Supporting Information

Total Synthesis and Structural Revision of Incargutines A and B

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Content

Experimental - - - - - - - - - - - - - - - - - - - - - - - - - - - - - 2

\textsuperscript{1}H and \textsuperscript{13}C NMR of New Compounds - - - - - - - - - - - - - - - - - - - - - - - - - - - - - 25
Experimental
Melting points (mp) were measured using a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were recorded using a JASCO FTIR-4100 instrument. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-AL300 or a Bruker AVANCE III 400 NanoBay instruments. Chemical shifts are given on the δ (ppm) scale using tetramethylsilane (TMS) as the internal standard (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; m, multiplet; br, broad). Mass spectra were measured on a JEOL JMS-MS700 V instrument by FAB⁺. Flash column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral) 40–50 μm.

4-Benzylxy-3-methylbutyl 2,4,6-trimethylbenzoate (8)
To a solution of alcohol 7 (20.8 g, 107 mmol) in CH₂Cl₂ (107 mL) were added 2,4,6-Me₃C₆H₂COCl (19.4 mL, 117 mmol), Et₃N (44.7 mL, 321 mmol), and DMAP (1.31 g, 10.7 mmol) at 0 °C under Ar atmosphere. The mixture was stirred at 25 °C for 18 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 20 : 1 to 10 : 1) to give mesitoate 8 (28.0 g, 77% yield) as a colorless oil.

IR (neat): 1720, 1612, 1454, 1262, 1080 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 7.29-7.37 (5H, m), 6.84 (2H, s), 4.50 (2H, s), 4.32-4.41 (2H, m), 3.34 (2H, d, J = 5.9 Hz), 2.28 (9H, s), 1.87-2.00 (2H, m), 1.57 (1H, m), 1.00 (3H, d, J = 6.6 Hz).
¹³C NMR (75 MHz, CDCl₃): δ = 170.4, 139.2, 138.6, 135.0, 135.0, 131.2, 128.4, 128.4, 128.4, 127.6, 127.6, 75.4, 73.0, 63.1, 32.5, 30.6, 21.0, 19.6, 19.6, 16.9.
MS-FAB: m/z 91, 147, 341 [M + H]⁺.

5,5-Dibromo-3-methylpent-4-enyl 2,4,6-trimethylbenzoate (9)
To a solution of mesitoate 8 (28.0 g, 82.2 mmol) in MeOH (548 mL) was added a 10% Pd on activated carbon (8.74 g, 8.22 mmol) at room temperature under Ar atmosphere, and the mixture was stirred under a balloon of H₂ at the 30 °C for 18 h. The mixture was filtered through celite pad. The filtrate was concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of (COCl)₂ (8.60 mL, 98.7 mmol) in CH₂Cl₂ (121 mL) was added
dropwise DMSO (14.0 mL, 197 mmol) at -78 °C under Ar atmosphere, and the mixture was stirred for 10 min at same temperature. To the reaction mixture was added dropwise a solution of the above crude product in CH₂Cl₂ (30.0 mL) at -78 °C, the mixture was stirred for 30 min at same temperature. To the reaction mixture was added Et₃N (42.3 mL, 304 mmol) at -78 °C, and the mixture was stirred for 1 h at 0 °C. The reaction was quenched by addition of water. The mixture was extracted with CH₂Cl₂, and the organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of PPh₃ (51.8 g, 197 mmol) in CH₂Cl₂ (140 mL) was added CBr₄ (32.7 g, 98.7 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred for 15 min at same temperature. To the reaction mixture was added dropwise a solution of the above crude product in CH₂Cl₂ (50.0 mL) at 0 °C, the mixture was stirred for 1 h at same temperature. The reaction mixture was treated with pyridine (76.0 mL) at 0 °C, and the mixture was stirred for 20 min at same temperature. The reaction was quenched by slow addition of saturated aqueous NaHCO₃ solution. The mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 50 : 1) to give dibromoolefin 9 (30.9 g, 93% yield) as a colorless oil.

IR (neat): 1720, 1611, 1454 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 6.85 (2H, s), 6.23 (1H, d, J = 9.5 Hz), 4.23-4.37 (2H, m), 2.66 (1H, m), 2.29 (6H, s), 2.28 (3H, s), 1.79 (2H, q, J = 6.8 Hz), 1.08 (3H, d, J = 6.8 Hz).

¹³C NMR (75 MHz, CDCl₃): δ = 170.2, 142.9, 142.9, 139.3, 135.2, 131.0, 128.4, 128.4, 88.7, 62.6, 35.4, 34.6, 21.0, 19.7, 19.7, 19.0.

MS-FAB: m/z 147, 401 [M]⁺.

5-(tert-Butyldimethylsilanyl)-3-methylpent-4-ynyl 2,4,6-trimethylbenzoate (10)

To a solution of dibromoolefin 9 (30.7 g, 75.9 mmol) in THF (122 mL) was added dropwise n-BuLi (1.62 M in hexane, 98.4 mL, 159 mmol) at -78 °C under Ar atmosphere, and the mixture was stirred for 1 h at same temperature. To the reaction mixture was added a solution of TBSCl (22.9 g, 152 mmol) in THF (30 mL) at -78 °C, the mixture was stirred for 30 min at room temperature. The reaction was quenched by addition of a saturated aqueous NH₄Cl solution. The mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and
concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 100 : 1 to 50 : 1) to give alkyne 10 (24.8 g, 91% yield) as a pale yellow oil.

IR (neat): 2166, 1727, 1612, 1461 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 6.85 (2H, s), 4.43-4.47 (2H, m), 2.67 (1H, m), 2.27-2.28 (9H, m), 1.73-1.94 (2H, m), 1.21 (3H, d, J = 7.0 Hz), 0.92 (9H, s), 0.07 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 170.2, 139.3, 135.0, 135.0, 131.2, 128.4, 128.4, 110.6, 83.4, 62.9, 35.5, 26.0, 26.0, 26.0, 23.8, 21.0, 20.9, 19.6, 19.6, 16.3, -4.6, -4.6.

MS-FAB: m/z 119, 359 [M + H]⁺.


5-[(tert-Butyldimethylsilyl)-3-methylpent-4-ynyl toluene-4-sulfonate (11)

To a solution of alkyne 10 (24.8 g, 69.2 mmol) in THF (173 mL) was added LAH (2.62 g, 69.2 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred for 2 h at room temperature. The reaction was quenched by addition of Na₂SO₄·10H₂O, and the mixture was stirred for 20 min at room temperature. The mixture was extracted with AcOEt, and the mixture was dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product and Et₃N (38.4 mL, 277 mmol) in CH₂Cl₂ (173 mL) were added TsCl (33.0 g, 173 mmol) and DMAP (845 mg, 6.92 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched by addition of a saturated aqueous NaHCO₃ solution. The mixture was extracted with AcOEt, and the mixture was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 50 : 1 to 20 : 1) to give tosylate 11 (21.3 g, 84% yield) as a white solid.

Mp 44-45 °C.

IR (neat): 2166, 1598, 1461, 1357, 1172 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.80 (2H, d, J = 8.3 Hz), 7.34 (2H, d, J = 8.3 Hz), 4.10-4.23 (2H, m), 2.57 (1H, m), 2.44 (3H, s), 1.65-1.87 (2H, m), 1.14 (3H, d, J = 7.0 Hz), 0.86 (9H, s), 0.01-0.02 (6H, m).

¹³C NMR (75 MHz, CDCl₃): δ = 144.8, 133.1, 129.9, 129.9, 127.9, 127.9, 109.9, 83.5, 68.6, 35.8, 25.9, 25.9, 25.9, 23.3, 21.5, 20.8, 16.2, -4.7, -4.7.

MS-FAB: m/z 367 [M + H]⁺.

**tert-Butyl-(5-iodo-3-methylpent-1-ynyl)dimethylsilane (12)**

To a solution of the tosylate 11 (21.3 g, 58.1 mmol) in acetone (145 mL) was added NaI (21.8 g, 145 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 1.5 h at 70 °C. The reaction was quenched by addition of water. The mixture was extracted with AcOEt, and the organic layer was washed with saturated aqueous NaHCO₃ solution and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane) to give iodide 12 (17.1 g, 91% yield) as a colorless oil.

IR (neat): 2169 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 3.24-3.38 (2H, m), 2.64 (1H, m), 1.87-1.94 (2H, m), 1.20 (3H, d, J = 6.8 Hz), 0.92 (9H, s), 0.07 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 110.0, 83.6, 40.2, 28.0, 26.0, 26.0, 20.4, 16.4, 3.9, -4.6, -4.6.

MS-FAB: m/z 321 [M - H]⁺.


**6-[5-(tert-Butyldimethylsilyl)-3-methylpent-4-ynyl]-3-ethoxycyclohex-2-enone (14)**

To a solution of LDA, which was prepared in situ by mixing i-Pr₂NH (12.4 mL, 88.2 mmol) and n-BuLi (1.62 M in hexane, 46.0 mL, 74.5 mmol) in THF (118 mL) at -78 °C for 1 h under Ar atmosphere, was added a solution of commercially available cyclohexenone 13 (10.0 mL, 74.5 mmol) at -78 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture was added a solution of iodide 12 (17.1 g, 53.1 mmol) and HMPA (22.0 mL, 126 mmol) in THF (85 mL) at -78 °C, and the mixture was stirred at 0 °C for 1.5 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution, the mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 5 : 1) to give cyclohexenone 14 which is inseparable diastereomeric mixture (13.2 g, 74% yield) as a colorless oil.

IR (neat): 2165, 1655, 1607, 1459, 1189 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.29 (1H, s), 3.88 (2H, q, J = 7.0 Hz), 2.39-2.47 (3H, m), 2.04-2.20 (2H, m), 1.91 (1H, m), 1.73 (1H, m), 1.44-1.54 (3H, m), 1.35 (3H, t, J = 7.0 Hz), 1.16-1.18 (3H, m), 0.91 (9H, s), 0.06 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 201.6, 176.7, 112.3, 102.1, 102.0, 82.2, 64.0, 45.0,
3-Ethoxy-6-(3-methylpent-4-ynyl)cyclohex-2-enone (15)
To a solution of cyclohexenone 14 (13.2 g, 39.3 mmol) in THF (39 mL) was added a TBAF (1.0 M in THF, 58.0 mL, 58.0 mmol) at room temperature, and the mixture was stirred for 18 h at 30 °C. The reaction was quenched by addition of water (150 mL), the mixture was extracted with AcOEt, and the organic layer was washed with brine, and dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 4 : 1) to give cyclohexenone 15 which is inseparable diastereomeric mixture (8.57 g, 99% yield) as a colorless oil.

IR (neat): 3303, 2110, 1650, 1604, 1454, 1188 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.30 (1H, s), 3.89 (2H, q, J = 7.0 Hz), 2.41-2.46 (3H, m), 1.87-2.24 (4H, m), 1.74 (1H, m), 1.48-1.55 (3H, m), 1.35 (3H, t, J = 7.0 Hz), 1.17-1.21 (3H, m).

¹³C NMR (75 MHz, CDCl₃): δ = 201.4, 201.3, 176.7, 102.1, 102.0, 88.8, 88.7, 68.3, 68.3, 64.0, 44.9, 44.6, 34.3, 33.7, 27.8, 27.6, 27.3, 27.0, 26.2, 26.1, 25.8, 25.5, 20.8, 20.6, 13.9.

MS-FAB: m/z 221 [M + H]⁺.

HRMS-FAB: m/z [M + H]⁺ calcd for C₁₄H₂₁O₂: 221.1542; found: 221.1531.

3-(4-Iodophenyl)-4-(3-methylpent-4-ynyl)cyclohex-2-enone (16)
To a solution of 1,4-diiodobenzene (41.6 g, 126 mmol) in THF (126 mL) was added i-PrMgCl (2.0 M in THF, 63.0 mL, 126 mmol) at 0 °C under Ar atmosphere and the mixture was stirred at the room temperature for 1 h. To the mixture was added a solution of cyclohexenone 15 (7.52 g, 34.1 mmol) in THF (45.0 mL) at the room temperature, and the mixture was stirred at 40 °C for 2 h. Then the reaction was quenched by addition of 10% HCl (126 mL) at 0 °C and the mixture was stirred at the same temperature for 30 min. The reaction mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous NaHCO₃ solution, H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 10 : 1 to 5 : 1) to give iodide 16 which is inseparable diastereomeric mixture (11.2 g, 87% yield, two steps) as
a white solid.
Mp 77-82 °C.
IR (neat): 3223, 1652, 1597, 1577, 1486, 1454 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 7.73-7.76 (2H, m), 7.21-7.25 (2H, m), 6.23 (1H, s),
2.92 (1H, m), 2.35-2.63 (3H, m), 2.10-2.26 (2H, m), 2.00 (1H, d, J = 2.4 Hz), 1.38-1.77
(4H, m), 1.10-1.16 (3H, m).
¹³C NMR (75 MHz, CDCl₃): δ = 199.5, 163.4, 163.3, 138.1, 138.0, 137.8, 128.4, 128.3,
125.7, 125.6, 96.1, 88.3, 88.0, 69.0, 68.7, 36.0, 35.5, 34.9, 34.8, 32.8, 32.7, 29.0, 28.9,
MS-FAB: m/z 379 [M + H]⁺.

7-(4-Iodophenyl)-8-(3-methylpent-4-ynyl)-1,4-dioxaspiro[4.5]dec-6-ene (17)
To a solution of iodide 16 (11.2 g, 29.6 mmol) and 1,2-bis(trimethylsilyloxy)ethane
(29.0 mL, 118 mmol) in CH₂Cl₂ (148 mL) was added TMSOTf (1.10 mL, 5.92 mmol)
at -70 °C under Ar atmosphere, and the mixture was stirred for 40 h at same temperature.
The reaction was quenched by addition of pyridine (29.6 mL). After concentration of
the solvent under reduced pressure, the residue was purified by a silica gel column
chromatography (hexane/ACOEt = 5 : 1) to give acetal 17 which is inseparable
diastereomeric mixture (9.40 g, 75% yield) as a colorless oil.
IR ( neat): 3300, 2110, 1484, 1098 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 7.62-7.65 (2H, m), 7.05-7.09 (2H, m), 5.69 (1H, s),
3.96-4.05 (4H, m), 2.63 (1H, m), 2.31 (1H, m), 1.76-2.02 (5H, m), 1.24-1.50 (4H, m),
1.04-1.10 (3H, m).
¹³C NMR (75 MHz, CDCl₃): δ = 146.7, 146.6, 140.4, 137.4, 137.3, 128.6, 128.5, 126.0,
125.8, 106.0, 92.9, 88.8, 88.4, 68.5, 68.2, 64.6, 64.4, 35.5, 35.2, 34.2, 34.1, 30.1, 29.9,
MS-FAB: m/z 423 [M + H]⁺.
HRMS-FAB: m/z [M + H]⁺ calcd for C₂₀H₂₄I₂O₂: 423.0821; found: 423.0828.

Ethyl 4-[6-(5-ethoxycarbonyl-3-methylpent-4-ynyl)-3-oxocyclohex-1-enyl]benzoate
(18)
To a solution of acetal 17 (9.40 g, 22.3 mmol) in THF (149 mL) was added a i-PrMgCl
(2.0 M in THF, 44.6 mL, 89.2 mmol) at -10 °C under Ar atmosphere, and the mixture
was stirred at the room temperature for 1 h. To the reaction mixture was added ethyl
chloroformate (17.1 mL, 178 mmol) at 0 °C, and the mixture was stirred at 40 °C for 1.5
h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution at 0 °C, the mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in acetone (223 mL) and water (15.9 mL) was added TsOH·H₂O (848 mg, 4.46 mmol) at 0 °C, and the mixture was stirred at room temperature for 14 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 3 : 1) to give cyclohexenone 18 which is inseparable diastereomeric mixture (4.82 g, 54% yield, two steps) as a pale yellow oil.

IR (neat): 2237, 1708, 1668, 1604, 1453 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.08 (2H, d, J = 7.9 Hz), 7.52-7.56 (2H, m), 6.27 (1H, s), 4.40 (2H, q, J = 7.2 Hz), 4.15-4.23 (2H, m), 3.01 (1H, m), 2.40-2.64 (3H, m), 2.09-2.33 (2H, m), 1.48-1.75 (4H, m), 1.40 (3H, t, J = 7.2 Hz), 1.25-1.31 (3H, m), 1.12-1.19 (3H, m).

¹³C NMR (75 MHz, CDCl₃): δ = 199.2, 166.0, 163.0, 142.8, 142.7, 131.5, 130.1, 126.9, 126.8, 126.6, 91.9, 91.6, 73.9, 73.6, 61.8, 61.1, 36.2, 35.7, 33.9, 33.0, 32.8, 29.1, 28.9, 25.8, 25.6, 25.4, 19.8, 19.4, 14.1, 13.9.

MS-FAB: m/z 323, 351, 397 [M + H]⁺.


Ethyl 7-(4-ethoxycarbonylphenyl)-5-hydroxy-3-methylindan-4-carboxylate (19)

To a solution of cyclohexenone 18 (3.11g, 7.85 mmol) in xylene (80%, 79 mL) was added In(OTf)₃ (882 mg, 1.57 mmol) at room temperature under Ar atmosphere, and the mixture was stirred at 130 °C for 5 h. After the reaction mixture was cooled to room temperature, the reaction mixture was passed through a silica gel (ca. 100 g) with hexane/AcOEt (1 : 0 to 1 : 2). The eluent was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 20 : 1) to give 4-phenylindane 19 (1.61 g, 56% yield) as a white solid.

Mp 96-97 ºC.

IR (neat): 1714, 1656, 1601, 1554, 1460 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 11.31 (1H, s), 8.10 (2H, d, J = 8.3 Hz), 7.51 (2H, d, J = 8.3 Hz), 6.86 (1H, s), 4.37-4.55 (4H, m), 3.86 (1H, m), 3.05 (1H, m), 2.61 (1H, m), 2.14 (1H, m), 1.81 (1H, m), 1.39-1.49 (6H, m), 1.23 (3H, d, J = 6.8 Hz).
Ethyl 4-(6-hydroxy-7-hydroxymethyl-1-methylindan-4-yl)benzoate (20)
To a solution of 4-phenylindane 19 (682 mg, 1.85 mmol) in THF (19.0 mL) was added BH₃·SMe₂ (90%, 0.23 mL, 2.22 mmol) at 0 °C, and the mixture was stirred at room temperature for 17 h. The reaction was quenched by slow addition of saturated aqueous NH₄Cl solution at 0 °C, and the mixture was stirred at the same temperature for 30 min. The mixture was extracted with AcOEt and the organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 3 : 1) to give diol 20 (503 mg, 84% yield) as a colorless oil.
IR (neat): 3343, 1692, 1607, 1561 cm⁻¹.

Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-6-hydroxy-1-methylindan-4-yl]benzoate (21)
To a solution of diol 20 (451 mg, 1.38 mmol) and Et₃N (0.960 mL, 6.90 mmol) in CH₂Cl₂ (14.0 mL) was added TBSCI (229 mg, 1.52 mmol) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched by addition of a saturated aqueous NH₄Cl solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 10 : 1) to give TBS ether 21 (542 mg, 89% yield) as a colorless oil.
IR (neat): 3350, 1715, 1608, 1471, 1270, 1101 cm⁻¹.
**1H NMR (300 MHz, CDCl3):** δ = 8.39 (1H, s), 8.08 (2H, d, J = 8.4 Hz), 7.51 (2H, d, J = 8.4 Hz), 6.79 (1H, s), 4.96-5.07 (2H, m), 4.46 (2H, q, J = 7.2 Hz), 3.23 (1H, m), 3.09 (1H, m), 2.67 (1H, m), 2.17 (1H, m), 1.79 (1H, m), 1.40 (3H, t, J = 7.2 Hz), 1.16 (3H, d, J = 7.0 Hz), 0.96 (9H, s), 0.20 (3H, s), 0.18 (3H, s).

**13C NMR (75 MHz, CDCl3):** δ = 166.7, 156.3, 147.3, 145.8, 137.2, 131.8, 129.5, 129.5, 128.9, 128.5, 128.5, 119.3, 115.3, 62.8, 60.9, 37.9, 34.0, 29.6, 25.7, 25.7, 25.6, 20.0, 18.0, 14.3, -5.6, -5.6.

**MS-FAB:** m/z 439 [M - H]+.

**HRMS-FAB:** m/z [M - H]+ calcd for C26H35O4Si: 439.2305; found: 439.2285.

**Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-1-methyl-6-trifluoromethanesulfonyloxyindan-4-yl]benzoate (22)**

To a solution of TBS ether 21 (508 mg, 1.15 mmol) and Et3N (1.6 mL, 11.5 mmol) in CH2Cl2 (12.0 mL) was added Tf2O (0.40 mL, 2.30 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction was quenched by addition of a saturated aqueous NaHCO3 solution, and the mixture was extracted with AcOEt. The organic layer was washed with H2O and brine, dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 30 : 1) to give triflate 22 (528 mg, 80% yield) as a pale yellow oil.

**IR (neat):** 1718, 1608, 1471, 1421, 1274, 1208, 1099 cm⁻¹.

**1H NMR (300 MHz, CDCl3):** δ = 8.11 (2H, d, J = 8.3 Hz), 7.48 (2H, d, J = 8.3 Hz), 7.11 (1H, s), 4.80 (2H, s), 4.41 (2H, q, J = 7.2 Hz), 3.59 (1H, m), 3.14 (1H, m), 2.75 (1H, m), 2.23 (1H, m), 1.84 (1H, m), 1.41 (3H, t, J = 7.2 Hz), 1.30 (3H, d, J = 7.2 Hz), 0.92 (9H, s), 0.14 (3H, s), 0.13 (3H, s).

**13C NMR (75 MHz, CDCl3):** δ = 166.4, 152.5, 147.1, 144.0, 141.8, 138.1, 129.8, 129.8, 128.5, 128.5, 128.3, 120.8, 119.7, 116.6, 61.1, 57.3, 38.5, 34.0, 30.1, 25.8, 25.7, 25.7, 19.9, 18.3, 14.2, -5.6, -5.7.

**MS-FAB:** m/z 515, 527, 573 [M + H]+.

**HRMS-FAB:** m/z [M + H]+ calcd for C27H36F3O6SSi: 573.1954; found: 573.1941.

**Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-1-methylindan-4-yl]benzoate (23)**

To a solution of triflate 22 (296 mg, 0.517 mmol), HCO2H (0.3 mL, 8.27 mmol) and Et3N (1.7 mL, 12.4 mmol) in DMF (5.2 mL) were added Pd(OAc)2 (11.6 mg, 0.0517 mmol) and PPh3 (27.1 mg, 0.103 mmol) at room temperature, and the mixture was
stirred at 60 °C for 2 h. After the reaction mixture was cooled to room temperature, the reaction was quenched by addition of brine, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 50 : 1) to give ethyl ester 23 (174 mg, 79% yield) as a colorless oil.

IR (neat): 1715, 1609, 1462, 1270, 1101 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.09 (2H, d, J = 8.3 Hz), 7.51 (2H, d, J = 8.3 Hz), 7.38 (1H, d, J = 8.0 Hz), 7.24 (1H, d, J = 8.0 Hz), 4.81 (2H, s), 4.40 (2H, q, J = 7.2 Hz), 3.37 (1H, m), 3.15 (1H, m), 2.76 (1H, m), 2.18 (1H, m), 1.79 (1H, m), 1.41 (3H, t, J = 7.2 Hz), 1.23 (3H, d, J = 7.0 Hz), 0.96 (9H, s), 0.13 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 166.8, 146.6, 146.2, 141.1, 136.6, 136.1, 129.6, 129.6, 128.8, 128.6, 128.6, 127.1, 125.3, 62.5, 60.9, 37.8, 34.0, 30.3, 25.9, 25.9, 25.9, 19.5, 18.4, 14.3, -5.4, -5.4.

MS-FAB: m/z 293, 379, 425 [M + H]⁺.


1-[4-(7-Hydroxymethyl-1-methylindan-4-yl)-phenyl]ethanone (24)
To a solution of ethyl ester 23 (232 mg, 0.546 mmol) in THF (5.0 mL) was added LiBH₄ (59.0 mg, 2.73 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred at 50 °C for 20 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution at 0 °C, and the mixture was stirred at room temperature for 30 min. The mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a suspension of the above crude product and NaHCO₃ (344 mg, 4.10 mmol) in CH₂Cl₂ (5.5 mL) was added Dess-Martin periodinane (347 mg, 0.819 mmol) at 0 °C, the mixture was stirred at room temperature for 3 h. The reaction was quenched by addition of 1 : 1 mixture saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in THF (5.5 mL) was added CH₃MgBr (0.99 M in THF, 0.72 mL, 0.710 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution, and the mixture was extracted with AcOEt. The organic layer was washed with
H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a suspension of the above crude product and NaHCO₃ (458 mg, 5.46 mmol) in CH₂Cl₂ (7.0 mL) was added Dess-Martin periodinane (463 mg, 1.09 mmol) at 0 °C, the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of 1 : 1 mixture saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in THF (7.0 mL) was added a TBAF (1.0 M in THF, 1.60 mL, 1.60 mmol) at 0 °C, and the mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 3 : 1) to give alcohol 24 (128 mg, 84% yield, five steps) as a white solid.

Mp 136-137 ºC.
IR (neat): 3384, 1651, 1602, 1454, 1417 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 8.02 (2H, d, J = 8.3 Hz), 7.54 (2H, d, J = 8.3 Hz), 7.37 (1H, d, J = 7.6 Hz), 7.26 (1H, d, J = 7.6 Hz), 4.73-4.85 (2H, m), 3.46 (1H, m), 3.17 (1H, m), 2.79 (1H, m), 2.64 (3H, m), 2.20 (1H, m), 1.82 (1H, m), 1.63 (1H, br), 1.27 (3H, m, J = 7.2 Hz).
¹³C NMR (75 MHz, CDCl₃): δ = 198.1, 147.8, 146.2, 141.6, 136.7, 136.1, 135.6, 128.8, 128.5, 128.5, 127.4, 126.2, 62.7, 37.9, 33.9, 30.4, 26.6, 20.1.
MS-FAB: m/z 281 [M + H]⁺.
HRMS-FAB: m/z [M + H]⁺ calcd for C₁₉H₂₁O₂: 281.1542; found: 281.1541.

7-(4-Hydroxyphenyl)-3-methylindan-4-carbaldehyde (1)
To a solution of alcohol 24 (61.5 mg, 0.220 mmol) in CH₂Cl₂ (5.0 mL) were added mCPBA (65%, 184 mg, 1.65 mmol) and Sc(OTf)₃ (54.0 mg, 0.110 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred at room temperature for 72 h. The reaction mixture was extracted with CH₂Cl₂, and the organic layer was washed with saturated aqueous NaHCO₃ solution at three times and 10% Na₂S₂O₃ aqueous solution. The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 6 : 1), to give a mixture of the product and unidentified contaminants, which was used next reaction without further purification.

To a suspension of the above mixture and NaHCO₃ (83 mg, 0.985 mmol) in CH₂Cl₂
(4.0 mL) was added Dess-Martin periodinane (84 mg, 0.197 mmol) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. The reaction was quenched by addition of 1:1 mixture saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification. To a solution of the above crude product in THF (3.0 mL) was added 10% HCl aqueous solution (3.0 mL) at 0 °C, and the mixture was stirred at room temperature for 24 h. The reaction mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous NaHCO₃ solution, H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a preparative TLC (hexane/AcOEt = 2 : 1) to give aldehyde 1 (22.7 mg, 41% yield, three steps) as a white solid.

Mp 142-143 ºC.

IR (neat): 3339, 1668, 1587, 1516, 1444 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 10.20 (1H, s), 7.72 (1H, d, J = 7.9 Hz), 7.37 (2H, d, J = 8.5 Hz), 7.33 (1H, d, J = 8.5 Hz), 6.92 (2H, d, J = 8.5 Hz), 4.93 (1H, s), 3.94 (1H, m), 3.16 (1H, m), 2.81 (1H, m), 2.21 (1H, m), 1.90 (1H, m), 1.29 (3H, d, J = 7.0 Hz).

¹³C NMR (100 MHz, CDCl₃): δ = 192.3, 155.6, 152.8, 143.8, 142.5, 132.7, 130.1, 129.9, 129.9, 129.9, 127.4, 115.4, 115.4, 38.0, 33.8, 30.0, 20.8.

MS-FAB: m/z 253 [M + H]+.

HRMS-FAB: m/z [M + H]+ calcd for C₁₇H₁₇O₂: 253.1229; found: 253.1240.

**Incargutine A (Reference 1)**

¹H NMR (400 MHz, CDCl₃): δ = 10.18 (1H, s), 7.69 (1H, d, J = 7.8 Hz), 7.30 (1H, d, J = 8.6 Hz), 7.30 (1H, d, J = 8.6 Hz), 7.24 (1H, d, J = 7.8 Hz), 6.92 (1H, d, J = 8.6 Hz), 3.55-3.62 (1H, m), 3.31-3.37 (2H, m), 2.31-2.35 (1H, m), 1.77-1.80 (1H, m), 0.80 (3H, d, J = 7.0 Hz).

¹³C NMR (100 MHz, CDCl₃): δ = 192.5, 155.6, 148.4, 146.4, 144.3, 132.9, 131.0, 129.8, 129.7, 129.7, 128.4, 115.4, 115.4, 115.4, 37.8, 33.4, 29.9, 19.8.

**4-(7-Dimethoxymethyl-1-methylindan-4-yl)phenol (2)**

To a solution of aldehyde 1 (11.1 mg, 0.0440 mmol) and CH(OCH₃)₃ (0.050 mL, 0.440 mmol) in CH₃CN (1.0 mL) was added Amberlyst-15 (7.7 mg) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The mixture was filtered and then extracted with AcOEt. The organic layer was washed with H₂O and brine, and dried over MgSO₄,
filtered and concentrated under reduced pressure. The residue was purified by a preparative TLC (hexane/AcOEt = 3 : 1) to give acetal 2 (10.8 mg, 82% yield) as a white solid.

Mp 137-138 °C.

IR (neat): 3303, 1610, 1591, 1520, 1269, 1103 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.41 (1H, d, J = 7.9 Hz), 7.32 (2H, d, J = 8.5 Hz), 7.18 (1H, d, J = 7.9 Hz), 6.88 (2H, d, J = 8.5 Hz), 5.51 (1H, s), 4.73 (1H, br), 3.48 (1H, m), 3.40 (3H, s), 3.35 (3H, s), 3.14 (1H, m), 2.75 (1H, m), 2.17 (1H, m), 1.80 (1H, m), 1.26 (3H, d, J = 6.8 Hz).

¹³C NMR (100 MHz, CDCl₃): δ = 154.6, 147.8, 141.3, 138.1, 133.9, 131.7, 129.9, 129.9, 126.7, 124.8, 115.1, 115.1, 102.0, 53.3, 53.2, 37.9, 34.3, 30.3, 20.0.

MS-FAB: m/z 267, 298 [M⁺].


Incargutine B (Reference 1)

¹H NMR (400 MHz, CDCl₃): δ = 7.36 (1H, d, J = 7.8 Hz), 7.24 (1H, d, J = 8.5 Hz), 7.24 (1H, d, J = 8.5 Hz), 7.07 (1H, d, J = 7.8 Hz), 6.87 (1H, d, J = 8.5 Hz), 6.87 (1H, d, J = 8.5 Hz), 5.41 (1H, s), 3.53-3.58 (1H, m), 3.37 (3H, s), 3.37 (3H, s), 2.95-2.99 (2H, m), 2.26-2.29 (1H, m), 1.67-1.71 (1H, m), 0.80 (3H, d, J = 6.9 Hz).

¹³C NMR (100 MHz, CDCl₃): δ = 155.4, 146.9, 141.9, 138.8, 133.5, 132.2, 129.7, 129.7, 127.6, 124.5, 115.2, 115.2, 102.7, 53.2, 53.2, 38.2, 33.3, 29.3, 19.9.

6-[5-(tert-Butyl-dimethyl-silanyl)-1-hydroxy-pent-4-ynyl]-3-ethoxy-cyclohex-2-eno ne (28)

To a solution of LDA, which was prepared in situ by mixing i-Pr₂NH (7.5 mL, 53.0 mmol) and n-BuLi (1.39 M in hexane, 35.0 mL, 48.9 mmol) in THF (116 mL) at -78 °C for 1 h under Ar atmosphere, was added a solution of commercially available cyclohexenone 13 (6.6 mL, 48.9 mmol) at -78 °C, and the mixture was stirred at the same temperature for 1 h. To the mixture was added a solution of aldehyde 27 (8.0 g, 40.8 mmol) and DMPU (9.9 mL, 81.6 mmol) in THF (20 mL) at -78 °C, and the mixture was stirred at -78 °C for 2.5 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution, the mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 5 : 1) to give alcohol 28 (10.1 g, 74% yield) as a colorless oil.

IR (neat): 3431, 2171, 1635, 1603, 1471, 1461, 1191 cm⁻¹.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 5.35$ (1H, m), 4.80 (1H, br), 3.86-3.97 (3H, m), 2.34-2.51 (4H, m), 1.91-2.26 (2H, m), 1.60-1.82 (3H, m), 1.37 (3H, t, $J = 7.0$ Hz), 0.91 (9H, s), 0.07 (6H, s).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 203.3, 201.4, 178.3, 178.1, 107.9, 107.6, 103.0, 102.5, 82.7, 82.4, 70.9, 69.7, 64.5, 64.4, 49.9, 49.4, 33.1, 32.1, 28.7, 28.6, 25.9, 23.6, 21.8, 16.8, 16.3, 15.5, 13.9, -4.7.

MS-FAB: $m/z$ 337 [$M + H]^+$.  
HRMS-FAB: $m/z$ [M + H]$^+$ calcd for C$_{19}$H$_{33}$O$_3$Si: 337.2199; found: 337.2197.

6-[5-(tert-Butyl-dimethyl-silanyl)-pent-4-ynylidene]-3-ethoxy-cyclohex-2-enone (29)

To a solution of alcohol 28 (10.1 g, 30.0 mmol) and Et$_3$N (6.2 mL, 45.0 mmol) in CH$_2$Cl$_2$ (100 mL) was added MsCl (2.8 mL, 36.0 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred at the same temperature for 1 h. The reaction was quenched by addition of saturated aqueous NaHCO$_3$ solution at 0 °C, and the mixture was extracted with AcOEt. The organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in toluene (100 mL) was added DBU (13.4 mL, 90.0 mmol) at room temperature, the mixture was stirred at 60 °C for 12 h. The reaction mixture was added a saturated aqueous NaHCO$_3$ solution at 0 °C, and the mixture was extracted with AcOEt. The organic layer was washed with H$_2$O and brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 5 : 1) to give cyclohexenone 29 (6.89 g, 72% yield, two steps) as a colorless oil.

IR (neat): 2172, 1668, 1604, 1471, 1191 cm$^{-1}$.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 6.60$ (1H, m), 5.46 (1H, m), 3.93 (2H, q, $J = 7.0$ Hz), 2.69 (2H, q, $J = 6.4$ Hz), 2.34-2.48 (6H, m), 1.37 (3H, t, $J = 7.0$ Hz), 0.91 (9H, s), 0.07 (6H, s).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 188.9, 176.8, 134.2, 133.8, 106.6, 103.0, 83.1, 64.2, 28.8, 27.3, 25.9, 25.9, 25.9, 23.7, 19.4, 16.3, 14.0, -4.7, -4.7.

MS-FAB: $m/z$ 319 [$M + H]^+$.  
HRMS-FAB: $m/z$ [M + H]$^+$ calcd for C$_{19}$H$_{31}$O$_2$Si: 319.2093; found: 319.2105.

6-[5-(tert-Butyl-dimethyl-silanyl)-1-methyl-pent-4-ynyl]-3-ethoxy-cyclohex-2-enone (30)
To a suspension of CuI (10.3 g, 54.0 mmol) in THF (78.0 mL) was added MeMgBr (0.99 M in THF, 109 mL, 108 mmol) at 0 °C, the mixture was stirred at same temperature for 20 min. The mixture was added to a solution of cyclohexenone 29 (6.89 g, 21.6 mmol) and DMPU (7.8 mL, 64.8 mmol) in THF (30 mL) at 0 °C, the mixture was stirred at same temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution at 0 °C, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 10 : 1) to give cyclohexenone 30 which is inseparable diastereomeric mixture (6.60 g, 91% yield, dr = 2.2 : 1) as a colorless oil.

IR (neat): 2170, 1650, 1605, 1471, 1461, 1187 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.32 (1H, m), 3.87 (2H, q, J = 7.0 Hz), 2.05-2.49 (6H, m), 1.51-1.99 (4H, m), 1.35 (3H, t, J = 7.0 Hz), 0.81-0.96 (12H, m), 0.06 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 200.6, 200.5, 176.8, 176.7, 108.0, 107.8, 102.9, 102.8, 82.4, 82.2, 64.0, 50.5, 49.3, 33.4, 32.4, 31.1, 30.5, 28.5, 28.2, 25.9, 22.5, 21.3, 18.1, 18.0, 16.7, 16.3, 15.3, 14.0, -4.7.

MS-FAB: m/z 335 [M + H]⁺.
HRMS-FAB: m/z [M + H]⁺ calcd for C₂₀H₃₅O₂Si: 335.2406; found: 335.2415.

3-Ethoxy-6-(1-methyl-pent-4-ynyl)-cyclohex-2-enone (31)

To a solution of cyclohexenone 30 (6.60 g, 19.7 mmol) in THF (20 mL) was added a TBAF (1.0 M in THF, 39.4 mL, 39.4 mmol) at room temperature, and the mixture was stirred for 18 h at 30 °C. The reaction was quenched by addition of water (150 mL), the mixture was extracted with AcOEt, and the organic layer was washed with brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 5 : 1) to give cyclohexenone 31 which is inseparable diastereomeric mixture (3.93 g, 91% yield) as a colorless oil.

IR (neat): 3298, 2116, 1649, 1604, 1454, 1428, 1187 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 5.33 (1H, s), 3.88 (2H, q, J = 7.0 Hz), 2.06-2.51 (6H, m), 1.50-2.02 (5H, m), 1.35 (3H, t, J = 7.0 Hz), 0.80-0.97 (3H, m).

¹³C NMR (75 MHz, CDCl₃): δ = 200.4, 200.4, 176.9, 176.8, 103.0, 102.9, 84.5, 84.3, 68.3, 68.0, 64.1, 50.5, 49.1, 33.2, 32.2, 30.9, 30.2, 28.6, 28.4, 22.2, 21.1, 16.8, 16.7, 16.5, 15.1, 14.0.

MS-FAB: m/z 221 [M + H]⁺.
HRMS-FAB: m/z [M + H]⁺ calcd for C₁₄H₂₁O₂: 221.1542; found: 221.1533.
3-(4-Iodo-phenyl)-4-(1-methyl-pent-4-ynyl)-cyclohex-2-enone (32)

To a solution of 1,4-diiodobenzene (23.6 g, 71.6 mmol) in 1,4-dioxane (70.0 mL) was added \( i-\text{PrMgCl} \) (2.0 M in THF, 35.8 mL, 71.6 mmol) at 0 °C under Ar atmosphere and the mixture was stirred at the room temperature for 1 h. To the mixture was added a solution of cyclohexenone 31 (3.93 g, 17.9 mmol) in 1,4-dioxane (20.0 mL) at the room temperature, and the mixture was stirred at 80 °C for 2 h. Then the reaction was quenched by addition of 10% HCl (90.0 mL) at 0 °C and the mixture was stirred at the same temperature for 30 min. The reaction mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous NaHCO\(_3\) solution, H\(_2\)O and brine, and dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 8 : 1) to give iodide 32 which is inseparable diastereomeric mixture (5.20 g, 77% yield, two steps) as a white solid.

Mp 92-95 ºC.

IR (neat): 3280, 2114, 1652, 1597, 1483 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.72-7.75 \) (2H, m), 7.12-7.17 (2H, m), 6.23 (1H, m), 2.89-3.07 (1H, m), 2.37-2.61 (2H, m), 1.72-2.25 (6H, m), 1.43-1.61 (1H, m), 1.26 (1H, m), 0.72-0.90 (3H, m).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 199.5, 199.4, 163.4, 163.2, 139.4, 138.8, 138.0, 137.9, 128.8, 128.4, 128.4, 95.3, 83.7, 83.3, 68.9, 68.5, 41.8, 39.3, 35.3, 34.8, 33.8, 33.3, 33.3, 31.5, 23.1, 21.6, 17.8, 16.3, 16.3, 15.0.

MS-FAB: \( m/z \) 379 [M + H]+.

HRMS-FAB: \( m/z \) [M + H]+ calcd for C\(_{18}\)H\(_{20}\)I0: 379.0559; found: 379.0559.

Ethyl 4-[6-(5-ethoxycarbonyl-1-methylpent-4-ynyl)-3-oxocyclohex-1-enyl]benzoate (33)

To a solution of iodide 32 (3.86 g, 10.2 mmol) and 1,2-bis(trimethylsilyloxy)ethane (10.0 mL, 40.8 mmol) in CH\(_2\)Cl\(_2\) (51.0 mL) was added TMSOTf (0.37 mL, 2.14 mmol) at -70 °C under Ar atmosphere, and the mixture was stirred for 40 h at same temperature. The reaction was quenched by addition of pyridine (4.3 mL). After concentration of the solvent under reduced pressure, the residue was purified by a silica gel column chromatography (hexane/AcOEt = 8 : 1), to give a mixture of the product and unidentified contaminants, which was used next reaction without further purification.

To a suspension of the above mixture in THF (57.0 mL) was added a \( i-\text{PrMgCl} \) (2.0 M in THF, 17.0 mL, 34.3 mmol) at -10 °C under Ar atmosphere, and the mixture was
stirred at the room temperature for 1 h. To the reaction mixture was added ethyl chloroformate (6.6 mL, 68.6 mmol) at 0 °C, and the mixture was stirred at 40 °C for 1 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution at 0 °C, the mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in acetone (86.0 mL) and water (6.0 mL) was added TsOH·H₂O (326 mg, 1.72 mmol) at 0 °C, and the mixture was stirred at room temperature for 18 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 3 : 1) to give cyclohexenone 33 which is inseparable diastereomeric mixture (1.70 g, 42% yield, three steps) as a colorless oil.

IR (neat): 2234, 1708, 1671, 1604, 1447 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.08 (2H, d, J = 8.1 Hz), 7.44-7.48 (2H, m), 6.25 (1H, s), 4.39 (2H, q, J = 7.0 Hz), 4.14-4.28 (2H, m), 3.05 (1H, m), 1.95-2.62 (5H, m), 1.49-1.67 (3H, m), 1.22-1.43 (7H, m), 0.70-0.92 (3H, m).

¹³C NMR (75 MHz, CDCl₃): δ = 199.2, 199.2, 166.0, 166.0, 163.0, 153.6, 153.5, 144.1, 143.6, 131.2, 131.1, 130.1, 130.0, 129.8, 129.3, 126.7, 126.6, 88.0, 87.8, 73.8, 73.3, 61.9, 61.7, 61.1, 61.1, 42.0, 39.6, 35.5, 34.8, 34.0, 33.2, 32.3, 30.5, 23.0, 21.4, 17.8, 16.6, 16.6, 14.7, 14.2, 13.9, 13.9.

MS-FAB: m/z 323, 351, 397 [M + H]⁺.


Ethyl 7-(4-ethoxycarbonylphenyl)-5-hydroxy-1-methylindan-4-carboxylate (34)

To a solution of cyclohexenone 33 (1.70 g, 4.29 mmol) in xylene (80%, 43 mL) was added In(OTf)₃ (482 mg, 0.858 mmol) at room temperature under Ar atmosphere, and the mixture was stirred at 130 °C for 5 h. After the reaction mixture was cooled to room temperature, the reaction mixture was passed through a silica gel (ca. 100 g) with hexane/AcOEt (1 : 0 to 1 : 2). The eluent was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/AcOEt = 20 : 1) to give 4-phenylindane 34 (822 mg, 52% yield) as a white solid.

Mp 100-101 °C.

IR (neat): 1715, 1658, 1602, 1557, 1456 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 11.20 (1H, s), 8.10 (2H, d, J = 8.3 Hz), 7.47 (2H, d, J
= 8.3 Hz), 6.76 (1H, s), 4.37-4.47 (4H, m), 3.44 (1H, m), 3.23-3.28 (2H, m), 2.29 (1H, m), 1.69 (1H, m), 1.39-1.47 (6H, m), 0.71 (3H, d, J = 6.8 Hz).

\[^{13}\text{C} \text{NMR} \left(75 \text{ MHz, } \text{CDCl}_3\right): \delta = 171.3, 166.5, 161.4, 146.9, 145.2, 144.4, 138.5, 129.7, 129.7, 128.3, 128.3, 116.7, 109.5, 61.4, 61.0, 41.0, 37.2, 33.5, 33.0, 20.3, 14.2, 14.2.\]

MS-FAB: m/z 323, 369 [M + H]^+.


Ethyl 4-(6-hydroxy-7-hydroxymethyl-3-methylindan-4-yl)benzoate (35)

To a solution of 4-phenylindane 34 (691 mg, 1.88 mmol) in THF (19.0 mL) was added BH\(_3\)-SMe\(_2\) (90%, 0.26 mL, 2.44 mmol) at 0 °C, and the mixture was stirred at room temperature for 18 h. The reaction was quenched by slow addition of saturated aqueous NH\(_4\)Cl solution at 0 °C, and the mixture was stirred at the same temperature for 30 min. The mixture was extracted with AcOEt and the organic layer was washed with H\(_2\)O and brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 3 : 1) to give diol 35 (590 mg, 96% yield) as a colorless oil.

IR (neat): 3314, 1692, 1605, 1563 cm\(^{-1}\).

\[^{1}\text{H} \text{NMR} \left(300 \text{ MHz, } \text{CDCl}_3\right): \delta = 8.07 (2H, d, J = 8.1 \text{ Hz}), 7.53 (1H, s), 7.46 (2H, d, J = 8.1 \text{ Hz}), 6.69 (1H, s), 4.96 (2H, d, J = 5.0 \text{ Hz}), 4.40 (2H, q, J = 7.2 \text{ Hz}), 3.50 (1H, m), 2.74-2.94 (2H, m), 2.25-2.37 (2H, m), 1.70 (1H, m), 1.41 (3H, t, J = 7.2 \text{ Hz}), 0.73 (3H, d, J = 7.0 \text{ Hz}).\]

\[^{13}\text{C} \text{NMR} \left(75 \text{ MHz, } \text{CDCl}_3\right): \delta = 166.9, 155.3, 146.1, 142.6, 138.1, 129.6, 129.6, 128.9, 128.5, 128.5, 120.0, 116.0, 61.7, 61.7, 61.0, 37.6, 33.4, 29.1, 20.3, 14.2.\]

MS-FAB: m/z 326 [M]^+.

HRMS-FAB: m/z [M]^+ calcd for C\(_{20}\)H\(_{22}\)O\(_4\): 326.1518; found: 326.1502.

Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-6-hydroxy-3-methylindan-4-yl]benzoate (36)

To a solution of diol 35 (590 mg, 1.81 mmol) and Et\(_3\)N (1.3 mL, 9.05 mmol) in CH\(_2\)Cl\(_2\) (18.0 mL) was added TBSCl (300 mg, 1.99 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of a saturated aqueous NH\(_4\)Cl solution, and the mixture was extracted with AcOEt. The organic layer was washed with H\(_2\)O and brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 15 : 1) to give TBS ether 36 (773 mg, 97% yield) as a colorless oil.
IR (neat): 3344, 1716, 1607, 1582, 1462, 1271, 1100 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.49\) (1H, s), 8.07 (2H, d, \(J = 8.3\) Hz), 7.48 (2H, d, \(J = 8.3\) Hz), 6.67 (1H, s), 4.96 (2H, s), 4.40 (2H, q, \(J = 7.2\) Hz), 3.48 (1H, m), 2.65-2.86 (2H, m), 2.32 (1H, m), 1.69 (1H, m), 1.41 (3H, t, \(J = 7.2\) Hz), 0.96 (9H, s), 0.72 (3H, d, \(J = 6.8\) Hz), 0.18 (6H, m).

\(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 166.7, 155.8, 146.2, 141.2, 137.8, 137.5, 129.6, 129.6, 129.0, 128.5, 128.5, 119.0, 116.2, 63.5, 60.9, 37.5, 33.4, 28.9, 25.6, 25.6, 25.6, 20.3, 18.0, 14.2, -5.8, -5.8.

MS-FAB: \(m/z\) 439 [M - H]\(^+\).

HRMS-FAB: \(m/z\) [M - H]\(^+\) calcd for C\(_{26}\)H\(_{35}\)O\(_4\)Si: 439.2305; found: 439.2285.

Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-3-methyl-6-trifluoromethanesulfonyloxyindan-4-yl]benzoate (37)

To a solution of TBS ether 36 (717 mg, 1.63 mmol) and pyridine (1.3 mL, 16.3 mmol) in CH\(_2\)Cl\(_2\) (16.3 mL) was added Tf\(_2\)O (0.53 mL, 3.26 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of a saturated aqueous NaHCO\(_3\) solution, and the mixture was extracted with AcOEt. The organic layer was washed with H\(_2\)O and brine, dried over MgSO\(_4\), filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 30 : 1) to give triflate 37 (888 mg, 95% yield) as a colorless oil.

IR (neat): 1708, 1608, 1471, 1420, 1200, 1073 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.11\) (2H, d, \(J = 8.3\) Hz), 7.45 (2H, d, \(J = 8.3\) Hz), 6.98 (1H, s), 4.77 (2H, s), 4.41 (2H, q, \(J = 7.2\) Hz), 3.54 (1H, m), 2.98-3.17 (2H, m), 2.37 (1H, m), 1.76 (1H, m), 1.42 (3H, t, \(J = 7.2\) Hz), 0.92 (9H, s), 0.77 (3H, d, \(J = 7.0\) Hz), 0.12 (6H, s).

\(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 166.4, 147.3, 147.2, 146.1, 144.3, 138.6, 129.8, 129.8, 128.6, 128.5, 128.5, 120.8, 120.3, 116.6, 61.0, 57.8, 38.1, 33.3, 29.8, 25.8, 25.8, 20.3, 19.7, 18.3, 14.2, -5.7, -5.7.

MS-FAB: \(m/z\) 515, 527, 571 [M - H]\(^+\).

HRMS-FAB: \(m/z\) [M - H]\(^+\) calcd for C\(_{27}\)H\(_{34}\)F\(_3\)O\(_6\)SSi: 571.1797; found: 571.1813.

Ethyl 4-[7-(tert-butyldimethylsilanyloxymethyl)-3-methylindan-4-yl]benzoate (38)

To a solution of triflate 37 (851 mg, 1.48 mmol), HCO\(_2\)H (0.9 mL, 23.8 mmol) and Et\(_3\)N (4.9 mL, 35.5 mmol) in DMF (15.0 mL) were added Pd(OAc)\(_2\) (33.2 mg, 0.148
mmol) and PPh₃ (77.6 mg, 0.296 mmol) at room temperature, and the mixture was stirred at 60 °C for 2 h. After the reaction mixture was cooled to room temperature, the reaction was quenched by addition of brine, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 50 : 1) to give ethyl ester 38 (518 mg, 83% yield) as a colorless oil.

IR (neat): 1716, 1609, 1462, 1270, 1099 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.08 (2H, d, J = 8.3 Hz), 7.48 (2H, d, J = 8.3 Hz), 7.33 (1H, d, J = 7.7 Hz), 7.12 (1H, d, J = 7.7 Hz), 4.73 (2H, s), 4.40 (2H, q, J = 7.2 Hz), 3.58 (1H, m), 3.15 (1H, m), 2.78-2.97 (2H, m), 2.33 (1H, m), 1.72 (1H, m), 1.41 (3H, t, J = 7.2 Hz), 0.96 (9H, s), 0.77 (3H, d, J = 7.0 Hz), 0.12 (6H, s).

¹³C NMR (75 MHz, CDCl₃): δ = 166.8, 146.6, 146.4, 141.0, 136.8, 136.6, 129.6, 129.6, 128.9, 128.7, 128.7, 127.8, 124.6, 63.2, 60.9, 38.1, 33.2, 28.7, 25.9, 25.9, 20.0, 18.3, 14.3, -5.4, -5.4.

MS-FAB: m/z 293, 379, 423 [M - H]+.


1-[4-(7-Hydroxymethyl-3-methylindan-4-yl)-phenyl]ethanone (39)
To a solution of ethyl ester 38 (385 mg, 0.908 mmol) in THF (9.0 mL) was added LiBH₄ (158 mg, 7.26 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred at 50 °C for 24 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution at 0 °C, and the mixture was stirred at room temperature for 30 min. The mixture was extracted with AcOEt, and the organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a suspension of the above crude product and NaHCO₃ (762 mg, 9.08 mmol) in CH₂Cl₂ (9.0 mL) was added Dess-Martin periodinane (770 mg, 1.82 mmol) at 0 °C, the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of 1 : 1 mixture saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in THF (9.0 mL) was added CH₃MgBr (0.97 M in THF, 1.2 mL, 1.18 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH₄Cl solution,
and the mixture was extracted with AcOEt. The organic layer was washed with H2O and brine, dried over MgSO4, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a suspension of the above crude product and NaHCO3 (762 mg, 9.08 mmol) in CH2Cl2 (9.0 mL) was added Dess-Martin periodinane (770 mg, 1.82 mmol) at 0 °C, the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of 1 : 1 mixture saturated aqueous Na2S2O3 solution and saturated aqueous NaHCO3 solution, and the mixture was extracted with AcOEt. The organic layer was washed with H2O and brine, dried over MgSO4, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in THF (9.0 mL) was added a TBAF (1.0 M in THF, 2.7 mL, 2.72 mmol) at 0 °C, and the mixture was stirred at 30 °C for 18 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 4 : 1) to give alcohol 39 (187 mg, 73% yield, five steps) as a colorless oil.

IR (neat): 3384, 1652, 1601, 1458, 1415 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 8.01 (2H, d, J = 8.3 Hz), 7.51 (2H, d, J = 8.3 Hz), 7.31 (1H, d, J = 7.7 Hz), 7.14 (1H, d, J = 7.7 Hz), 4.73 (2H, d, J = 5.7 Hz), 3.60 (1H, m), 2.88-3.08 (2H, m), 2.65 (3H, s), 2.36 (1H, m), 1.75 (1H, m), 1.60 (1H, m), 0.79 (3H, d, J = 7.0 Hz).

13C NMR (75 MHz, CDCl3): δ = 198.1, 146.9, 146.7, 142.2, 137.3, 136.3, 135.7, 128.9, 128.5, 128.5, 128.0, 125.6, 63.4, 38.2, 33.1, 28.8, 26.5, 20.0.

MS-FAB: m/z 281 [M + H]+.


2,3-Dihydro-7-(4-hydroxyphenyl)-1-methyl-1H-inden-4-carboxaldehyde [(±)-Incargutine A, 25]

To a solution of alcohol 39 (85.5 mg, 0.305 mmol) in CH2Cl2 (5.0 mL) were added mCPBA (65%, 306 mg, 2.75 mmol) and Sc(OTf)3 (75.1 mg, 0.153 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred at room temperature for 96 h. The reaction mixture was extracted with CH2Cl2, and the organic layer was washed with saturated aqueous NaHCO3 solution at three times and 10% Na2S2O3 aqueous solution. The organic layer was dried over MgSO4, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 4 : 1), to give a mixture of the product and unidentified contaminants, which was used next reaction without further purification.
To a suspension of the above mixture and NaHCO₃ (156 mg, 1.86 mmol) in CH₂Cl₂ (5.0 mL) was added Dess-Martin periodinane (157 mg, 0.371 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of 1:1 mixture saturated aqueous Na₂S₂O₃ solution and saturated aqueous NaHCO₃ solution, and the mixture was extracted with AcOEt. The organic layer was washed with H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

To a solution of the above crude product in THF (3.0 mL) was added 10% HCl aqueous solution (3.0 mL) at 0 °C, and the mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous NaHCO₃ solution, H₂O and brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a preparative TLC (hexane/AcOEt = 8 : 1) to give (±)-Incargutine A 25 (30.8 mg, 40% yield, three steps) as a white solid.

Mp 166-167 ºC.

IR (neat): 3259, 1663, 1610, 1585, 1515, 1438 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 10.18 (1H, s), 7.69 (1H, d, J = 7.8 Hz), 7.31 (2H, d, J = 8.5 Hz), 7.24 (1H, m), 6.91 (2H, d, J = 8.5 Hz), 4.91 (1H, m), 3.59 (1H, m), 3.26-3.40 (2H, m), 2.36 (1H, m), 1.79 (1H, m), 0.82 (3H, d, J = 6.9 Hz).

¹³C NMR (100 MHz, CDCl₃): δ = 192.7, 155.3, 148.4, 146.5, 144.3, 133.0, 130.9, 129.9, 129.7, 129.7, 128.4, 115.4, 115.4, 37.7, 33.3, 29.9, 19.7.

MS-FAB: m/z 253 [M + H]⁺.


4-[2,3-Dihydro-7-(dimethoxymethyl)-3-methyl-1H-inden-4-yl]phenol [(±)-Incargutine B, 26]

To a solution of (±)-Incargutine A 25 (10.5 mg, 0.0416 mmol) and CH(OCH₃)₃ (0.050 mL, 0.440 mmol) in CH₃CN (2.0 mL) was added Amberlyst-15 (7.3 mg) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ solution. The mixture was filtered and then extracted with AcOEt. The organic layer was washed with H₂O and brine, and dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by a preparative TLC (hexane/AcOEt = 5 : 1) to give (±)-Incargutine B 26 (11.5 mg, 93% yield) as a colorless oil.

IR (neat): 3375, 1612, 1592, 1519, 1214, 1108 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.36 (1H, d, J = 7.8 Hz), 7.27 (2H, m), 7.08 (1H, d, J
= 7.8 Hz), 6.86 (2H, d, \( J = 8.4 \) Hz), 5.41 (1H, s), 4.81 (1H, m), 3.55 (1H, m), 3.37 (6H, s), 2.92-3.04 (2H, m), 2.30 (1H, m), 1.71 (1H, m), 0.80 (3H, d, \( J = 6.9 \) Hz).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 154.6, 146.9, 142.0, 138.7, 134.1, 132.2, 129.8, 129.8, 127.6, 124.6, 115.1, 115.1, 102.7, 53.2, 53.2, 38.2, 33.3, 29.3, 19.9.\)

MS-FAB: \( m/z \) 267, 298 \([M]^+\).

HRMS-FAB: \( m/z \) [M]\(^+\) calcd for C\(_{19}\)H\(_{22}\)O\(_3\): 298.1569; found: 298.1579.
$^1$H and $^{13}$C NMR of New Compounds

**$^1$H NMR Spectra**

- Chemical Shift (ppm): 3.08, 3.76, 2.08, 9.45, 2.06, 2.07, 2.05, 2.00, 4.71, 0.99, 1.01, 1.52, 1.55, 1.56, 1.59, 1.91, 1.94, 1.94, 1.96, 1.98, 2.00, 2.28, 3.33, 3.35, 4.34, 4.36, 4.37, 4.38, 4.40, 4.50

**$^{13}$C NMR Spectra**

- Chemical Shift (ppm): 16.85, 19.62, 20.99, 30.57, 32.50, 63.13, 72.97, 75.35, 77.43, 127.55, 128.40, 131.24, 135.03, 138.64, 139.20, 170.36

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Note: The spectra and chemical shifts are typical of organic compounds, indicating the presence of functional groups such as alcohols, ethers, and aromatic rings.