9, 131.7, 134.4, 134.6; IR (neat) 3419, 1643, 1382, 910 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{ClO}_2$ (M^+) 264.0917, found 264.0913.

exo-7-Bromobicyclo[4.1.0]heptane-7-carbaldehyde (14i) (*cis*-adduct)

(Method A) BuLi (1.52 M in hexane, 3.62 mL, 5.50 mmol) was added to a stirred solution of 7,7-dibromobicyclo[4.1.0]heptane (1.27 g, 5.00 mmol) in THF (10 mL) at -100 $^{\circ}\text{C}$ under an Ar atmosphere, followed by being stirred at the same temperature for 30 min. DMF (2.50 mL, 32.3 mmol) was added to the mixture at the same temperature, which was stirred for 1 h. Water was added to the mixture, which was extracted three times with Et_2O . The combined organic phase was washed with water,

brine, dried (Na₂SO₄), and concentrated. The obtained crude oil was purified by SiO₂-column chromatography (hexane/Et₂O = 50/1) to give the desired product **14i** (705 mg, 65%). The relative configuration of aldehyde **14i** was determined as *cis*-adduct by the comparison of chemical shift (CHO) of **2i** (another stereoisomer) with that of **14i**. Based on the deshielding effect of alkyl group, the chemical shift (CHO: 9.55 ppm) of aldehyde **14i** was assigned to that of *cis*-adduct. **14i**: pale yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 1.33-1.56 (m, 4H), 1.77-1.92 (m, 2H), 1.95-2.11 (m, 2H), 2.17-2.30 (m, 2H), 9.55 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 18.7, 20.9, 32.6, 44.1, 195.4; IR (KBr) 2936, 1707, 1447, 1283, 1263, 1181, 1125, 893, 777 cm⁻¹; HRMS (EI) calcd for C₈H₁₁BrO (M⁺) 201.9993, found 201.9991.

Methyl *exo*-7-bromobicyclo[4.1.0]heptane-7-carboxylate (**14ii**) (*cis*-adduct)

(**Method B**) In a similar manner using CO₂ (dry ice; c.a. 2.5 g) instead of DMF for the preparation of **14i**, the mixture was quenched with water, which was extracted twice with Et₂O. Separated aqueous layer was acidified using 6 M-HCl aqueous solution, which was re-extracted three times with Et₂O. The combined organic phase was washed with water and brine, dried (Na₂SO₄) and concentrated. The obtained crude carboxylic acid (solid) was used for the next step without purification. MeI (747 μL, 12.0 mmol) was added to a stirred solution of the carboxylic acid (1.10 g, 5.00 mmol) and K₂CO₃ (1.66 g, 12.0 mmol) in DMF (5.0 mL) at 20 - 25 °C under an Ar atmosphere, followed by being stirred at same temperature for 1 h. The mixture was quenched with water, which was extracted three times with Et₂O. The combined organic phase was washed with water, brine, dried (Na₂SO₄), and concentrated. The obtained crude oil was purified by SiO₂-column chromatography (hexane/AcOEt = 60/1) to give the desired product **14ii** (860 mg, 64%). In order to determine the relative configuration, ester **14ii** derived from aldehyde **14i** (*cis*-adduct) [2 steps: (1) Jones' oxidation (2) methylation]. Thus, the relative configuration of **14ii** was assigned as *cis*-adduct. **14ii**: pale yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 0.97-1.11 (m, 2H), 1.14-1.34 (m, 2H), 1.65-1.78 (m, 2H), 1.82-1.98 (m, 4H), 3.79 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 19.3, 20.4, 25.1, 31.8, 52.6, 167.9; IR (neat) 3007, 2948, 2870, 1734, 1437, 1319, 1273, 1204, 1101 cm⁻¹; HRMS (EI) calcd for C₉H₁₃BrO₂ (M⁺) 232.0099, found 232.0108.

exo-7-Chlorobicyclo[4.1.0]heptane-7-carbaldehyde (**14l**) (*cis*-adduct)

Following the procedure of method A, the reaction of 7-bromo-7-chlorobicyclo[4.1.0]heptane (2.10 g, 10.0 mmol) with ⁿBuLi (1.52 M in hexane, 7.23 mL, 11.0 mmol) and DMF (5.00 mL, 64.6 mmol) gave the desired product **14l** (675 mg, 43%). Relative structure of **14l** was determined based on the comparison between NMR spectrum of **2g** and **14l**. The relative configuration of aldehyde **14l** was determined as *cis*-adduct by the comparison of chemical shift (CHO) of **14l** with that of **2g** (another

stereoisomer). Based on the deshielding effect of alkyl group, the chemical shift (CHO 9.72 ppm) of aldehyde **14l** was assigned to that of *cis*-adduct. **14l**: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.34-1.57 (m, 4H), 1.75-1.88 (m, 2H), 1.94-2.09 (m, 2H), 2.11-2.19 (m, 2H), 9.72 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.3, 20.8, 33.0, 53.2, 196.1; IR (neat) 2940, 2861, 1713, 1447, 1287, 1267, 1186, 1128, 982, 631 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{11}\text{ClO}$ (M^+) 158.0498, found 158.0503.

Methyl *exo*-7-chlorobicyclo[4.1.0]heptane-7-carboxylate (14II**) (*cis*-adduct)**

Following the procedure of method B, the reaction of 7-bromo-7-chlorobicyclo[4.1.0]heptane (2.10 g, 10.0 mmol) with $n\text{BuLi}$ (1.52 M in hexane, 7.23 mL, 11.0 mmol) and CO_2 (dry ice; c.a. 5.0 g) gave the crude solid (654 mg, 3.75 mmol). The reaction of crude solid with K_2CO_3 (1.24 g, 9.00 mmol) and MeI (570 μL , 9.00 mmol) gave the product **14II** (334 mg, 47%). In order to determine the relative configuration, ester **14II** derived from aldehyde **14l** (*cis*-adduct) [2 steps: (1) Jones' oxidation (2) methylation]. Thus, the relative configuration of **14II** was assigned as *cis*-adduct. **14II**: pale yellow oil; ^1H NMR (300MHz, CDCl_3) δ 1.07-1.36 (m, 4H), δ 1.68-1.74 (m, 2H), 1.75-1.99 (m, 4H), 3.80 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 18.9, 20.4, 26.3, 44.2, 52.6, 168.0; IR (neat) 2940, 2861, 1738, 1437, 1321, 1206, 1165, 1103 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{13}\text{ClO}_2$ (M^+) 188.0604, found 188.0607.

(1*R,2*S**)-1-Bromo-2-phenylcyclopropane-1-carbaldehyde (**14p**) (*cis*-adduct)**

Following the procedure of method A, the reaction of 1,1-dibromo-2-phenylcyclopropane (2.10 g, 10.0 mmol) with DMF (5.00 mL, 64.6 mmol) and $n\text{BuLi}$ (1.52 M in hexane, 7.23 mL, 11.0 mmol) gave the product **14p** (675 mg, 64%). Based on the analogy of spectra data of **3a**, the relative configuration of **14p** was determined as *cis*-adduct. **14p**: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.93 (*exo*, dd, $J = 6.2$ Hz, $J = 8.6$ Hz, 0.05H), 2.05 (*endo*, dd, $J = 6.9$ Hz, $J = 9.6$ Hz, 0.95H), 2.27 (*exo*, dd, $J = 6.2$ Hz, $J = 10.3$ Hz, 0.05H), 2.45 (*endo*, dd, $J = 6.9$ Hz, $J = 8.3$ Hz, 0.95H), 2.91 (*exo*, t, $J = 9.3$ Hz, 0.05H), 3.33 (*endo*, t, $J = 9.3$ Hz, 0.95H), 7.21-7.39 (m, 5H), 8.70 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.0, 38.3, 40.3, 127.8, 128.6, 128.6, 133.2, 193.5; IR (neat) 3030, 2838, 1715, 1497, 1451, 1263, 1200, 926, 889, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_9\text{BrO}$ (M^+) 223.9873, found 223.9875.

(1*R,2*S**)-Methyl-1-bromo-2-phenylcyclopropane-1-carboxylate (**14pp**) (*cis*-adduct)**

Following the procedure of method B, the reaction of 1,1-dibromo-2-phenylcyclopropane (1.10 g, 4.00 mmol) with $n\text{BuLi}$ (1.52 M in hexane, 2.89 mL, 4.40 mmol) and CO_2 (dry ice; c.a. 2.0 g) gave the crude solid (866 mg, 3.60 mmol). The reaction of crude solid with K_2CO_3 (1.20 g, 8.64 mmol) and MeI

(537 μ L, 8.64 mmol) gave the desired product **14pp** (582 mg, 57%). **14pp**: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 1.79 (dd, $J = 6.5$ Hz, $J = 10.0$ Hz, 1H), 2.37 (dd, $J = 6.5$ Hz, $J = 8.6$ Hz, 1H), 3.07 (t, $J = 9.3$ Hz, 1H), 3.42 (s, 3H), 7.19-7.33 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.1, 31.3, 36.7, 52.9, 127.3, 128.1, 128.6, 134.3, 167.3; IR (neat) 3030, 2953, 1738, 1499, 1437, 1314, 1217, 1121, 1069, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}_2$ (M^+) 253.9942, found 253.9944.

(1*R*,2*R)-Methyl -1-bromo-2-butylcyclopropane-1-carboxylate (14qq) (cis-adduct)**

Following the procedure of method B, the reaction of 1,1-dibromo-2-butylpropane (512 mg, 2.00 mmol) with $n\text{BuLi}$ (1.52 M in hexane, 1.45 ml, 2.20 mmol) and CO_2 (dry ice; c.a. 1.0 g) gave the crude solid (224 mg, 1.10 mmol).

The reaction of crude solid with K_2CO_3 (365 mg, 2.64 mmol) and MeI (164 μ L, 2.64 mmol) gave the desired product **14qq** (160 mg, 36%). **14qq**: pale yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.22-1.38 (m, 4H), 1.43-1.52 (m, 3H), 1.62 (dd, $J = 6.2$ Hz, $J = 8.3$ Hz, 1H), 1.71-1.84 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.2, 24.7, 27.3, 29.7, 31.0, 34.1, 53.2, 169.3; IR (neat) 2957, 2930, 2863, 1725, 1437, 1316, 1209, 1127 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{15}\text{BrO}_2$ (M^+) 234.0255, found 234.0261.