**Palladium-catalyzed intramolecular decarboxylative allylic arylation of α-aryl-γ-methylidene-δ-valerolactones**

Ryo Shintani,* Takaoki Tsuji, Soyoung Park and Tamio Hayashi*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

**Supporting Information**

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

MeOH was distilled over Mg turnings under nitrogen. CH₂Cl₂ and CHCl₃ were distilled over CaH₂ under vacuum. THF, Et₂O, and toluene were purified by passing through neutral alumina columns under nitrogen. Diisopropylamine was distilled over NaOH under vacuum.

Dimethyl carbonate (Wako Chemicals), dimethyl malonate (Wako Chemicals), methyl propiolate (Wako Chemicals), 4-(dimethylamino)pyridine (Wako Chemicals), triethylamine (Wako Chemicals), N,N'-dicyclohexylcarbodiimide (Wako Chemicals), tert-butyl alcohol (Wako Chemicals), tert-butyl bromide (TCI), methyl chloroformate (TCI), 3,5-dimethoxyphenylacetic acid (Fluka; 55% purity), p-toluenesulfonic acid (Nacalai Tesque; monohydrate), thionyl chloride (Wako Chemicals), TBAF (Aldrich; 1.0 M solution in THF), NaH (Kanto Chemicals; 60 wt% in mineral oil), n-BuLi (Kanto Chemical; 1.59 M solution in hexane), KOH (Kishida Chemical), KOᵗ-Bu (Wako Chemicals), LiAlH₄ (Wako Chemicals), Ag₂O (Wako Chemicals), and alumina (Nacalai Tesque; activated 200) were used as received.

1a, 1b, 1d, 2e, 1h, 1l, 1m, N-benzyl-3-indolylacetic acid, 2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl methanesulfonate, 6-methoxy-2-naphthlacetonitrile, 6-bromo-2-naphthlacetonitrile, 5-methylene-[1,3,2]dioxathian-2-one, and Pd(PPh₃)₄ were synthesized following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

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II. Synthesis of Substrates

α-tert-Butoxycarbonyl-α-(N-benzyl-3-indolyl)-γ-methylidene-δ-valerolactone (1c)

Thionyl chloride (3.06 mL, 42.0 mmol) was added to a solution of N-benzyl-3-indolylacetic acid (7.50 g, 28.3 mmol) in MeOH (80 mL) at 0 °C, and the mixture was stirred for 14 h at room temperature. After removal of the volatiles under vacuum, the residue was dissolved in dimethyl carbonate (30 mL). This solution was then added to a suspension of NaH (2.25 g, 56.3 mmol; 60 wt% in mineral oil) in dimethyl carbonate (5 mL) at 0 °C. The resulting mixture was stirred for 24 h at room temperature and the reaction was quenched with water. After extraction with Et2O, the organic layer was washed successively with saturated NaClaq and with saturated NH4Claq, dried over MgSO4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH2Cl2/Et2O/hexane = 1/1/6 to afford dimethyl (N-benzyl-3-indolyl)malonate (CAS 458529-83-4) as a red oil (5.08 g, 15.1 mmol; 53% yield).

1H NMR (CDCl3): δ 7.65 (d, 3JHH = 7.3 Hz, 1H), 7.32-7.25 (m, 5H), 7.21-7.14 (m, 4H), 5.31 (s, 2H), 4.98 (s, 1H), 3.76 (s, 6H).

A solution of 1 M KOH in MeOH (13.5 mL, 13.5 mmol) was added to a solution of dimethyl (N-benzyl-3-indolyl)malonate (5.08 g, 15.1 mmol) in MeOH (14 mL), and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum and the residue was dissolved in 5% NaHCO3aq. This was washed with EtOAc and the organic layer was extracted with 5% NaHCO3aq (2 times). The combined aqueous layer was acidified with 2 M HClaq and extracted with EtOAc (4 times). The organic layer was dried over MgSO4, filtered, and concentrated under vacuum to afford monomethyl (N-benzyl-3-indolyl)malonate as a red oil (3.44 g, 10.6 mmol; 70% yield).

1H NMR (CDCl3): δ 7.66 (d, 3JHH = 7.5 Hz, 1H), 7.33 (s, 1H), 7.32-7.26 (m, 4H), 7.21-7.12 (m, 4H), 5.30 (s, 2H), 4.98 (s, 1H), 3.78 (s, 3H).

tert-Butyl alcohol (1.07 mL, 11.2 mmol) was added to a solution of monomethyl (N-benzyl-3-indolyl)malonate (3.44 g, 10.6 mmol) and 4-(dimethylamino)pyridine (31.8 mg, 0.260 mmol) in CH2Cl2 (25 mL) at 0 °C. N,N'-dicyclohexylcarbodiimide (2.26 g, 11.0 mmol) was then added to it with additional CH2Cl2 (10 mL). The mixture was stirred for 9 h at 0 °C and the precipitate that formed was filtered off through celite with Et2O. After removing the solvent under vacuum, the residue was chromatographed on silica gel with CH2Cl2/Et2O/hexane = 1/1/6 to afford tert-butyl methyl (N-benzyl-3-indolyl)malonate as a red oil (3.11 g, 8.20 mmol; 77% yield).

1H NMR (CDCl3): δ 7.66 (d, 3JHH = 7.5 Hz, 1H), 7.35 (s, 1H), 7.31-7.24 (m, 4H), 7.19-7.11 (m, 4H), 5.31 (s, 2H), 4.87 (s, 1H), 3.76 (s, 3H), 1.45 (s, 9H).

A solution of tert-butyl methyl (N-benzyl-3-indolyl)malonate (3.11 g, 8.20 mmol) in THF (10 mL) was added to a suspension of NaH (330 mg, 8.25 mmol; 60 wt% in mineral oil) in THF (5 mL) at 0 °C. The mixture was stirred for 20 min at 0 °C and a solution of 2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl methanesulfonate (2.67 g, 9.52 mmol) in THF (10 mL) was added to it. DMF (2 mL) was then added to this mixture and it was stirred for 46 h at 50 °C. The reaction was quenched with water and extracted with Et2O. The organic layer
was washed with saturated NaCl, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/10 to afford tert-butyl methyl (2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl)(N-benzyl-3-indolyl)malonate as a colorless oil (3.87 g, 6.86 mmol; 84% yield).

1H NMR (CDCl₃): δ 7.74 (s, 1H), 7.63 (d, 3J_HH = 7.9 Hz, 1H), 7.28-7.22 (m, 3H), 7.20 (d, 3J_HH = 8.0 Hz, 1H), 7.11 (td, 3J_HH = 7.6 Hz and 4J_HH = 1.1 Hz, 1H), 7.08-7.03 (m, 3H), 5.30 (s, 2H), 5.05 (q, 3J_HH = 1.8 Hz, 1H), 4.69 (s, 1H), 3.71 (s, 3H), 3.70 (s, 2H), 3.21 (d, 3J_HH = 15.0 Hz, 1H), 3.17 (d, 3J_HH = 14.0 Hz, 1H), 1.39 (s, 9H), 0.81 (s, 9H), –0.11 (s, 6H).

TBAF (6.90 mL, 6.90 mmol; 1.0 M solution in THF) was added to a solution of tert-butyl methyl (2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl)(N-benzyl-3-indolyl)malonate (3.70 g, 6.56 mmol) in THF (17 mL) at –78 °C. The mixture was stirred for 11 h while gradually raising the temperature to 10 °C and the reaction was quenched with water. After extraction with Et₂O, the organic layer was washed with saturated NaCl, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/4 and the solid thus obtained was washed with hexane to afford 1c as a white solid (1.87 g, 4.48 mmol; 68% yield).

1H NMR (CDCl₃): δ 7.68 (d, 3J_HH = 7.9 Hz, 1H), 7.31-7.24 (m, 4H), 7.17 (td, 3J_HH = 7.6 Hz and 4J_HH = 1.1 Hz, 1H), 7.12 (td, 3J_HH = 7.5 Hz and 4J_HH = 1.1 Hz, 1H), 7.09-7.07 (m, 3H), 5.29 (s, 2H), 5.06 (t, 3J_HH = 1.6 Hz, 1H), 5.04 (t, 3J_HH = 1.6 Hz, 1H), 4.84 (d, 3J_HH = 14.3 Hz, 1H), 4.78 (d, 2J_HH = 14.4 Hz, 1H), 3.50 (d, 2J_HH = 16.0 Hz, 1H), 3.27 (d, 2J_HH = 16.0 Hz, 1H), 1.43 (s, 9H). 13C NMR (CDCl₃): δ 169.0, 168.4, 137.10, 137.06, 136.9, 128.7, 127.7, 126.5, 126.4, 122.2, 121.2, 119.7, 111.8, 111.0, 109.8, 83.3, 71.3, 55.4, 50.1, 36.5, 27.7. M.p. 110–111 °C (Et₂O). Anal. Calcd for C₂₆H₂₇NO₄: C, 74.80; H, 6.52. Found: C, 74.83; H, 6.54.

**α-tert-Butoxycarbonyl-α-(6-methoxy-2-naphthyl)-γ-methylidene-δ-valerolactone (1f)**

![Image of α-tert-Butoxycarbonyl-α-(6-methoxy-2-naphthyl)-γ-methylidene-δ-valerolactone (1f)](image)

6 M NaOHaq (7.80 mL, 46.8 mmol) was added to a solution of 6-methoxy-2-naphthylacetonitrile (2.34 g, 11.9 mmol) in MeOH (30 mL) and the mixture was refluxed for 40 h. After removal of the MeOH under vacuum, the residue was acidified with 4 M HCl and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and concentrated to afford 6-methoxy-2-naphthylacetic acid (CAS 2471-70-7) as a pale yellow solid (2.50 g, 11.6 mmol; 97% yield).

1H NMR (CDCl₃): δ 7.33-7.68 (m, 3H), 7.40-7.37 (m, 1H), 7.16-7.12 (m, 2H), 3.91 (s, 3H), 3.79 (s, 2H). 6-Methoxy-2-naphthylacetic acid was converted to 1e following the procedure for 1c. White solid. 12% yield.

1H NMR (CDCl₃): δ 7.75 (d, 3J_HH = 8.8 Hz, 1H), 7.71 (d, 3J_HH = 9.0 Hz, 1H), 7.68 (d, 3J_HH = 1.9 Hz, 1H), 7.45 (dd, 3J_HH = 8.6 Hz and 4J_HH = 2.0 Hz, 1H), 7.15 (dd, 3J_HH = 8.8 Hz and 4J_HH = 2.4 Hz, 1H), 7.12 (d, 3J_HH = 2.4 Hz, 1H), 5.13 (t, 3J_HH = 1.7 Hz, 1H), 5.02 (t, 3J_HH = 1.7 Hz, 1H), 4.79 (d, 3J_HH = 14.5 Hz, 1H), 4.64 (d, 3J_HH = 14.4 Hz, 1H), 3.92 (s, 3H), 3.53 (d, 3J_HH = 16.1 Hz, 1H), 3.34 (d, 3J_HH = 16.2 Hz, 1H), 1.46 (s, 9H). 13C NMR (CDCl₃): δ 169.5, 168.3, 158.2, 136.5, 134.0, 130.5, 129.7, 128.5, 127.1, 125.93, 125.86, 119.1, 111.9, 105.5,

α-tert-Butoxycarbonyl-α-(6-bromo-2-naphthyl)-γ-methylidene-δ-valerolactone (1g)

![Chemical Structure](image)

6 M NaOHq (8.90 mL, 53.4 mmol) was added to a solution of 6-bromo-2-naphthylacetonitrile (4.30 g, 17.5 mmol) in MeOH (50 mL) and the mixture was refluxed for 27 h. After removal of the MeOH under vacuum, the residue was acidified with 6 M HClaq and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and concentrated to afford 6-bromo-2-naphthylacetic acid (CAS 32721-06-5) as a white solid (3.65 g, 13.8 mmol; 79% yield).

1H NMR (CDCl₃): δ 7.99 (s, 1H), 7.77-7.66 (m, 3H), 7.54 (dd, 3J_HH = 8.6 Hz and 4J_HH = 1.8 Hz, 1H), 7.44 (d, 3J_HH = 8.4 Hz, 1H), 3.81 (s, 2H).

t-Butyl bromide (2.50 mL, 22.3 mmol) was added to a mixture of 6-bromo-2-naphthylacetic acid (2.46 g, 9.28 mmol) in CHCl₃ (100 mL) and this was warmed to reflux. Ag₂O (5.20 g, 22.4 mmol) was added portionwise (1.04 g per every 10 min x 5 times) and the resulting mixture was further refluxed for 1 h. After cooled to room temperature, the precipitate was filtered off through celite with Et₂O, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with CH₂Cl₂/EtOAc/hexane =1/1/1 to afford tert-butyl 6-bromo-2-naphthylacetate as a pale yellow solid (716 mg, 2.23 mmol; 24% yield).

1H NMR (CDCl₃): δ 7.98 (s, 1H), 7.72-7.66 (m, 3H), 7.53 (dd, 3J_HH = 8.7 Hz and 4J_HH = 1.8 Hz, 1H), 7.44 (d, 3J_HH = 8.6 Hz and 4J_HH = 1.7 Hz, 1H), 3.67 (s, 2H), 1.44 (s, 9H).

n-BuLi (1.86 mL, 2.96 mmol; 1.59 M solution in hexane) was added dropwise to a solution of disopropylamine (380 µL, 2.71 mmol) in THF (35 mL) at –78 °C, and the mixture was stirred for 10 min at –78 °C. A solution of tert-butyl 6-bromo-2-naphthylacetate (790 mg, 2.46 mmol) in THF (10 mL) was then added to it dropwise, and this mixture was stirred for 30 min at –78 °C. A solution of methyl chloroformate (227 µL, 2.95 mmol) in THF (3 mL) was then added to it dropwise, and the resulting mixture was stirred for 30 min at –78 °C. The reaction was quenched with saturated NH₄Claq and warmed to room temperature. After dilution with water, this was extracted with Et₂O, and the organic layer was washed with saturated NaClq, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH₂Cl₂/EtOAc/hexane = 1/1/10 to afford tert-butyl methyl (6-bromo-2-naphthyl)malonate as a pale yellow solid (631 mg, 1.66 mmol; 67% yield).

1H NMR (CDCl₃): δ 8.00 (d, 4J_HH = 1.8 Hz, 1H), 7.80 (s, 1H), 7.75 (d, 3J_HH = 8.6 Hz, 1H), 7.70 (d, 3J_HH = 8.8 Hz, 1H), 7.57-7.54 (m, 2H), 4.70 (s, 1H), 3.77 (s, 3H), 1.46 (s, 9H).

tert-Butyl methyl (6-bromo-2-naphthyl)malonate was converted to 1f following the procedure for 1c. White solid. 45% yield.

1H NMR (CDCl₃): δ 8.00 (d, 4J_HH = 1.8 Hz, 1H), 7.77 (d, 3J_HH = 8.8 Hz, 1H), 7.73 (s, 1H), 7.69 (d, 3J_HH = 8.5 Hz, 1H), 7.57 (dd, 3J_HH = 8.8 Hz and 4J_HH = 2.0 Hz, 1H), 7.52 (dd, 3J_HH = 8.7 Hz and 4J_HH = 2.1 Hz, 1H), 5.14 (t, J_HH = 1.8 Hz, 1H), 5.05 (t, J_HH = 1.7 Hz, 1H), 4.83 (d,
\(\text{H} = 14.8 \text{ Hz}, 1\text{H})\), 4.66 (d, \(\text{H} = 14.9 \text{ Hz}, 1\text{H})\), 3.54 (d, \(\text{H} = 16.0 \text{ Hz}, 1\text{H})\), 3.32 (d, \(\text{H} = 16.0 \text{ Hz}, 1\text{H})\), 1.46 (s, 9H). 13C NMR (CDCl3): \(\delta 169.1, 167.9, 136.1, 133.8, 133.6, 131.4, 129.8, 129.7, 129.6, 127.3, 126.6, 126.0, 120.6, 112.3, 83.7, 71.2, 60.0, 35.9, 27.7.\) M.p. 115–116 °C (Et2O). Anal. Calcd for C21H21BrO4: C, 60.44; H, 5.07. Found: C, 60.63; H, 4.99.

\(\alpha\text{-}\text{tert-Butoxycarbonyl-}\alpha\text{-}(3,5\text{-dimethoxyphenyl)-}\gamma\text{-methylidene-}\delta\text{-valerolactone (1i)}\)

This was synthesized from 3,5-dimethoxyphenylacetic acid, following the procedure for 1c. White solid. 19% yield.

1H NMR (CDCl3): \(\delta 6.48 (d, \text{J} = 2.1 \text{ Hz}, 2\text{H}), 6.42 (t, \text{J} = 2.1 \text{ Hz}, 1\text{H}), 5.10 (t, \text{J} = 1.7 \text{ Hz}, 1\text{H}), 5.02 (t, \text{J} = 1.7 \text{ Hz}, 1\text{H}), 4.75 (d, \text{J} = 14.7 \text{ Hz}, 1\text{H}), 4.63 (d, \text{J} = 14.6 \text{ Hz}, 1\text{H}), 3.78 (s, 6\text{H}), 3.40 (d, \text{J} = 16.2 \text{ Hz}, 1\text{H}), 3.19 (d, \text{J} = 16.3 \text{ Hz}, 1\text{H}), 1.46 (s, 9\text{H}).\) 13C NMR (CDCl3): \(\delta 169.1, 167.8, 137.4, 136.5, 111.8, 105.9, 99.9, 83.3, 71.1, 59.8, 55.3, 35.7, 27.7.\) M.p. 73–74 °C (Et2O). Anal. Calcd for C19H24O6: C, 65.50; H, 6.94. Found: C, 65.21; H, 6.81.

\(\alpha\text{-}\text{tert-Butoxycarbonyl-}\alpha\text{-}(3,4,5\text{-trimethoxyphenyl)-}\gamma\text{-methylidene-}\delta\text{-valerolactone (1j)}\)

This was synthesized from 3,4,5-trimethoxyphenylacetic acid, following the procedure for 1c. White solid. 12% yield.

1H NMR (CDCl3): \(\delta 6.56 (s, 2\text{H}), 5.12 (t, \text{J} = 1.8 \text{ Hz}, 1\text{H}), 5.05 (t, \text{J} = 1.6 \text{ Hz}, 1\text{H}), 4.77 (d, \text{J} = 14.7 \text{ Hz}, 1\text{H}), 4.65 (d, \text{J} = 14.4 \text{ Hz}, 1\text{H}), 3.85 (s, 3\text{H}), 3.84 (s, 6\text{H}), 3.43 (d, \text{J} = 16.3 \text{ Hz}, 1\text{H}), 3.18 (d, \text{J} = 16.3 \text{ Hz}, 1\text{H}), 1.48 (s, 9\text{H}).\) 13C NMR (CDCl3): \(\delta 169.2, 167.9, 153.1, 138.0, 136.6, 130.6, 111.8, 105.1, 83.4, 71.1, 60.8, 59.8, 56.2, 36.0, 27.7.\) M.p. 124–125 °C (Et2O). Anal. Calcd for C20H26O7: C, 63.48; H, 6.93. Found: C, 63.41; H, 6.92.

\(\alpha\text{-Methoxycarbonyl-}\alpha\text{-}(2\text{-methoxycarbonyl-1-ethenyl)-}\gamma\text{-methylidene-}\delta\text{-valerolactone (1k)}\)

A solution of dimethyl malonate (5.31 mL, 46.5 mmol) in THF (15 mL) was added to a suspension of NaH (1.92 g, 48.0 mmol; 60 wt% in mineral oil) in THF (30 mL) at 0 °C and the mixture was stirred for 15 min at room temperature. The solvent was removed under
vacuum and the residue was dissolved in DMF (40 mL). 5-Methylene-[1,3,2]dioxathian-2-one (2.50 g, 18.6 mmol) was then added to it with additional DMF (5 mL), and the mixture was stirred for 66 h at 60 °C. The reaction was diluted with EtOAc and quenched with 10% H2SO4aq. After extraction with EtOAc, the organic layer was washed successively with water and with saturated NaClaq, dried over MgSO4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5→1/3→1/1 and the solid thus obtained was washed with Et2O/hexane to afford α-methoxycarbonyl-γ-methylidene-δ-valerolactone as a white solid (1.53 g, 8.98 mmol; 48% yield).

1H NMR (CDCl3): δ 5.16 (s, 1H), 5.13 (s, 1H), 4.81 (s, 2H), 3.79 (s, 3H), 3.73 (dd, JHH = 8.8 and 7.2 Hz, 1H), 3.00 (dd, JHH = 16.0 Hz and JHH = 9.2 Hz, 1H), 2.89 (dd, JHH = 16.0 Hz and JHH = 7.0 Hz, 1H).

Triethylamine (164 μL, 1.18 mmol) and methyl propiolate (156 μL, 1.75 mmol) were successively added to a solution of α-methoxycarbonyl-γ-methylidene-δ-valerolactone (201 mg, 1.18 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 5 h at room temperature. After removal of the solvent under vacuum, the residue was chromatographed on silica gel with EtOAc/hexane = 1/2 to afford 1j as a colorless oil (205 mg, 0.806 mmol; 68% yield, E/Z = 76/24).

1H NMR (CDCl3): δ 7.21 (d, JHH = 16.2 Hz, 0.76H), 6.77 (d, JHH = 11.9 Hz, 0.24H), 6.06 (d, JHH = 11.7 Hz, 0.24H), 5.98 (d, JHH = 16.2 Hz, 0.76H), 5.17 (d, JHH = 12.7 Hz, 0.24H), 5.14-5.11 (m, 1.76H), 5.00 (s, 0.24H), 4.81 (d, JHH = 13.0 Hz, 0.24H), 4.80 (d, JHH = 15.1 Hz, 0.76H), 4.77 (d, JHH = 15.3 Hz, 0.76H), 3.80 (s, 2.28H), 3.75 (s, 3H), 3.72 (s, 0.72H), 3.31 (d, JHH = 15.5 Hz, 0.76H), 3.14 (d, JHH = 13.5 Hz, 0.24H), 2.81 (d, JHH = 14.0 Hz, 0.24H), 2.72 (d, JHH = 15.5 Hz, 0.76H). 13C NMR (CDCl3): δ 171.3, 168.1, 167.0, 166.4, 165.9, 165.5, 145.4, 142.2, 135.3, 134.2, 123.6, 121.6, 114.0, 113.8, 73.0, 71.7, 58.1, 56.4, 53.7, 53.1, 51.8, 51.7, 39.9, 35.7. Anal. Calcd for C12H14O6: C, 56.69; H, 5.55. Found: C, 56.63; H, 5.54.

III. Catalytic Reactions

Procedure for Equation 1.

A solution of Pd(PPh3)4 (11.6 mg, 10.0 μmol) and lactone 1 (0.200 mmol) in toluene (2.0 mL) was stirred for 24 h at 30 °C. The reaction mixture was directly passed through a pad of silica gel with Et2O and the solvent was removed under vacuum. The residue was chromatographed on silica gel to afford compound 2.

X = S (2a). Colorless oil. 92% yield.

1H NMR (CDCl3): δ 7.46 (d, JHH = 6.1 Hz, 1H), 6.39 (d, JHH = 5.9 Hz, 1H), 4.74 (quint, JHH = 1.7 Hz, 1H), 4.62 (t, JHH = 1.9 Hz, 1H), 4.12-4.06 (m, 1H), 3.43 (dd, JHH = 20.8 Hz and JHH = 3.4 and 1.0 Hz, 1H), 2.45 (dd, JHH = 13.3 Hz and JHH = 5.0 Hz, 1H), 2.24-2.17 (m, 1H), 1.41 (s, 9H). 13C NMR (CDCl3): δ 165.1, 156.7, 141.5, 139.3, 124.5, 119.8, 110.7, 79.8, 52.2, 36.6, 33.3, 28.2. HRMS (ESI-
TOF) calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{2}SNa (M+Na\textsuperscript{+}) 273.0920 found 273.0912.

\begin{center}
\includegraphics[width=0.5\textwidth]{chemical_structure}
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\textbf{X = O (2b).} Colorless oil. 93\% yield.

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): \( \delta 6.66 \) (s, 1H), 6.57 (s, 1H), 4.83 (t, \( J_{\text{HH}} = 1.7 \) Hz, 1H), 4.71 (s, 1H), 4.63-4.58 (m, 1H), 3.50 (d, \( J_{\text{HH}} = 20.5 \) Hz, 1H), 2.93 (d, \( J_{\text{HH}} = 20.2 \) Hz, 1H), 2.73 (dd, \( J_{\text{HH}} = 12.8 \) Hz and \( J_{\text{HH}} = 5.6 \) Hz, 1H), 2.09-2.04 (m, 1H), 1.45 (s, 9H). \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}): \( \delta 165.4, 158.4, 154.5, 139.3, 112.7, 112.2, 106.4, 84.0, 79.4, 36.3, 32.8, 28.3 \). HRMS (ESI-TOF) calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{3}Na (M+Na\textsuperscript{+}) 257.1148 found 257.1154.

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\textbf{Procedure for Equation 2.}

Alumina (1.0 g) was added to a solution of 2a (46.0 mg, 0.184 mmol) in toluene (2.0 mL), and the mixture was stirred for 3 h at room temperature. The alumina was then filtered off with Et\textsubscript{2}O and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with CH\textsubscript{2}Cl\textsubscript{2}/Et\textsubscript{2}O/hexane = 1/1/15 to afford 3a as a colorless oil (41.6 mg, 0.166 mmol; 90\% yield).

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): \( \delta 6.96 \) (d, \( J_{\text{HH}} = 5.3 \) Hz, 1H), 6.80 (d, \( J_{\text{HH}} = 5.1 \) Hz, 1H), 4.84 (d, \( J_{\text{HH}} = 1.3 \) Hz, 1H), 4.76 (d, \( J_{\text{HH}} = 1.3 \) Hz, 1H), 3.58 (dd, \( J_{\text{HH}} = 7.2 \) and \( 6.0 \) Hz, 1H), 3.26 (d, \( J_{\text{HH}} = 18.1 \) Hz, 1H), 3.18 (d, \( J_{\text{HH}} = 18.1 \) Hz, 1H), 2.78 (dd, \( J_{\text{HH}} = 13.0 \) Hz and \( J_{\text{HH}} = 7.2 \) Hz, 1H), 2.38 (dd, \( J_{\text{HH}} = 13.1 \) Hz and \( J_{\text{HH}} = 6.0 \) Hz, 1H), 1.34 (s, 9H). \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}): \( \delta 171.7, 142.1, 136.3, 132.8, 127.3, 122.5, 111.1, 80.3, 45.0, 34.9, 32.9, 28.0 \). Anal. Calcd for C\textsubscript{14}H\textsubscript{18}O\textsubscript{2}S: C, 67.16; H, 7.25. Found: C, 67.36; H, 7.29.

\begin{center}
\includegraphics[width=0.5\textwidth]{chemical_structure}
\end{center}

\textbf{General Procedure for Table 1 and Equation 3.}

A solution of Pd(PPh\textsubscript{3})\textsubscript{4} (11.6 mg, 10.0 \textmu mol) and lactone 1 (0.200 mmol) in toluene (2.0 mL) was stirred for 24 h at 30 °C. The reaction mixture was passed through a pad of silica gel with Et\textsubscript{2}O and the solvent was removed under vacuum. The residue was dissolved in toluene (2.0 mL), and alumina (500 mg) was added to it. The mixture was stirred for 3 h at room temperature and the alumina was filtered off with Et\textsubscript{2}O. After removal of the solvent under vacuum, the residue was purified by silica gel preparative TLC to afford compound 3.

\begin{center}
\includegraphics[width=0.5\textwidth]{chemical_structure}
\end{center}

\textbf{Entry 1.} No treatment with alumina after the cyclization reaction. Yellow viscous oil. 96\%
yield.

$^1$H NMR (C$_6$D$_6$): $\delta$ 8.94 (d, $^3$J$_{HH} = 7.9$ Hz, 1H), 7.14-7.05 (m, 5H), 7.02 (t, $^3$J$_{HH} = 7.6$ Hz, 1H), 6.79 (td, $^3$J$_{HH} = 7.6$ Hz and $^4$J$_{HH} = 0.8$ Hz, 1H), 6.36 (d, $^3$J$_{HH} = 7.9$ Hz, 1H), 4.85 (t, $^3$J$_{HH} = 1.6$ Hz, 1H), 4.71 (s, 1H), 3.95 (s, 2H), 3.86-3.81 (m, 1H), 3.60 (d, $^2$J$_{HH} = 20.0$ Hz, 1H), 3.03 (dd, $^2$J$_{HH} = 13.0$ Hz and $^3$J$_{HH} = 11.6$ Hz, 1H), 2.02 (dd, $^2$J$_{HH} = 13.0$ Hz and $^3$J$_{HH} = 6.9$ Hz, 1H), 1.47 (s, 9H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 166.5, 156.5, 147.2, 140.9, 139.0, 131.7, 128.8, 128.6, 127.3, 127.2, 124.7, 119.2, 118.4, 110.9, 108.2, 80.0, 68.4, 51.2, 36.1, 35.7, 28.3. HRMS (ESI-TOF) calcd for C$_{25}$H$_{27}$NO$_2$Na (M+Na$^+$) 396.1939 found 396.1945.

**Entry 2.** The reaction was conducted at 20 °C. Colorless oil. 73% yield.

$^1$H NMR (C$_6$D$_6$): $\delta$ 6.85 (d, $^3$J$_{HH} = 5.1$ Hz, 1H), 6.78 (d, $^3$J$_{HH} = 5.1$ Hz, 1H), 4.84 (d, $^2$J$_{HH} = 1.3$ Hz, 1H), 4.76 (d, $^2$J$_{HH} = 1.5$ Hz, 1H), 3.59 (t, $^3$J$_{HH} = 6.5$ Hz, 1H), 3.30 (s, 3H), 3.24 (d, $^2$J$_{HH} = 18.1$ Hz, 1H), 3.17 (d, $^2$J$_{HH} = 17.7$ Hz, 1H), 2.74 (dd, $^2$J$_{HH} = 13.1$ Hz and $^3$J$_{HH} = 6.9$ Hz, 1H), 2.33 (dd, $^2$J$_{HH} = 13.0$ Hz and $^3$J$_{HH} = 5.9$ Hz, 1H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 172.7, 141.7, 136.5, 132.2, 127.4, 122.7, 111.4, 51.4, 43.9, 34.7, 32.9. Anal. Calcd for C$_{11}$H$_{12}$O$_2$: C, 63.43; H, 5.81. Found: C, 63.03; H, 6.05.

**Entry 3.** White solid. 90% yield.

$^1$H NMR (C$_6$D$_6$): $\delta$ 7.68 (d, $^3$J$_{HH} = 8.0$ Hz, 1H), 7.64 (d, $^3$J$_{HH} = 7.4$ Hz, 1H), 7.51 (d, $^3$J$_{HH} = 8.4$ Hz, 1H), 7.32-7.27 (m, 3H), 4.96 (s, 2H), 3.84 (t, $^3$J$_{HH} = 5.4$ Hz, 1H), 3.68 (d, $^2$J$_{HH} = 18.9$ Hz, 1H), 3.62 (d, $^2$J$_{HH} = 18.9$ Hz, 1H), 2.92 (dd, $^2$J$_{HH} = 12.9$ Hz and $^3$J$_{HH} = 5.2$ Hz, 1H), 2.48 (dd, $^2$J$_{HH} = 12.8$ Hz and $^3$J$_{HH} = 6.0$ Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 172.3, 142.5, 133.2, 132.5, 131.9, 131.8, 128.7, 127.9, 126.3, 126.1, 125.6, 123.4, 110.6, 80.2, 49.1, 35.5, 34.0, 28.0. M.p. 100–101 °C (Et$_2$O). Anal. Calcd for C$_{20}$H$_{22}$O$_2$: C, 81.60; H, 7.53. Found: C, 81.36; H, 7.70.

**Entry 5.** Colorless oil. 89% yield.

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**Supplementary Material (ESI) for Chemical Communications**

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$^1$H NMR (C$_6$D$_6$): $\delta$ 7.58 (d, $^3J_{HH} = 9.1$ Hz, 1H), 7.50 (d, $^3J_{HH} = 8.4$ Hz, 1H), 7.36 (d, $^3J_{HH} = 8.5$ Hz, 1H), 7.23 (dd, $^3J_{HH} = 9.3$ Hz and $^4J_{HH} = 2.7$ Hz, 1H), 6.97 (d, $^4J_{HH} = 2.5$ Hz, 1H), 4.96 (s, 2H), 3.87 (t, $^3J_{HH} = 5.6$ Hz, 1H), 3.66 (d, $^2J_{HH} = 18.8$ Hz, 1H), 3.60 (d, $^2J_{HH} = 18.9$ Hz, 1H), 3.43 (s, 3H), 2.93 (dd, $^2J_{HH} = 12.8$ Hz and $^3J_{HH} = 5.6$ Hz, 1H), 2.51 (dd, $^2J_{HH} = 12.9$ Hz and $^3J_{HH} = 5.9$ Hz, 1H), 1.36 (s, 9H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 172.5, 157.9, 142.7, 134.5, 132.01, 132.00, 129.6, 128.5, 125.4, 125.1, 118.7, 110.5, 107.0, 80.1, 54.8, 48.9, 35.6, 34.1, 28.1.

Anal. Calcd for C$_{21}$H$_{24}$O$_3$: C, 77.75; H, 7.46. Found: C, 77.51; H, 7.38.

**Entry 6.** Colorless oil. 85% yield.

$^1$H NMR (C$_6$D$_6$): $\delta$ 7.77 (d, $^4J_{HH} = 2.1$ Hz, 1H), 7.41 (dd, $^3J_{HH} = 8.8$ Hz and $^4J_{HH} = 2.1$ Hz, 1H), 7.28 (d, $^3J_{HH} = 8.8$ Hz, 1H), 7.21 (d, $^3J_{HH} = 9.4$ Hz, 1H), 7.20 (d, $^3J_{HH} = 8.8$ Hz, 1H), 4.94 (s, 1H), 4.93 (s, 1H), 3.73 (t, $^3J_{HH} = 5.6$ Hz, 1H), 3.48 (d, $^2J_{HH} = 18.9$ Hz, 1H), 3.41 (d, $^2J_{HH} = 18.9$ Hz, 1H), 2.87 (dd, $^2J_{HH} = 12.8$ Hz and $^3J_{HH} = 5.2$ Hz, 1H), 2.41 (dd, $^2J_{HH} = 12.8$ Hz and $^3J_{HH} = 6.1$ Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 172.0, 142.0, 134.3, 132.2, 132.1, 130.8, 130.7, 129.3, 129.0, 125.33, 125.31, 119.8, 110.8, 80.4, 48.9, 35.3, 33.8, 28.0.

Anal. Calcd for C$_{20}$H$_{21}$BrO$_2$: C, 64.35; H, 5.67. Found: C, 64.33; H, 5.63.

**Entry 7.** The reaction was conducted at 50 °C with no treatment with alumina after the cyclization reaction. Colorless oil. 19% yield.

$^1$H NMR (C$_6$D$_6$): $\delta$ 7.23 (dd, $^3J_{HH} = 5.7$ Hz and $^4J_{HH} = 3.3$ Hz, 1H), 7.05-7.02 (m, 2H), 6.88 (dd, $^3J_{HH} = 5.4$ Hz and $^4J_{HH} = 3.3$ Hz, 1H), 4.86 (s, 2H), 3.70 (t, $^3J_{HH} = 5.9$ Hz, 1H), 3.43 (d, $^2J_{HH} = 18.4$ Hz, 1H), 3.27 (d, $^2J_{HH} = 18.6$ Hz, 1H), 2.84 (dd, $^2J_{HH} = 13.6$ Hz and $^3J_{HH} = 5.9$ Hz, 1H), 2.42 (dd, $^2J_{HH} = 13.5$ Hz and $^3J_{HH} = 5.9$ Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (C$_6$D$_6$): $\delta$ 172.3, 142.7, 136.8, 134.8, 129.1, 128.9, 127.2, 125.9, 110.0, 80.1, 48.2, 36.9, 35.3, 28.0.

Anal. Calcd for C$_{16}$H$_{20}$O$_2$: C, 78.65; H, 8.25. Found: C, 78.84; H, 8.43.

**Entry 8.** The reaction was conducted at 50 °C with no treatment with alumina after the cyclization reaction. White solid. 65% yield.
$^1$H NMR (CD$_2$D$_6$): δ 6.52 (d, $^4$J$_{HH}$ = 2.3 Hz, 1H), 6.35 (d, $^4$J$_{HH}$ = 2.3 Hz, 1H), 4.97 (d, $^3$J$_{HH}$ = 1.3 Hz, 1H), 4.90 (d, $^3$J$_{HH}$ = 1.4 Hz, 1H), 3.77 (t, $^3$J$_{HH}$ = 5.9 Hz, 1H), 3.55 (s, 2H), 3.42 (s, 3H), 3.26 (s, 3H), 2.87 (dd, $^2$J$_{HH}$ = 13.1 Hz and $^3$J$_{HH}$ = 6.0 Hz, 1H), 2.50 (dd, $^2$J$_{HH}$ = 13.1 Hz and $^3$J$_{HH}$ = 5.8 Hz, 1H), 1.36 (s, 9H). $^{13}$C NMR (CD$_2$D$_6$): δ 172.3, 159.1, 158.3, 143.0, 136.1, 118.2, 110.2, 104.5, 97.6, 80.1, 54.9, 54.7, 48.9, 35.6, 31.2, 28.1. M.p. 79–80 °C (Et$_2$O). Anal. Calcd for C$_{18}$H$_{24}$O$_4$: C, 71.03; H, 7.95. Found: C, 71.14; H, 7.94.

**Entry 9.** The reaction was conducted at 50 °C with no treatment with alumina after the cyclization reaction. White solid. 57% yield.

$^1$H NMR (CD$_2$D$_6$): δ 6.59 (s, 1H), 4.97 (s, 1H), 4.92 (d, $^3$J$_{HH}$ = 1.4 Hz, 1H), 3.72 (t, $^3$J$_{HH}$ = 5.9 Hz, 1H), 3.67 (s, 3H), 3.57 (s, 2H), 3.41 (s, 3H), 2.88 (dd, $^2$J$_{HH}$ = 12.8 Hz and $^3$J$_{HH}$ = 6.1 Hz, 1H), 2.49 (dd, $^2$J$_{HH}$ = 12.8 Hz and $^3$J$_{HH}$ = 5.8 Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (CD$_2$D$_6$): δ 172.4, 152.2, 151.6, 142.6, 142.1, 129.8, 123.2, 110.4, 108.3, 80.1, 60.5, 60.0, 55.6, 48.5, 35.6, 31.5, 28.1. M.p. 57–58 °C (Et$_2$O). Anal. Calcd for C$_{19}$H$_{26}$O$_5$: C, 68.24; H, 7.84. Found: C, 68.48; H, 7.81.

**Equation 3.** No treatment with alumina after the cyclization reaction. Colorless oil. 90% yield.

$^1$H NMR (CD$_2$D$_6$): δ 7.18 (d, $^3$J$_{HH}$ = 1.9 Hz, 1H), 4.77 (s, 1H), 4.75 (s, 1H), 3.36 (s, 3H), 3.24 (s, 3H), 2.99-2.94 (m, 3H), 2.43 (dd, $^2$J$_{HH}$ = 13.1 Hz and $^3$J$_{HH}$ = 8.3 Hz, 1H), 2.31 (dd, $^2$J$_{HH}$ = 13.1 Hz and $^3$J$_{HH}$ = 5.9 Hz, 1H). $^{13}$C NMR (CD$_2$D$_6$): δ 171.9, 166.3, 141.4, 135.6, 131.6, 111.2, 51.6, 51.3, 43.8, 33.2, 32.7. Anal. Calcd for C$_{11}$H$_{14}$O$_4$: C, 62.85; H, 6.71. Found: C, 62.88; H, 6.69.

**Procedure for Equation 4.**

A solution of Pd(PPh$_3$)$_4$ (23.1 mg, 20.0 μmol) and lactone 1l (98.5 mg, 0.400 mmol) in THF (0.5 mL) was stirred for 10 h at 30 °C. The reaction mixture was directly passed through a pad of silica gel with Et$_2$O and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et$_2$O/hexane = 1/6 to afford compound 4 as a white solid (69.6 mg, 0.172 mmol; 86% yield, dr = 57/43).

S10
1H NMR (CDCl₃): δ 7.34-7.29 (m, 4H), 7.25-7.22 (m, 6H), 4.75 (s, 2.28H), 4.70 (s, 1.72H), 3.67 (s, 2.58H), 3.62 (s, 3.42H), 3.06 (d, 2J_HH = 14.6 Hz, 1.72H), 3.00 (s, 2J_HH = 14.8 Hz, 2.28H), 2.93 (d, 2J_HH = 14.7 Hz, 2.28H), 2.85 (d, 2J_HH = 14.5 Hz, 1.72H). 13C NMR (CDCl₃): δ 175.6, 175.5, 144.8, 143.0, 141.8, 141.7, 128.4, 128.2, 126.74, 126.71, 126.4, 125.8, 119.3, 118.6, 54.6, 54.2, 52.1, 51.9, 43.6, 42.6. M.p. 92–93 °C (Et₂O). HRMS (ESI-TOF) calcd for C₂₆H₂₈O₄Na (M+Na+) 427.1882 found 427.1880.

**Procedure for Equation 5.**

A solution of Pd(PPh₃)₄ (11.6 mg, 10.0 μmol) and lactone 1m (52.2 mg, 0.200 mmol) in toluene (2.0 mL) was stirred for 14 h at 80 °C. After cooled to room temperature, the reaction mixture was passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/10 to afford compound 5 (CAS 116145-61-0 for (E)-isomer) as a colorless oil (34.6 mg, 0.160 mmol; 80% yield, E/Z = 95/5).¹⁰

(E)-isomer: ¹H NMR (CDCl₃): δ 7.84 (s, 1H), 7.40-7.31 (m, 5H), 4.85 (quint, 2J_HH = 1.4 Hz, 1H), 4.69 (s, 1H), 3.81 (s, 3H), 3.19 (s, 2H), 1.85 (s, 3H). ¹³C NMR (CDCl₃): δ 168.8, 143.4, 140.6, 135.4, 130.3, 129.2, 128.6, 128.4, 110.3, 52.1, 35.3, 23.5.

**Procedure for Equations 6 and 7.**

A solution of compound 3 (0.200 mmol) and KOt-Bu (18.0 mg, 0.160 mmol) in DMSO (2.0 mL) was stirred for 1 h at room temperature. The reaction mixture was bubbled with air for 5 min and quenched with saturated NH₄Claq. This was extracted with CH₂Cl₂ and the organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane to afford compound 6.

![Equation 6](attachment:image.png)

**Equation 6.** 85% yield, colorless oil.

¹H NMR (CDCl₃): δ 8.13 (d, 2J_HH = 5.6 Hz, 1H), 7.90 (d, 4J_HH = 0.9 Hz, 1H), 7.83 (d, 2J_HH = 0.8 Hz, 1H), 7.49 (d, 3J_HH = 5.6 Hz, 1H), 2.51 (s, 3H), 1.67 (s, 9H). ¹³C NMR (CDCl₃): δ 166.1, 141.5, 136.4, 133.3, 129.0, 126.9, 126.6, 126.3, 124.5, 81.3, 28.3, 21.2. Anal. Calcd for C₁₄H₁₆O₂S: C, 67.71; H, 6.49. Found: C, 67.44; H, 6.70.

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Equation 7. 87% yield, white solid.

\[ \text{Me-C}^2\text{t-Bu-}6\text{e} \]

\[ \text{87\% yield, white solid.} \]

\[ \text{1H NMR (CDCl}_3\text{): } \delta 8.68 (d, 3J_{HH} = 8.2 \text{ Hz, 1H}), 8.65 (s, 1H), 8.63 (d, 3J_{HH} = 9.4 \text{ Hz, 1H}), 7.93 (s, 1H), 7.89 (d, 3J_{HH} = 7.7 \text{ Hz, 1H}), 7.78 (d, 3J_{HH} = 9.3 \text{ Hz, 1H}), 7.65 (td, 3J_{HH} = 7.5 \text{ Hz and } 4J_{HH} = 1.3 \text{ Hz, 1H}), 7.61 (t, 3J_{HH} = 7.4 \text{ Hz, 1H}), 2.65 (s, 3H), 1.71 (s, 9H). \]

\[ \text{13C NMR (CDCl}_3\text{): } \delta 167.6, 134.9, 131.7, 131.0, 130.7, 130.4, 129.8, 128.4, 128.2, 127.3, 126.7, 126.5, 126.1, 123.7, 122.7, 81.6, 28.3, 21.9. \]

\[ \text{M.p. 105–106 °C (Et}_2\text{O). HRMS (ESI-TOF) calcd for } C_{20}H_{20}O_2Na (M+Na^+) 315.1356 \text{ found 315.1361.} \]

Procedure for Equation 8.

\[ \text{8} \]

A solution of compound \( \text{3e} \) (354 mg, 1.20 mmol) in Et\(_2\)O (29 mL) was added to a suspension of LiAlH\(_4\) (91.7 mg, 2.42 mmol) in Et\(_2\)O (1 mL) at room temperature. The resulting mixture was stirred for 6 h at room temperature and quenched with 1 M NaOH\(_{aq}\) (0.6 mL). This mixture was passed through celite with Et\(_2\)O and the solvent was removed under vacuum. The residue was chromatographed on silica gel with Et\(_2\)O/hexane = 1/2→1/1 to afford compound \( \text{7} \) as a white solid (262 mg, 1.17 mmol; 97% yield).

\[ \text{1H NMR (C}_6\text{D}_6\text{): } \delta 7.71 (dd, 3J_{HH} = 8.1 \text{ Hz and } 4J_{HH} = 1.2 \text{ Hz, 1H}), 7.67 (dd, 3J_{HH} = 7.8 \text{ Hz and } 4J_{HH} = 1.6 \text{ Hz, 1H}), 7.50 (d, 3J_{HH} = 8.4 \text{ Hz, 1H}), 7.35-7.29 (m, 2H), 7.11 (d, 3J_{HH} = 8.4 \text{ Hz, 1H}), 4.99 (t, 3J_{HH} = 1.6 \text{ Hz, 1H}), 4.93 (t, 3J_{HH} = 1.6 \text{ Hz, 1H}), 3.62 (s, 2H), 3.51 (dd, 3J_{HH} = 6.8 \text{ and 5.4 Hz, 2H}), 2.93 (tdd, 3J_{HH} = 6.7, 5.5, \text{ and } 2.7 \text{ Hz, 1H}), 2.67 (dd, 3J_{HH} = 12.9 \text{ Hz and } 3J_{HH} = 2.6 \text{ Hz, 1H}), 2.35 (dd, 3J_{HH} = 12.8 \text{ Hz and } 3J_{HH} = 5.1 \text{ Hz, 1H}), 0.80 (t, 3J_{HH} = 5.2 \text{ Hz, 1H}). \]

\[ \text{13C NMR (CDCl}_3\text{): } \delta 142.6, 133.9, 132.5, 131.9, 131.6, 128.5, 127.6, 126.2, 126.1, 125.3, 122.8, 110.9, 66.5, 43.2, 34.0, 33.7. \]


\[ \text{m-Chloroperbenzoic acid (393 mg, 1.25 mmol; 55\% purity) was added to a solution of compound } \text{7} \text{ (224 mg, 1.00 mmol) in CH}_2\text{Cl}_2 \text{ (20 mL) and the mixture was stirred for 5 h at room temperature. The reaction was quenched with saturated NaHSO}_3\text{aq (1.3 mL) and the mixture was further stirred for 30 min. This was extracted with CH}_2\text{Cl}_2 \text{, and the organic layer} \]
was washed with water and then with saturated NaHCO₃aq, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was dissolved in CH₂Cl₂ (15 mL) and a solution of p-toluenesulfonylic acid (13.8 mg, 72.5 μmol; monohydrate) in CH₂Cl₂ (5 mL) was added to it at 0 °C. The mixture was stirred for 4 h at 0 °C and quenched with saturated NH₄Cl aq (20 mL). This was further stirred for 50 min at 0 °C and extracted with CH₂Cl₂. The organic layer was washed with saturated NaHCO₃aq and then with saturated NaCl aq, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/2→1/1 to afford compound 8 as a white solid (183 mg, 0.762 mmol; 76% yield).

¹H NMR (CDCl₃): δ 7.85 (d, ³JHH = 7.9 Hz, 1H), 7.82 (d, ³JHH = 7.4 Hz, 1H), 7.69 (d, ³JHH = 8.2 Hz, 1H), 7.50 (ddd, ³JHH = 8.4 and 6.8 Hz and ⁴JHH = 1.3 Hz, 1H), 7.45 (ddd, ³JHH = 8.0 and 6.8 Hz and ⁴JHH = 1.2 Hz, 1H), 7.25 (d, ³JHH = 7.3 Hz, 1H), 4.14 (dd, ²JHH = 7.2 Hz and ³JHH = 3.9 Hz, 1H), 4.01 (d, ²JHH = 7.2 Hz, 1H), 3.97 (d, ²JHH = 11.5 Hz, 1H), 3.84 (d, ²JHH = 11.5 Hz, 1H), 3.47 (t, ³JHH = 3.8 Hz, 1H), 3.24 (d, ²JHH = 17.1 Hz, 1H), 3.20 (d, ²JHH = 17.1 Hz, 1H), 2.35 (dd, ²JHH = 10.9 Hz and ³JHH = 3.9 Hz, 1H), 1.91 (d, ²JHH = 11.0 Hz, 1H).

¹³C NMR (CDCl₃): δ 139.5, 132.6, 132.5, 128.6, 128.5, 126.6, 126.2, 125.6, 125.1, 123.0, 83.1, 77.8, 66.8, 43.1, 37.9, 35.7. M.p. 135–136 °C (Et₂O). Anal. Calcd for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 79.73; H, 6.76.
IV. $^1$H NMR Spectra