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Supporting Information

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Tandem Ring Expansion of Alkenylbenzocyclobutenol Derivatives into Substituted Naphthols

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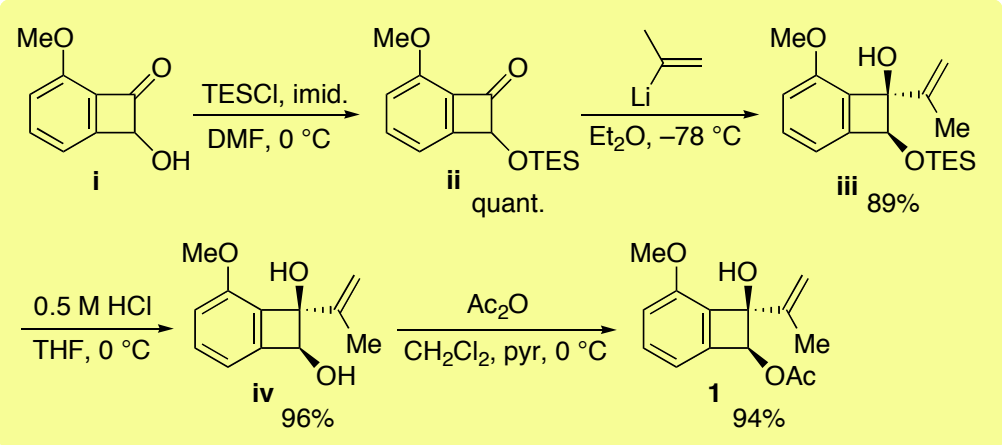
General Experimental Procedures

Ethereal solvents (anhydrous; *Kanto Chemical Co., Inc.*) were used as received. CH_3CN was distilled from CaH_2, and stored over 4Å molecular sieves. CH_2Cl_2 was successively distilled from P_2O_5 and CaH_2, and stored over 4Å molecular sieves. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 (Merck Art 7734, 70–230 mesh) was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF_{254} (Art 7747).

Melting point (mp) determinations were performed by using a Yanako MP-S3 instrument and are uncorrected. ^1H NMR and ^{13}C NMR were measured on a JEOL JNM lambda-400, and a Bruker DRX-500 spectrometer. Infrared (IR) spectra were recorded on a Jasco IR-Report-100, a Horiba FT-710 spectrometer. Mass spectra were obtained with a JEOL JMS 700 spectrometer.

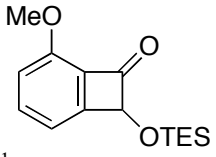
1. General Procedures for the Synthesis of Alkenylbenzocyclobutenes

Scheme I. Synthesis of alkenylbenzocyclobutene **1**



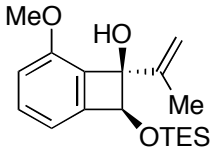
*Synthesis of siloxyketone **ii***:

To a solution of the hydroxyketone **i**[1)] (1.00 g, 6.09 mmol) in DMF (20 mL) was added imidazole (1.25 g, 18.3 mmol) and TESCl (1.81 g, 12.0 mmol) in DMF (5.0 mL) at 0 °C. After 10 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with Et_2O (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to afford **ii** (1.69 g, quant.) as a colorless oil.



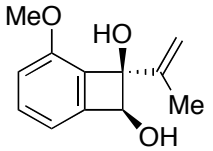
^{1}H NMR (500 MHz, $CDCl_3$, δ)
0.73 (q, 6H, J = 7.6 Hz), 1.03 (t, 9H, J = 7.6 Hz), 4.13 (s, 3H), 5.70 (s, 1H), 6.90 (d, 1H, J = 8.4 Hz), 7.17 (d, 1H, J = 7.2 Hz), 7.50 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
4.9, 6.7, 59.8, 84.9, 114.7, 117.4, 131.6, 138.0, 154.3, 157.2, 186.5;
IR (neat)
2950, 2900, 2875, 1760, 1595, 1570, 1480, 1450, 1430, 1405, 1350, 1275, 1235, 1190, 1160, 1140, 1120, 1040, 1025, 1010, 970, 940, 880, 865, 790, 770, 740 cm^{-1};
Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.71; H, 7.96. Found: C, 64.96; H, 8.11.

*Synthesis of silyl ether **iii***:
To a solution of 2-bromopropene (0.15 mL, 1.69 mmol) in Et_2O (2.0 mL) was added *t*-BuLi (1.57 M in pentane, 2.0 mL, 3.14 mmol) at –78 °C, and the reaction was further stirred for 1 h, to which was added ketone **ii** (306 mg, 1.10 mmol) in Et_2O (2.5 mL). After 10 min, the reaction was quenched with water. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 95/5) to afford **iii** (314 mg, 89.1%) as a colorless oil.



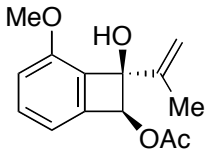
^{1}H NMR (400 MHz, $CDCl_3$, δ)
0.73 (q, 6H, J = 7.6 Hz), 1.03 (t, 9H, J = 7.6 Hz), 1.75 (s, 3H), 3.87 (s, 1H), 3.91 (s, 3H), 4.96 (s, 1H), 5.02 (s, 1H), 5.04 (s, 1H), 6.81 (d, 1H, J = 8.4 Hz), 6.82 (d, 1H, J = 7.2 Hz), 7.25 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz);
^{13}C NMR (100 MHz, acetone-d_6, δ)
5.3, 6.9, 19.1, 57.8, 78.4, 84.6, 112.1, 116.1, 116.8, 131.9, 134.3, 148.0, 148.5, 156.1;
IR (neat)
3480, 2950, 2905, 2875, 1600, 1575, 1475, 1430, 1345, 1265, 1230, 1200, 1145, 1110, 1090, 1055, 1030, 1010, 960, 900, 830, 780, 745 cm^{-1};
Anal. Calcd for $C_{18}H_{28}O_3Si$: C, 67.46; H, 8.81. Found: C, 67.21; H, 9.09.

*Synthesis of diol **iv**:*
To a solution of silyl ether **iii** (292 mg, 0.911 mmol) in MeOH (5.0 mL) was added 0.5 M HCl (1.0 mL) at 0 °C. After 10 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 7/3) to afford **iv** (180 mg, 95.8%). Recrystallization from hexane–EtOAc gave **iv** as colorless prisms: mp 64.2–64.8 °C.



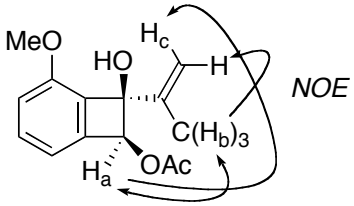
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.78 (s, 3H), 3.11 (d, 1H, J = 7.6 Hz), 3.40 (s, 1H), 3.87 (s, 3H), 4.98 (s, 1H), 5.04 (s, 1H), 5.05 (d, 1H, J = 7.6 Hz), 6.83 (d, 1H, J = 8.0 Hz), 6.93 (d, 1H, J = 7.2 Hz), 7.29 (dd, 1H, J_1 = 7.2, = 8.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
18.8, 57.0, 77.3, 84.0, 112.4, 115.3, 115.7, 131.6, 132.3, 145.5, 147.0, 154.8;
IR (KBr)
3421, 3384, 3083, 3056, 3010, 2946, 2919, 2844, 1650, 1608, 1577, 1481, 1436, 1367, 1332, 1255, 1199, 1143, 1072, 1029, 939, 923, 798, 752, 703 cm^{-1};
Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.83; H, 6.97.

*Synthesis of acetate **1**:*
To a solution of diol **iv** (382 mg, 1.85 mmol) in CH_2Cl_2–pyridine (5.0/1.0 mL) was added Ac_2O (1.0 mL, 9.8 mmol) and 4-dimethylaminopyridine (20 mg, 0.16 mmol) at 0 °C. After 30 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with Et_2O (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 8/2) to afford **1** (432 mg, 94.1%) as a colorless oil.



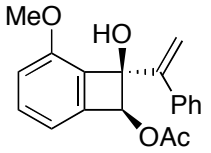
^{1}H NMR (400 MHz, $CDCl_3$, δ)
1.85 (s, 3H), 2.19 (s, 3H), 2.91 (s, 1H), 3.90 (s, 3H), 4.98 (s, 1H), 5.02 (s, 1H), 5.89 (s, 1H), 6.87 (d, 1H, J = 8.4 Hz), 6.93 (d, 1H, J = 7.5 Hz), 7.31 (dd, 1H, J_1 = 7.5, J_2 = 8.4 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ)
18.6, 21.1, 57.4, 79.2, 84.8, 113.4, 116.3, 116.6, 131.9, 133.0, 143.2, 145.3, 154.8, 170.0;
IR (neat)
3470, 2970, 2940, 1740, 1600, 1570, 1480, 1430, 1365, 1270, 1220, 1140, 1070, 1050, 1030, 950, 920, 900, 790, 760, 740 cm^{-1};
FAB-MS: 249 ($[M+H]^+$);
Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.75; H, 6.21.

[#1]The stereochemistry of **1** was determined on the basis of the observed NOE shown below.

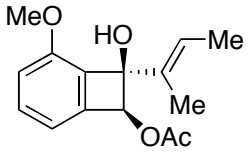


H_a: 5.89 ppm, H_b: 1.85 ppm, H_c: 4.98 ppm

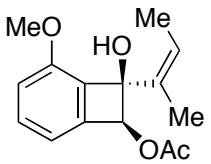
Starting compounds **6–8**, **14** and **17** were also prepared via addition of stereodefined alkenyl lithium to siloxy ketone **ii**.



acetate **6** (colorless prisms)
Mp 92.3–93.0 °C (hexane)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.14 (s, 3H), 3.26 (s, 1H), 3.96 (s, 3H), 5.39 (s, 1H), 5.40 (s, 1H), 5.90 (s, 1H), 6.89 (d, 1H, J = 8.4 Hz), 6.90 (d, 1H, J = 7.5 Hz), 7.25–7.36 (m, 6H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
20.9, 57.4, 79.5, 84.0, 116.0, 116.8, 117.0, 127.6, 127.8, 127.9, 132.0, 133.0, 138.6, 143.4, 149.8, 154.6, 170.2;
IR (KBr)
3465, 3073, 3062, 3016, 2970, 2945, 2843, 1725, 1604, 1579, 1443, 1438, 1371, 1151, 1074, 1047, 1027, 920, 821, 781, 758 cm^{-1};
FAB-MS: 311 ($[M+H]^+$);
Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.79; H, 6.06.

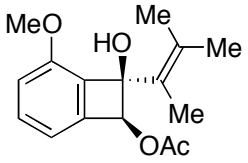


acetate **7** (colorless prisms)
Mp 87.3–88.1 °C (hexane)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.63 (d, 3H, J = 6.7 Hz), 1.74 (q, 3H, J = 1.0 Hz), 2.17 (s, 3H), 2.91 (s, 1H), 3.89 (s, 3H), 5.51 (qq, 1H, J_1 = 1.0, J_2 = 6.7 Hz), 5.85 (s, 1H), 6.87 (d, 1H, J = 8.4 Hz), 6.92 (d, 1H, J = 7.2 Hz), 7.30 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
12.1, 13.5, 21.1, 57.3, 79.3, 86.0, 115.9, 116.8, 122.8, 131.8, 133.5, 135.9, 143.3, 155.1, 170.2;
IR (KBr)
3480, 3072, 3027, 2998, 2969, 2933, 2856, 1749, 1614, 1583, 1482, 1442, 1378, 1349, 1303, 1259, 1222, 1145, 1064, 1031, 925, 867, 788 cm^{-1};
FAB-MS: 263 ($[M+H]^+$);
Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.51; H, 7.15.

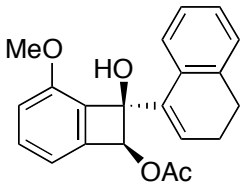


acetate **8** (colorless oil)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.51 (d, 3H, J = 7.3 Hz), 1.78 (d, 3H, J = 1.4 Hz), 2.18 (s, 3H), 2.76 (s, 1H), 3.92 (s, 3H), 5.51 (qq, 1H, J_1 = 1.4, J_2 = 7.3 Hz), 5.64 (s, 1H), 6.84 (d, 1H, J = 8.4 Hz), 6.92 (d, 1H, J = 7.2 Hz), 7.31 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
14.1, 21.1, 22.4, 56.8, 80.5, 83.5, 115.3, 116.6, 124.1, 131.9, 134.9, 136.0, 143.6, 154.5, 170.0;
IR (neat)

3470, 2960, 2940, 2850, 1740, 1600, 1575, 1480, 1430, 1362, 1270, 1230, 1140, 1070, 1030, 910, 785, 760 cm^{-1};
FAB-MS: 263 ($[M+H]^+$);
Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.96; H, 6.80.



acetate **14** (colorless oil)
^{1}H NMR (500 MHz, acetone-d_6, δ)
1.69 (s, 3H), 1.70 (s, 6H), 2.08 (s, 3H), 3.88 (s, 3H), 4.53 (s, 1H), 5.81 (s, 1H), 6.84 (d, 1H, J = 7.2 Hz), 6.88 (d, 1H, J = 8.3 Hz), 7.28 (dd, 1H, J_1 = 7.2, J_2 = 8.3 Hz);
^{13}C NMR (125 MHz, acetone-d_6, δ)
17.3, 20.9, 21.9, 22.4, 56.9, 81.7, 85.6, 115.3, 117.3, 130.0, 131.0, 132.1, 137.5, 145.3, 155.6, 170.6;
IR (neat)
3467, 2998, 2938, 2915, 2859, 2842, 1741, 1606, 1581, 1484, 1438, 1373, 1270, 1230, 1072, 1037, 941, 910, 786, 748 cm^{-1};
FAB-MS: 276 (M^+);
Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.81; H, 7.52.



acetate **17** (colorless prisms)[a]
Mp 188.7–189.3 °C (hexane)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.17–2.37 (m, 2H), 2.23 (s, 3H), 2.66–2.84 (m, 2H), 3.29 (s, 1H), 3.97 (s, 3H), 5.91 (s, 1H), 6.08 (dd, 1H, J_1 = 4.2, J_2 = 5.2 Hz), 6.92 (d, 1H, J = 8.3 Hz), 6.97 (d, 1H, J = 7.2 Hz), 7.14–7.22 (m, 3H), 7.32 (dd, 1H, J_1 = 7.2, J_2 = 8.3 Hz), 7.44 (d, 1H, J = 7.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
21.2, 23.2, 28.1, 57.4, 79.9, 84.4, 115.5, 117.7, 124.8, 126.3, 127.0, 127.8, 130.5, 131.9, 132.0, 133.9, 136.9, 137.2, 144.1, 154.9, 170.2;
IR (KBr)
3500, 3059, 3016, 2995, 2948, 2881, 2833, 1731, 1606, 1484, 1436, 1405, 1373, 1268, 1250, 1238, 1153, 1089, 1041, 933, 895, 839, 777, 733, 717 cm^{-1};
FAB-MS: 336 (M^+);
Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.74; H, 5.76.

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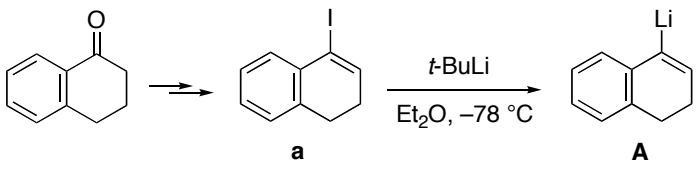
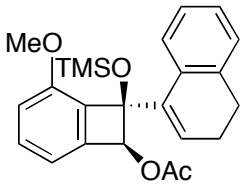
[a] Alkenyllithium **A** was generated by halogen–lithium exchange of iodoalkene **a**,[2] prepared from 1-tetralone.

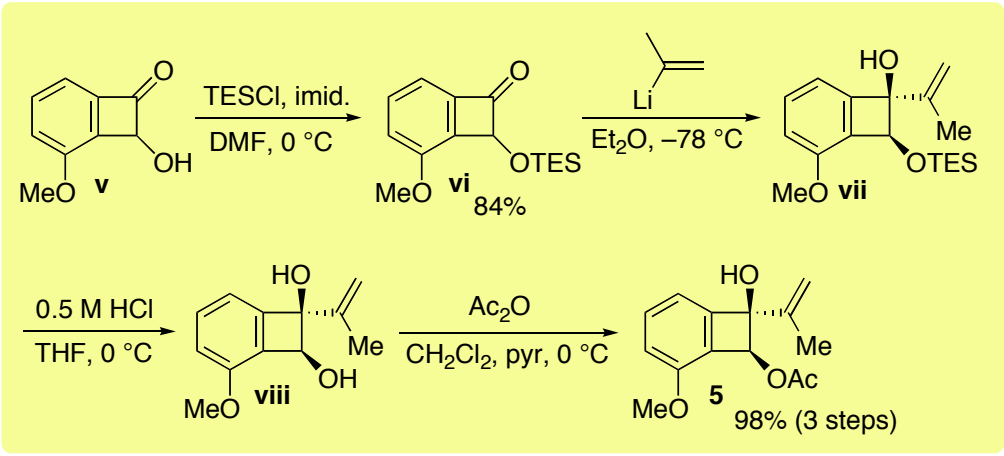


*Synthesis of silyl ether **19**:*
To a solution of acetate **17** (45.6 mg, 0.136 mmol) in DMF (1.5 mL) was added imidazole (33.2 mg, 0.488 mmol) and TMSCl (26.6 mg, 0.245 mmol) at 0 °C. After stirred for 30 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with Et_2O (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 9/1) to afford silyl ether **19** (53.1 mg, 95.6%) as a colorless oil.

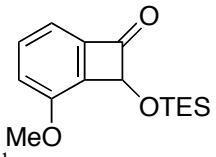


^{1}H NMR (500 MHz, $CDCl_3$, δ)
0.11 (s, 9H), 2.23 (s, 3H), 2.20–2.34 (m, 2H), 2.64–2.80 (m, 2H), 3.92 (s, 3H), 5.76 (s, 1H), 6.14 (t, 1H, J = 4.7 Hz), 6.89 (d, 1H, J = 8.4 Hz), 6.97 (d, 1H, J = 7.2 Hz), 7.12–7.19 (m, 3H), 7.36 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz), 7.58 (d, 1H, J = 7.2 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
1.2, 21.3, 23.2, 28.1, 55.2, 79.8, 86.3, 112.0, 117.6, 125.6, 126.0, 126.6, 127.4, 128.2, 131.7, 132.7, 134.3, 136.8, 138.5, 145.1, 153.9, 170.7;
IR (neat)
3057, 3016, 2954, 2939, 2893, 2835, 1745, 1606, 1485, 1456, 1439, 1371, 1273, 1247, 1230, 1157, 1115, 1078, 1045, 1034, 957, 937, 870, 843, 806, 769, 746 cm^{-1};
EI-MS (70ev) *m/z* 408 (M^+), 408 (base peak), 349, 318, 215;
HRMS *m/z* 408.1741 (408.1757 calcd for $C_{24}H_{28}O_4Si$, M^+).

Scheme II. Synthesis of alkenylbenzocyclobutene **5**

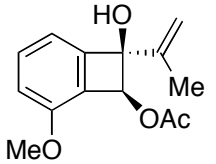


*Synthesis of siloxy ketone **vi**:*
To a solution of the hydroxyketone **v**[1)] (300 mg, 1.83 mmol) in DMF (6.0 mL) was added imidazole (435 mg, 6.39 mmol) and TESCl (393 mg, 2.61 mmol) in DMF (1.0 mL) at 0 °C. After 20 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with Et_2O (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 96/4) to afford **vi** (426 mg, 83.6%) as a colorless oil.



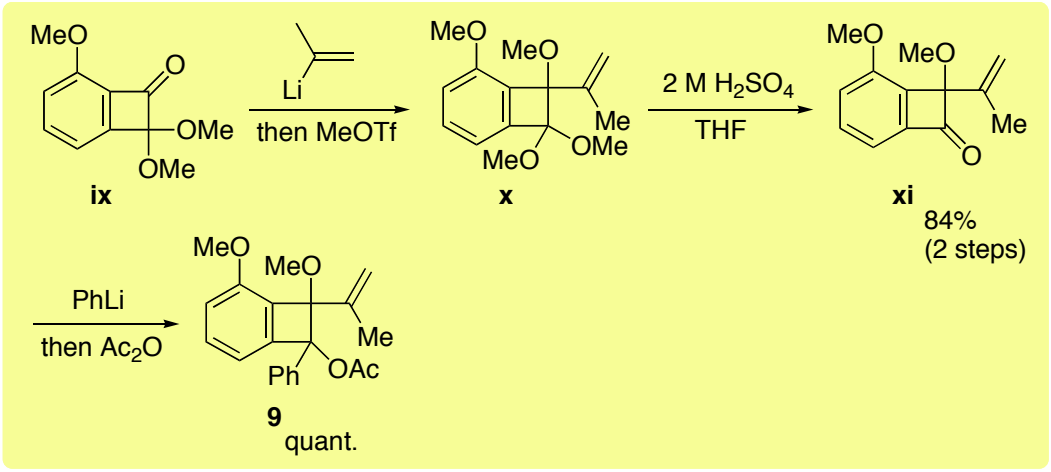
^{1}H NMR (500 MHz, $CDCl_3$, δ)
0.73 (q, 6H, J = 7.8 Hz), 1.00 (t, 9H, J = 7.8 Hz), 4.01 (s, 3H), 5.85 (s, 1H), 7.01 (d, 1H, J = 8.4 Hz), 7.06 (d, 1H, J = 7.2 Hz), 7.43 (dd, 1H, J_1 = 7.2, J_2 = 8.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
4.9, 6.7, 57.0, 85.8, 113.2, 120.8, 132.9, 142.2, 148.7, 156.4, 190.6;
IR (neat)
2956, 2911, 2877, 1768, 1600, 1575, 1486, 1459, 1438, 1272, 1232, 1189, 1164, 1105, 1056, 1006, 976, 866, 786, 744 cm^{-1};
Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.71; H, 7.96. Found: C, 64.47; H, 7.68.

*Synthesis of acetate **5**:*
To a solution of 2-bromopropene (545 mg, 4.50 mmol) in Et_2O (3.0 mL) was added t-BuLi (1.47 M in pentane, 5.4 mL, 7.9 mmol) at –78 °C, and the reaction was further stirred for 1 h, to which was added siloxyketone **vi** (331 mg, 1.19 mmol) in Et_2O (2.0 mL). After 10 min, the reaction was quenched with water. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4). Evaporation of the solvents gave the crude alcohol **vii**.
To a solution of the crude product **vii** in MeOH (4.0 mL) was added 0.5 M HCl (0.5 mL) at 0 °C. After 30 min, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4). Evaporation of the solvents gave the crude diol **viii**.
To a solution of the crude diol **viii** in pyridine (2.0 mL) was added Ac_2O (1.0 mL) at 0 °C. After 0.5 h, the reaction was stopped by adding sat. aq. $NaHCO_3$. The products were extracted with Et_2O (×3), and the combined organic extracts were successively washed with 0.5 M HCl and brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 8/2) to afford **5** (290 mg, 98.2%) as white solid. Recrystallization from hexane gave **5** as colorless prisms: mp 75.6–76.1 °C.



^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.91 (s, 3H), 2.21 (s, 3H), 2.58 (s, 1H), 3.86 (s, 3H), 4.99–5.01 (m, 2H), 6.21 (s, 1H), 6.84 (d, 1H, J = 8.3 Hz), 6.93 (d, 1H, J = 7.2 Hz), 7.36 (dd, 1H, J_1 = 7.2, J_2 = 8.3 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
18.4, 21.2, 56.4, 78.8, 85.1, 113.8, 114.8, 115.5, 125.0, 132.5, 144.3, 150.6, 155.7, 169.9;
IR (KBr)
3502, 3002, 2973, 2923, 2840, 1720, 1612, 1486, 1442, 1376, 1340, 1280, 1228, 1137, 1064, 1039, 908, 782, 740 cm^{-1};
FAB-MS: 249 ($[M+H]^+$);
Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.45; H, 6.25.

Scheme III. Synthesis of acetate **9**



*Synthesis of alkenylbenzocyclobutenone **xi**:*[3)]

To a solution of 2-bromopropene (746 mg, 6.25 mmol) in Et_2O (3.0 mL) was slowly added t-BuLi (1.62 M in pentane, 5.6 ml, 2.56 mmol) at –78 °C, and the reaction mixture was further stirred for 1 h, to which was added ketone **ix**[1)] (746 mg, 3.58 mmol) in Et_2O (3.0 ml) and then methyl trifluoromethanesulfonate (1.44 g, 8.78 mmol) in Et_2O (0.5 mL). After the reaction was warmed to room temperature in 2 h, the solution was recooled to 0 °C. For removal of excess methyl trifluoromethanesulfonate, N, N-dimethylethylenediamine (1.8 ml, 1.1 mmol) was added, and the reaction was further stirred for 10 min. After the reaction mixtures were acidified with 2 M HCl, the products were extracted with EtOAc and the combined organic extracts were washed with sat. aq. $NaHCO_3$, brine, and dried with Na_2SO_4. Evaporation of the solvents gave the crude product **x** .

To a solution of the crude product **x** in THF (2.0 mL) was added 2 M H_2SO_4 (0.5 mL) at 0 °C. After the reaction was warmed up to room temperature, and further stirred for 8 h, the reaction was stopped by adding sat. $NaHCO_3$. The products were extracted with Et_2O and combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 96/4) to give **xi** (552 mg, 84%) as a colorless oil.

ketone **xi**

^{1}H NMR (500 MHz, $CDCl_3$, δ)

1.85 (s, 3H), 3.35 (s, 3H), 3.92 (s, 3H), 4.99 (s, 1H), 5.09 (s, 1H), 7.07 (d, 1H, J = 8.3 Hz), 7.12 (d, 1H, J = 7.6 Hz), 7.50 (dd, 1H, J_1 = 7.6, J_2 = 8.3 Hz);

^{13}C NMR (125 MHz, $CDCl_3$, δ)

19.5, 53.8, 56.9, 104.2, 113.3, 115.1, 120.0, 133.2, 142.3, 142.9, 149.3, 156.9, 192.3;

IR (neat)

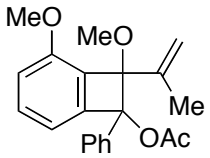
3075, 2940, 2825, 1760, 1660, 1640, 1595, 1565, 1480, 1450, 1430, 1370, 1340, 1270, 1220, 1180, 1150, 1110, 1065, 1030, 940, 905, 870, 830, 820, 790, 740, 680 cm^{-1};

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.28; H, 6.35.

*Synthesis of acetate **9**:*

To a solution of bromobenzene (259 mg, 1.65 mmol) in Et_2O (2.0 mL) was slowly added t-BuLi (1.46 M in pentane, 1.8 mL, 2.63 mmol) at –78 °C, and the reaction mixture was further stirred for 1 h; to the stirred solution was added ketone **xi** (188 mg, 0.859 mmol) in Et_2O (4.0 mL) and Ac_2O (267 mg, 2.62 mmol) in Et_2O (2.0 mL). After the mixture was warmed to room temperature in 1 h and stirred for an additional 30 min, the reaction was quenched with sat. aq. $NaHCO_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and

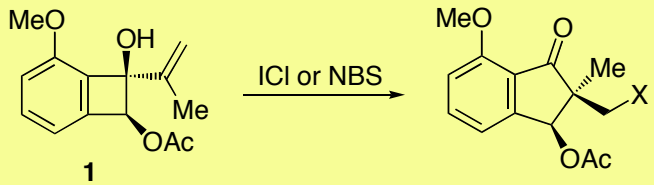
concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 95/5) to afford **9** (295 mg, quant.) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.98 (s, 3H), 1.99 (s, 3H), 3.10 (s, 3H), 3.86 (s, 3H), 4.99 (s, 1H), 5.20 (s, 1H), 6.94 (d, 1H, J = 8.6 Hz), 7.28–7.33 (m, 5H), 7.33 (d, 1H, J = 7.3 Hz), 7.45 (dd, 1H, J_1 = 7.3, J_2 = 8.6 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
18.7, 21.5, 53.7, 55.2, 91.1, 94.7, 111.7, 116.7, 120.0, 127.4, 127.5, 127.7, 131.5, 131.8, 138.4, 142.6, 145.1, 154.9, 169.4;
IR (neat)
3085, 3027, 2937, 2832, 1743, 1606, 1484, 1440, 1367, 1278, 1236, 1095, 1025, 958, 902, 786, 746 cm^{-1};
FAB-MS: 339 ($[M+H]^+$);
Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.28; H, 6.27.

2. General Procedures for the Halonium Ion Induced Ring Expansion

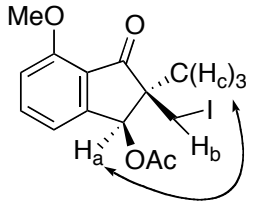
Scheme IV. Ring expansion of alkenylbenzocyclobutene **1** into halomethly indanone **2**



*Synthesis of iodomethlindanone **2a**:*
To a solution of ICl (30.5 mg, 0.188 mmol) in THF (1.5 mL) was added acetate **1** (31.1 mg, 0.125 mmol) in THF (1.5 mL) at 0 °C. After the mixture was warmed to room temperature and stirred for an additional 20 min, the reaction was quenched with 10% aq. $Na_2S_2O_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 8/2 ×4) to afford **2a-cis** (26.2 mg, 56.0%) and **2a-trans** (15.9 mg, 34.0%).

indanone **2a-cis** (colorless oil)
Rf 0.64 (hexane/acetone = 6/4)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.37 (s, 3H), 2.14 (s, 3H), 3.44 (d 1H, J = 10.3 Hz), 3.48 (d, 1H, J = 10.3 Hz), 3.97 (s, 3H), 6.02 (s, 1H), 6.96 (d, 1H, J = 8.2 Hz), 7.22 (d, 1H, J = 7.7 Hz), 7.63 (dd, 1H, J_1 = 7.7, J_2 = 8.2 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
9.0, 21.2, 25.3, 52.2, 56.0, 76.3, 112.0, 119.0, 122.5, 137.7, 151.0, 158.1, 170.5, 200.8;
IR (neat)
3014, 2975, 2929, 2875, 2840, 1737, 1716, 1596, 1482, 1375, 1309, 1282, 1236, 1209, 1037, 985, 777 cm^{-1};
EI-MS (70ev) *m/z* 374 (M^+), 374 (base peak), 315, 247, 205, 187, 161;
Anal. Calcd for $C_{14}H_{15}IO_4$: C, 44.94; H, 4.04. Found: C, 44.66; H, 4.16.

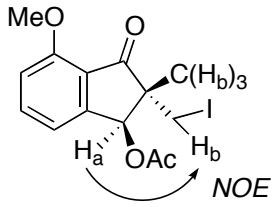
[#2] The stereochemistry of **2a-cis** was determined on the basis of the observed NOE shown below.



H_a: 6.02 ppm, H_c: 1.37 ppm

indanone **2a-trans** (colorless prisms)
Mp 147.5–148.2 °C (hexane/Et_2O)
Rf 0.55 (hexane/acetone = 6/4)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.22 (s, 3H), 2.19 (s, 3H), 3.49 (d, 1H, J = 10.0 Hz), 3.53 (d, 1H, J = 10.0 Hz), 3.98 (s, 3H), 6.31 (s, 1H), 6.94 (d, 1H, J = 8.4 Hz), 7.14 (d, 1H, J = 7.7 Hz), 7.63 (dd, 1H, J_1 = 7.7, J_2 = 8.4 Hz);
^{13}C NMR (125 MHz, acetone-d_6, δ)
12.5, 20.2, 20.7, 53.6, 56.1, 77.2, 112.7, 118.4, 123.4, 138.3, 152.6, 158.8, 171.5, 200.4;
IR (KBr)
3025, 2979, 2933, 2842, 1731, 1708, 1598, 1482, 1436, 1407, 1371, 1282, 1228, 1159, 1072, 1033, 977, 892, 798, 769, 717 cm^{-1};
EI-MS (70ev) *m/z* 374 (M^+), 374 (base peak), 247, 205, 187, 161;
Anal. Calcd for $C_{14}H_{15}IO_4$: C, 44.94; H, 4.04. Found: C, 45.24; H, 4.32.

[#3]The stereochemistry of **2a-trans** was determined on the basis of the observed NOE shown below.



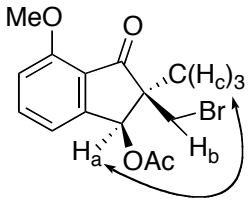
H_a: 6.31 ppm, H_b: 3.49, 3.53 ppm

*Synthesis of bromomethyl indanone **2b**:*
To a solution of NBS (40.7 mg, 0.229 mmol) in CH_2Cl_2 (1.9 mL) was added acetate **1** at –78 °C. After the mixture was warmed up to –10 °C, and further stirred for 1 h, the reaction was stopped by adding water. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 8/2 ×3) to afford **2b-cis** (38.7 mg, 76.1%) and **2b-trans** (12.0 mg, 23.6%).

indanone **2b-cis** (colorless oil)
Rf 0.55 (hexane/acetone = 6/4)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.40 (s, 3H), 2.13 (s, 3H), 3.62 (d, 1H, J = 10.4 Hz), 3.68 (d, 1H, J = 10.4 Hz), 3.97 (s, 3H), 6.10 (s, 1H), 6.96 (d, 1H, J = 8.3 Hz), 7.20 (d, 1H, J = 7.5 Hz), 7.63 (dd, 1H, J_1 = 7.5, J_2 = 8.3 Hz) ;
^{13}C NMR (125 MHz, $CDCl_3$, δ)
21.1, 22.9, 35.2, 53.2, 56.0, 75.9, 112.0, 118.9, 122.7, 137.7, 151.4, 158.1, 170.6, 201.7;
IR (neat)
3018, 2969, 2935, 2842, 1747, 1716, 1597, 1482, 1454, 1373, 1284, 1234, 1189, 1081, 983, 946, 923, 854, 808, 779, 755 cm^{-1};
EI-MS (70ev) *m/z* 326, 328 (M^+), 326, 328 (base peak), 247, 205, 161, 146, 129;

Anal. Calcd for $C_{14}H_{15}BrO_4$: C, 51.40; H, 4.62. Found: C, 51.61; H, 4.91.

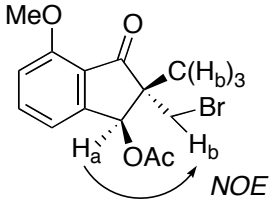
[#4]The stereochemistry of **2b-cis** was determined on the basis of the observed NOE shown below.



H_a: 6.10 ppm, H_c: 1.40 ppm

indanone **2b-trans** (colorless oil)
Rf 0.54 (hexane/acetone = 6/4)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.17 (s, 3H), 2.19 (s, 3H), 3.69 (d, 1H, J = 9.9 Hz), 3.75 (d, 1H, J = 9.9 Hz), 3.98 (s, 3H), 6.42 (s, 1H), 6.94 (d, 1H, J = 8.3 Hz), 7.14 (d, 1H, J = 7.6 Hz), 7.65 (dd, 1H, J_1 = 7.6, J_2 = 8.3 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
18.9, 20.8, 37.1, 54.1, 56.0, 75.1, 111.4, 117.8, 123.1, 137.5, 152.1, 158.0, 171.0, 201.0;
IR (neat)
3018, 2973, 2935, 2842, 1738, 1716, 1598, 1483, 1454, 1413, 1373, 1282, 1234, 1174, 1078, 1035, 980, 904, 802, 775 cm^{-1};
EI-MS (70ev) *m/z* 326, 328 (M^+), 326, 328 (base peak), 247, 205, 161, 146, 129;
Anal. Calcd for $C_{14}H_{15}BrO_4$: C, 51.40; H, 4.62. Found: C, 51.62; H, 4.86.

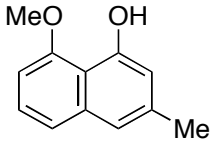
[#5]The stereochemistry of **2b-trans** was determined on the basis of the observed NOE shown below.



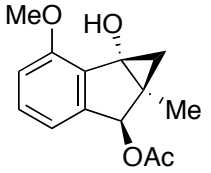
H_a: 6.42 ppm, H_b: 3.69, 3.75 ppm

3. General experimental procedures for the synthesis of naphthols (one-pot procedure)
*Synthesis of naphthol **4***:
To a solution of ICl (114 mg, 0.702 mmol) in THF (1.5 mL) was added acetate 1 (121 mg, 0.489 mmol) in THF (2.0 mL) at 0 °C, and the reaction was further stirred for 40 min at room temperature. SmI_2 (0.07 M in CH_3CN, 24 mL, 1.7 mmol)[b] was added to the reaction mixture at 0 °C and the temperature raised to room temperature. After 4 h, the reaction was quenched with sat. aq. NH_4Cl. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel flash column chromatography (hexane/EtOAc = 9/1) to give naphthol **4** (89.3 mg, 97.0%). Recrystallization from hexane–EtOAc gave **4** as colorless prisms: mp 91.9–92.7 °C.

[b] **Preparation of SmI_2 in CH_3CN**: A mixture of samarium powder (722 mg, 4.80 mmol) and 1,2-diiodomethane (677 mg, 2.40 mmol) in CH_3CN (20 mL) was stirred at room temperature. After 4h, the mixture turned dark green and a solution of SmI_2 was obtained. The concentration of SmI_2 was determined by iodometric titration (0.074 M).

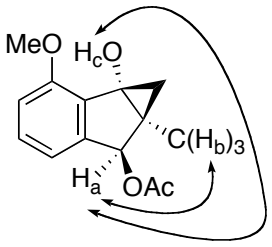


^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.42 (s, 3H), 4.04 (s, 3H), 6.70 (d, 1H, J = 7.6 Hz), 6.73 (d, 1H, J = 1.2 Hz), 7.09 (br s, 1H), 7.26 (dd, 1H, $J_1 = J_2 = 7.6$ Hz), 7.32 (d, 1H, J = 7.6 Hz), 9.23 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
21.7, 56.0, 103.0, 112.2, 113.2, 118.2, 121.2, 125.6, 136.8, 137.8, 154.1, 156.0;
IR (KBr)
3361, 3052, 2971, 2938, 2834, 1641, 1577, 1508, 1438, 1371, 1280, 1234, 1187, 1160, 1093, 1056, 964, 838, 792, 750, 717 cm^{-1};
EI-MS (70ev) *m/z* 188 (M^+), 188 (base peak), 173, 145, 127, 115;
Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.83; H, 6.54.



cyclopropanol **3** (colorless oil)
^{1}H NMR (500 MHz, acetone-d_6, δ)
0.92 (d, 1H, J = 5.0 Hz), 1.01 (d, 1H, J = 5.0 Hz), 1.37 (s, 3H), 2.05 (s, 3H), 3.82 (s, 3H), 4.83 (s, 1H), 6.21 (s, 1H), 6.73 (d, 1H, J = 7.5 Hz), 6.86 (d, 1H, J = 8.2 Hz), 7.12 (dd, 1H, $J_1 = 7.5$, $J_2 = 8.2$ Hz);
^{13}C NMR (125 MHz, acetone-d_6, δ)
15.6, 21.0, 29.0, 29.9, 55.9, 68.7, 82.9, 112.4, 118.5, 129.3, 135.2, 140.8, 157.0, 171.7;
IR (neat)
3401, 2992, 2952, 2933, 2871, 2836, 1733, 1594, 1484, 1438, 1371, 1268, 1236, 1139, 1089, 1029, 1020, 987, 906, 804, 765 cm^{-1};
EI-MS (70ev) *m/z* 248 (M^+), 248 (base peak), 220, 205, 189, 174, 145;
Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.51; H, 6.63.

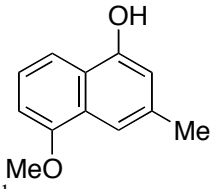
[#6]The stereochemistry of cyclopropanol **3** was determined on the basis of the observed NOE shown below.



NOE

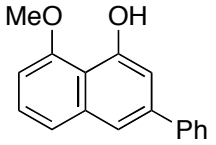
H_a: 6.21 ppm, H_b: 1.37 ppm, H_c: 4.83 ppm

*Synthesis of naphthol **10**:*
According to the procedure described for the synthesis of **4**, acetate **5** (49.5 mg, 0.119 mmol) gave, after purified by silica-gel flash column chromatography (hexane/EtOAc = 8/2), naphthol **10** (31.7 mg, 84.6%). Recrystallization from hexane–EtOAc gave **10** as colorless prisms: mp 157.3–158.3 °C.



^{1}H NMR (400 MHz, $CDCl_3$, δ)
2.46 (s, 3H), 3.99 (s, 3H), 5.13 (s, 1H), 6.70 (s, 1H), 6.81 (d, 1H, J = 7.6 Hz), 7.32 (dd, 1H, J_1 = 7.6, J_2 = 8.5 Hz), 7.63 (s, 1H), 7.66 (d, 1H, J = 8.5 Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ)
22.0, 55.5, 104.5, 111.5, 113.4, 113.8, 123.5, 124.2, 126.9, 135.2, 150.9, 154.8;
IR (KBr)
3423, 3062, 2998, 2962, 2917, 2834, 1637, 1602, 1521, 1448, 1398, 1348, 1259, 1199, 1124, 1049, 983, 889, 842, 800, 719 cm^{-1};
EI-MS (70ev) *m*/*z* 188 (M^+), 188 (base peak), 173, 145, 115;
Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.32; H, 6.46.

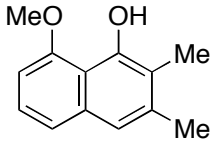
*Synthesis of arylnaphthalene **11**:*
According to the procedure described for the synthesis of **4**, acetate **6** (34.7 mg, 0.112 mmol) gave, after purified by PTLC (hexane/EtOAc = 8/2), arylnaphthalene **11** (26.9 mg, 96.0%). Recrystallization from hexane–EtOAc gave **11** as colorless prisms: mp 112.2–112.9 °C.



^{1}H NMR (500 MHz, $CDCl_3$, δ)
4.07 (s, 3H), 6.77 (d, 1H, J = 7.6 Hz), 7.17 (d, 1H, J = 2.0 Hz), 7.30–7.38 (m, 2H), 7.44–7.48 (m, 3H), 7.52 (d, 1H, J = 2.0 Hz), 7.70–7.72 (m, 2H), 9.35 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
56.1, 103.9, 109.7, 114.1, 116.9, 122.1, 126.0, 127.2, 127.4, 128.7, 136.9, 140.3, 140.5, 154.7, 156.0;
IR (KBr)
3355, 3052, 3004, 2937, 2842, 1635, 1612, 1573, 1519, 1496, 1442, 1384, 1294, 1241, 1091, 1037, 973, 858, 794, 755 cm^{-1};
EI-MS (70ev) *m*/*z* 250 (M^+), 250 (base peak), 207, 178;
Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.53; H, 5.44.

*Synthesis of naphthol **12**:*
According to the procedure described for the synthesis of **4**, acetate **8** (71.1 mg, 0.271 mmol) gave, after purified by PTLC (hexane/EtOAc = 8/2), naphthol **12** (42.2 mg, 77.0%). Recrystallization from hexane gave **12** as colorless prisms: mp 120.4–121.0 °C.

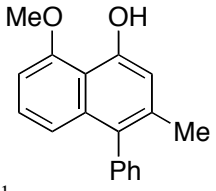
*Synthesis of naphthol **12** (from **7**):*
According to the procedure described for the synthesis of **4**, acetate **7** (45.4 mg, 0.173 mmol) gave, after purified by PTLC (hexane/EtOAc = 8/2), naphthol **12** (30.8 mg, 88.0%).



^{1}H NMR (500 MHz, $CDCl_3$, δ)

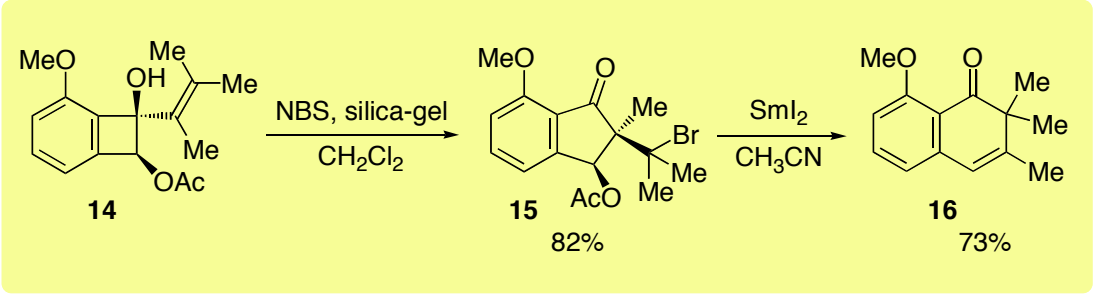
2.28 (s, 3H), 2.39 (s, 3H), 4.04 (s, 3H), 6.69 (d, 1H, J = 7.6 Hz), 7.13 (s, 1H), 7.21 (dd, 1H, J_1 = 7.6, J_2 = 8.4 Hz), 7.29 (d, 1H, J = 8.4 Hz), 9.56 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
11.6, 20.8, 56.1, 103.1, 113.2, 118.5, 118.7, 121.1, 124.5, 134.4, 137.6, 150.8, 155.5;
IR (KBr)
3363, 3058, 3021, 2971, 2944, 2844, 1635, 1610, 1581, 1504, 1452, 1355, 1317, 1274, 1240, 1145, 1095, 1006, 964, 840, 792, 756 cm^{-1};
EI-MS (70ev) *m/z* 202 (M^+), 202 (base peak), 187, 159, 141, 115;
Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 6.83.

*Synthesis of arylnaphthalene **13**:*
According to the procedure described for the synthesis of **4**, acetate **9** (16.7 mg, 0.049 mmol) gave, after purified by PTLC (hexane/EtOAc = 8/2), arylnaphthalene **13** (10.2 mg, 78.3%). Recrystallization from hexane–EtOAc gave **13** as colorless prisms: mp 151.6–152.5 °C.



^{1}H NMR (400 MHz, $CDCl_3$, δ)
2.14 (s, 3H), 4.07 (s, 3H), 6.73 (d, 1H, J = 7.6 Hz), 6.84 (s, 1H), 6.96 (dd, 1H, J_1 = 0.7 Hz, J_2 = 8.5 Hz), 7.12–7.23 (m, 3H), 7.36–7.49 (m, 3H), 9.40 (s, 1H);
^{13}C NMR (100 MHz, $CDCl_3$, δ)
20.9, 56.2, 103.1, 112.7, 113.4, 120.3, 125.4, 126.8, 128.4, 129.7, 130.7, 135.7, 136.0, 140.2, 153.4, 156.2;
IR (KBr)
3403, 3054, 3019, 2942, 2918, 2850, 1612, 1575, 1511, 1463, 1427, 1398, 1353, 1292, 1255, 1184, 1081, 962, 879, 808, 756, 703 cm^{-1};
EI-MS (70ev) *m/z* 264 (M^+), 264 (base peak), 221;
Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.52; H, 6.23.

Scheme V. Two-step synthesis of ketone **16**

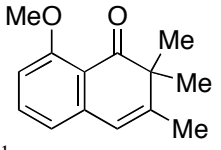


*Synthesis of indanone **15**:*
To a suspension of NBS (48.5 mg, 0.273 mmol) and silica-gel (Micro Bead 5D, Fuji Silysia chemical Ltd., 265 mg)[4)] in CH_2Cl_2 (1.0 mL) was added acetate **14** (24.7 mg, 0.0894 mmol) in CH_2Cl_2 (1.5 mL) at –78 °C. After the mixture was warmed to 10 °C in 1 h, the reaction was quenched with 10% aq. $Na_2S_2O_3$. The products were extracted with CH_2Cl_2 (×3), and the combined organic extracts were

washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to give indanone **15** (26.0 mg, 81.9%, cis/trans = 6/1) as a colorless oil.

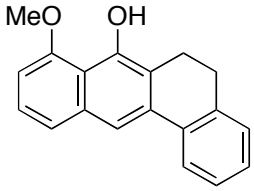
[#] *the underline's data corresponds to minor isomer's*

^{1}H NMR (500 MHz, acetone-d_6, δ)
1.46 (s, 3H), 1.58 (s, 3H), 1.89 (br-s, 3H), 2.06 (br-s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 3.92 (s, 3H), 3.93 (s, 3H), 6.17 (s, 1H), 6.21 (s, 1H), 7.05–7.12 (m, 2H), 7.12 (d, 1H, J = 8.4 Hz), 7.13 (d, 1H, J = 7.5 Hz), 7.70 (dd, 1H, J_1 = 7.5, J_2 = 8.4 Hz), 7.71–7.75 (m, 1H);
^{13}C NMR (125 MHz, acetone-d_6, δ)
21.5, 21.6, 24.2, 29.9, 30.0, 32.3, 33.7, 56.16, 56.23, 60.2, 60.7, 78.9, 79.2, 113.1, 113.3, 118.4, 118.5, 123.8, 138.4, 138.8, 152.0, 152.7, 158.9, 159.1, 170.6, 199.7;
IR (neat)
2999, 2974, 2939, 2875, 1743, 1714, 1597, 1483, 1458, 1437, 1373, 1292, 1280, 1228, 1198, 1097, 1030, 978, 895, 806, 777, 756 cm^{-1};
FAB-MS: 355, 357 ($[M+H]^+$);
Anal. Calcd for $C_{16}H_{19}BrO_4$: C, 54.10; H, 5.39. Found: C, 53.86; H, 5.41.
*Synthesis of ketone **16**:*
To a solution of indanone **15** (20.1 mg, 0.0566 mmol) in CH_3CN (1.0 mL) was added SmI_2 (0.07 M in CH_3CN, 1.5 ml, 0.105 mmol) at 0 °C. After the reaction was warmed to room temperature, and stirred for 45 min., the reaction was quenched with sat. aq. NH_4Cl. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified with PTLC (hexane/CH_2Cl_2/Et_2O = 5/2/3) to give ketone **16** (8.9 mg, 72.7%) as a colorless oil.



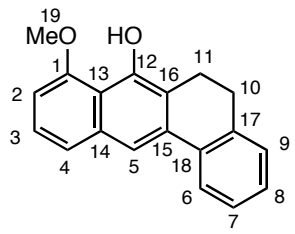
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.28 (s, 6H), 1.95 (s, 3H), 3.92 (s, 3H), 6.26 (s, 1H), 6.71 (d, 1H, J = 7.8 Hz), 6.82 (d, 1H, J = 8.3 Hz), 7.43 (dd, 1H, J_1 = 7.8, J_2 = 8.3 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
19.4, 23.7, 49.6, 56.0, 110.2, 116.7, 119.0, 121.2, 134.7, 140.8, 147.9, 160.3, 203.3;
IR (neat)
3006, 2958, 2921, 2840, 1675, 1589, 1571, 1473, 1434, 1317, 1284, 1251, 1189, 1122, 1078, 973, 881, 846, 802, 771, 701 cm^{-1};
EI-MS (70ev) *m/z* 216 (M^+), 216 (base peak), 201;
Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.00; H, 7.76.

*Synthesis of tetracycle **18**:*
To a solution of ICl (25.0 mg, 0. 154 mmol) in THF (1.2 mL) was added acetate **17** (34.1 mg, 0.101 mmol) in THF (1.5 mL) at 0 °C, and the reaction was further stirred for 30 min at room temperature, to which was added HMPA (0.15 mL) and SmI_2 (0.1 M in THF, 5.0 mL, 0.50 mmol) at 40 °C. After 10 min, the reaction was quenched with sat. aq. NH_4Cl. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 8/2) to give tetracycle **18** (20.8 mg, 75.3%). Recrystallization from hexane gave **18** as colorless prisms: mp 135.9–136.7 °C.



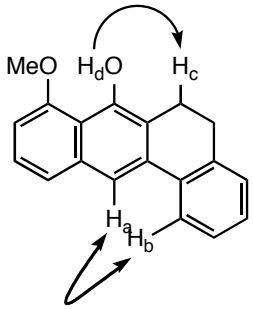
^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.88–2.92 (m, 2H), 3.03–3.06 (m, 2H), 4.05 (s, 3H), 6.73 (d, 1H, J = 7.6 Hz), 7.23–7.34 (m, 4H), 7.44 (d, 1H, J = 8.2 Hz), 7.73 (s, 1H), 7.89 (d, 1H, J = 7.7 Hz), 9.60 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
21.0, 28.8, 56.2, 104.0, 113.6, 114.3, 119.2, 122.3, 124.5, 125.0, 126.8, 127.7, 128.2, 134.4, 134.7, 135.2, 138.2, 150.1, 155.8;
IR (KBr)
3384, 3060, 3025, 2975, 2918, 2867, 2825, 1631, 1585, 1448, 1363, 1311, 1243, 1214, 1095, 1070, 1001, 978, 871, 771, 705 cm^{-1};
EI-MS (70ev) *m/z* 276 (M^+), 276 (base peak), 261, 215;
Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.36; H, 5.60.

[#7]The structure of tetracycle **18** was determined by NMR study (HMBC, NOE) as shown below.



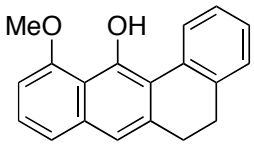
Key 2- and 3-bond HMBC correlations

position	δH (ppm)	carbon no. (ppm)
11	3.03–3.06	C-12 (150.1)
2	6.73	C-13 (114.3), C-1 (155.8)
5	7.73	C-13 (114.3), C-16 (119.2)
O<u>H</u>	9.60	C-13 (114.3), C-16 (119.2), C-12 (150.1)



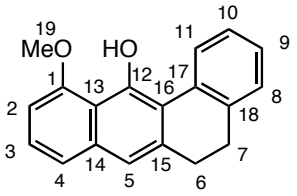
H_a: 7.73 ppm, H_b: 7.89 ppm,
H_c: 3.03–3.06 ppm, H_d: 9.60 ppm

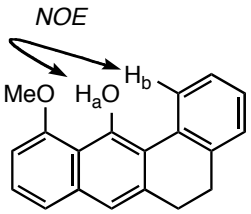
*Synthesis of tetracycle **20**:*
A solution of sily ether **19** (41.0 mg, 0.100 mmol) in xylene (2.0 mL) was heated at 140 °C for 13 h. After cooled to room temperature, the reaction mixture was evaporated to give crude ring expanded product.
To a solution of crude silyl ether in MeOH (1.5 mL) was added PPTS (5.0 mg, 0.020 mmol) at room temperature. After stirred for 1 h, the reaction was quenched with sat. aq. $NaHCO_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 9/1) to give tetracycle **20** (21.1 mg, 76.4%) as a colorless oil.



^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.81–2.85 (m, 2H), 2.90–2.93 (m, 2H), 4.07 (s, 3H), 6.74 (d, 1H, J = 7.6 Hz), 7.17–7.34 (m, 6H), 8.57 (d, 1H, J = 8.0 Hz), 10.2 (s, 1H);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
30.1, 31.1, 56.3, 104.0, 114.8, 116.8, 117.0, 121.3, 125.8, 126.1, 126.4, 127.5, 129.0, 133.1, 135.6, 138.8, 139.7, 151.7, 156.5;
IR (neat)
3346, 3055, 3014, 2939, 2895, 2839, 1631, 1583, 1485, 1450, 1431, 1362, 1267, 1234, 1092, 1061, 980, 951, 845, 800, 752, 706 cm^{-1};
EI-MS (70ev) *m/z* 276 (M^+), 276 (base peak), 261, 233, 215;
Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.75; H, 6.04.

[#8]The structure of tetracycle **20** was determined by NMR study (HMBC, NOE) as shown below.



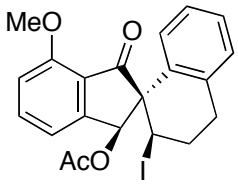


H_a: 10.2 ppm, H_b: 8.57 ppm

Key 2- and 3-bond HMBC correlations

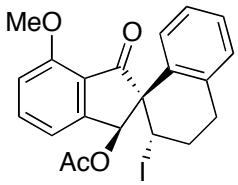
position	δH (ppm)	carbon no. (ppm)
6	2.90–2.93	C-5 (116.8), C-16 (117.0)
2	6.74	C-13 (114.8), C-1 (156.5)
11	8.57	C-16 (117.0)
OH	10.2	C-13 (114.8), C-16 (117.0), C-12 (151.7)

*Synthesis of spiro-indanone **21**:*
To a solution of ICl (55.2 mg, 0.341 mmol) in THF (2.5 mL) was added acetate **17** (58.4 mg, 0.174 mmol) in THF (2.5 mL) at 0 °C. After the mixture was warmed to room temperature and stirred for an additional 20 min, the reaction was quenched with 10% aq. $Na_2S_2O_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/acetone = 8/2 ×4) to afford **21-cis** (53.5 mg, 66.7%) and **21-trans** (22.8 mg, 28.2%).[c]



[c] When acetate **17** was treated with $BnMe_3N^+ICl_2^-$ (3.0 equiv.) in the presence of $NaHCO_3$ (CH_2Cl_2–MeOH, 0 °C, 2 h), the *cis* selectivity increased to 5.6/1 (89.9%).

indanone **21** (major, colorless prisms)
Mp >132 °C (decomposed)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
2.23 (s, 3H), 2.58–2.64 (m, 1H), 2.74–2.80 (m, 1H), 2.95 (ddd, 1H, J_1 = 4.9, J_2 = 12.6, J_3 = 17.1 Hz), 3.22 (ddd, 1H, J_1 = 4.7, J_2 = 12.7 Hz, J_3 = 17.1 Hz), 3.98 (s, 3H), 4.39 (dd, 1H, J_1 = 3.4 Hz, J_2 = 12.8 Hz), 6.60 (s, 1H), 6.71 (d, 1H, J = 8.0 Hz), 7.00–7.19 (m, 5H), 7.69 (dd, 1H, J_1 = 7.8, J_2 = 8.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
21.0, 25.6, 32.2, 33.5, 56.1, 58.6, 79.7, 112.0, 117.5, 123.0, 126.88, 126.94, 127.0, 129.3, 136.24, 136.27, 137.5, 152.5, 158.5, 170.7, 200.1;
IR (KBr)
3064, 3019, 2942, 2888, 2838, 1735, 1710, 1594, 1482, 1452, 1375, 1301, 1278, 1224, 1056, 1025, 989, 889, 800, 763, 736 cm^{-1};
FAB-MS: 463 ($[M+H]^+$);
Anal. Calcd for $C_{21}H_{19}IO_4$: C, 54.56; H, 4.14. Found: C, 54.35; H, 3.95.



indanone **21** (minor, colorless prisms)
Mp >148 °C (decomposed)
^{1}H NMR (500 MHz, $CDCl_3$, δ)
1.71 (s, 3H), 2.53–2.59 (m, 1H), 2.75–2.80 (m, 1H), 2.96 (ddd, 1H, J_1 = 4.8, J_2 = 12.2, J_3 = 16.9 Hz), 3.28 (ddd, 1H, J_1 = 4.8, J_2 = 12.7, J_3 = 16.9 Hz), 3.97 (s, 3H), 5.22 (dd, 1H, J_1 = 3.5, J_2 = 12.8), 6.20 (s, 1H), 6.59 (d, 1H, J = 7.9 Hz), 6.88–7.10 (m, 4H), 7.22 (d, 1H, J = 7.6 Hz), 7.71 (dd, 1H, J_1 = 7.6, J_2 = 7.9 Hz);
^{13}C NMR (125 MHz, $CDCl_3$, δ)
20.4, 31.9, 33.0, 35.0, 56.0, 60.7, 79.7, 111.7, 117.2, 124.2, 124.9, 126.9, 129.5, 129.9, 130.7, 137.2, 137.4, 152.1, 158.6, 170.6, 199.8;
IR (KBr)
3066, 3016, 2937, 2838, 1743, 1716, 1596, 1508, 1482, 1455, 1373, 1272, 1228, 1149, 1093, 1054, 1025, 956, 912, 863, 819, 777 cm^{-1};
FAB-MS: 463 ($[M+H]^+$);
Anal. Calcd for $C_{21}H_{19}IO_4$: C, 54.56; H, 4.14. Found: C, 54.29; H, 4.39.

Table 1. Crystal data and structure refinement for **21**.

Identification code	**21**
Empirical formula	$C_{21}\ H_{19}\ I\ O_4$
Formula weight	462.26
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C* 2/*c*
Unit cell dimensions	a = 32.804(6) Å α = 90.00°
	b = 7.6082(6) Å β = 95.754(5)°
	c = 14.8643(13) Å γ = 90.00°
Volume	3691.1(8) $Å^3$
Z, Calculated density	8, 1.664 Mg/m^3
Absorption coefficient	1.758 mm^{-1}
F(000)	1840
Crystal size	0.18 x 0.15 x 0.05 mm
Theta range for data collection	1.25 to 27.55° .
Limiting indices	–42<=h<=42, –9<=k<=9, –19<=l<=18
Reflections collected / unique	16502 / 4215 [R(int) = 0.0217]
Completeness to θ = 27.55	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9172 and 0.7425
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4215 / 0 / 237
Goodness-of-fit on F^2	1.080
Final R indices [3747refs. I>2σ (I)]	R1 = 0.0233, wR2 = 0.0532
R indices (all data)	R1 = 0.0288, wR2 = 0.0561
Largest diff. peak and hole	0.505 and -0.380 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **21**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8647(1)	4874(3)	662(1)	23(1)
C(2)	8292(1)	3594(3)	760(1)	26(1)
C(3)	8296(1)	1964(3)	323(2)	30(1)
C(4)	7991(1)	736(3)	394(2)	37(1)
C(5)	7677(1)	1093(3)	925(2)	42(1)
C(6)	7672(1)	2686(3)	1365(2)	39(1)
C(7)	7972(1)	3954(3)	1287(1)	31(1)
C(8)	7945(1)	5690(3)	1759(2)	39(1)
C(9)	8361(1)	6560(3)	1954(2)	35(1)
C(10)	8562(1)	6673(3)	1076(1)	28(1)
C(11)	9039(1)	3982(3)	1149(1)	23(1)
C(12)	9322(1)	3598(3)	465(1)	24(1)
C(13)	9713(1)	2822(3)	568(1)	26(1)
C(14)	9925(1)	2686(3)	–193(1)	31(1)
C(15)	9752(1)	3286(3)	–1028(2)	35(1)
C(16)	9365(1)	4030(3)	–1140(1)	31(1)
C(17)	9156(1)	4180(3)	–381(1)	24(1)
C(18)	8739(1)	4980(3)	–351(1)	24(1)
C(19)	10270(1)	1572(3)	1506(2)	35(1)
C(20)	8421(1)	7364(3)	–1197(1)	32(1)
I(1)	9106(1)	8333(1)	1327(1)	34(1)
O(1)	9079(1)	3648(2)	1949(1)	32(1)
O(2)	9861(1)	2279(2)	1401(1)	33(1)
O(3)	8762(1)	6735(2)	–721(1)	27(1)
O(4)	8094(1)	6674(2)	–1203(1)	51(1)
C(21)	8510(1)	8994(3)	–1702(2)	43(1)

Table 3. Bond lengths [Å] and angles [°] for **21**.

C(1)-C(2)	1.536(3)
C(1)-C(10)	1.537(3)
C(1)-C(11)	1.566(3)
C(1)-C(18)	1.566(2)
C(2)-C(7)	1.397(3)
C(2)-C(3)	1.401(3)
C(3)-C(4)	1.381(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.386(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.378(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.391(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.503(3)

C(8)-C(9)	1.519(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.522(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-I(1)	2.188(2)
C(10)-H(10)	1.0000
C(11)-O(1)	1.211(2)
C(11)-C(12)	1.474(3)
C(12)-C(17)	1.392(3)
C(12)-C(13)	1.404(3)
C(13)-O(2)	1.350(2)
C(13)-C(14)	1.391(3)
C(14)-C(15)	1.390(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.385(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.383(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.501(3)
C(18)-O(3)	1.450(2)
C(18)-H(18)	1.0000
C(19)-O(2)	1.439(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(4)	1.193(3)
C(20)-O(3)	1.352(3)
C(20)-C(21)	1.493(3)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(2)-C(1)-C(10)	110.89(16)
C(2)-C(1)-C(11)	106.08(15)
C(10)-C(1)-C(11)	112.01(16)
C(2)-C(1)-C(18)	110.16(15)
C(10)-C(1)-C(18)	113.48(16)
C(11)-C(1)-C(18)	103.76(15)
C(7)-C(2)-C(3)	118.5(2)
C(7)-C(2)-C(1)	123.19(19)
C(3)-C(2)-C(1)	118.32(18)
C(4)-C(3)-C(2)	121.5(2)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	119.8(2)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(6)-C(5)-C(4)	119.1(2)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5

C(5)-C(6)-C(7)	122.0(2)
C(5)-C(6)-H(6)	119.0
C(7)-C(6)-H(6)	119.0
C(6)-C(7)-C(2)	119.2(2)
C(6)-C(7)-C(8)	119.6(2)
C(2)-C(7)-C(8)	121.2(2)
C(7)-C(8)-C(9)	112.13(19)
C(7)-C(8)-H(8A)	109.2
C(9)-C(8)-H(8A)	109.2
C(7)-C(8)-H(8B)	109.2
C(9)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9
C(8)-C(9)-C(10)	108.62(18)
C(8)-C(9)-H(9A)	110.0
C(10)-C(9)-H(9A)	110.0
C(8)-C(9)-H(9B)	110.0
C(10)-C(9)-H(9B)	110.0
H(9A)-C(9)-H(9B	108.3
C(9)-C(10)-C(1)	113.84(17)
C(9)-C(10)-I(1)	107.57(14)
C(1)-C(10)-I(1)	113.87(13)
C(9)-C(10)-H(10)	107.0
C(1)-C(10)-H(10)	107.0
I(1)-C(10)-H(10)	107.0
O(1)-C(11)-C(12)	128.42(18)
O(1)-C(11)-C(1)	123.30(17)
C(12)-C(11)-C(1)	108.24(15)
C(17)-C(12)-C(13)	120.24(18)
C(17)-C(12)-C(11)	109.99(17)
C(13)-C(12)-C(11)	129.74(17)
O(2)-C(13)-C(14)	123.97(19)
O(2)-C(13)-C(12)	118.05(17)
C(14)-C(13)-C(12)	117.96(18)
C(15)-C(14)-C(13)	120.5(2)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	122.0(2)
C(16)-C(15)-H(15)	119.0
C(14)-C(15)-H(15)	119.0
C(17)-C(16)-C(15)	117.40(19)
C(17)-C(16)-H(16)	121.3
C(15)-C(16)-H(16)	121.3
C(16)-C(17)-C(12)	121.87(19)
C(16)-C(17)-C(18)	125.91(18)
C(12)-C(17)-C(18)	112.21(17)
O(3)-C(18)-C(17)	106.16(15)
O(3)-C(18)-C(1)	115.81(15)
C(17)-C(18)-C(1)	105.78(15)
O(3)-C(18)-H(18)	109.6
C(17)-C(18)-H(18)	109.6
C(1)-C(18)-H(18)	109.6
O(2)-C(19)-H(19A)	109.5

O(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(4)-C(20)-O(3)	123.0(2)
O(4)-C(20)-C(21)	125.7(2)
O(3)-C(20)-C(21)	111.2(2)
C(13)-O(2)-C(19)	117.41(16)
C(20)-O(3)-C(18)	116.87(16)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	25(1)	25(1)	21(1)	2(1)	3(1)	1(1)
C(2)	24(1)	28(1)	25(1)	6(1)	1(1)	1(1)
C(3)	30(1)	27(1)	34(1)	3(1)	2(1)	3(1)
C(4)	39(1)	27(1)	44(1)	5(1)	–4(1)	0(1)
C(5)	35(1)	41(1)	48(1)	16(1)	0(1)	–8(1)
C(6)	31(1)	47(1)	41(1)	11(1)	8(1)	–1(1)
C(7)	27(1)	36(1)	30(1)	6(1)	5(1)	2(1)
C(8)	36(1)	44(1)	40(1)	–3(1)	16(1)	3(1)
C(9)	38(1)	37(1)	30(1)	–7(1)	11(1)	2(1)
C(10)	28(1)	27(1)	28(1)	–2(1)	4(1)	3(1)
C(11)	25(1)	24(1)	21(1)	–1(1)	2(1)	1(1)
C(12)	26(1)	26(1)	20(1)	–1(1)	2(1)	0(1)
C(13)	28(1)	26(1)	23(1)	0(1)	3(1)	0(1)
C(14)	30(1)	34(1)	30(1)	–2(1)	8(1)	6(1)
C(15)	41(1)	40(1)	26(1)	–1(1)	12(1)	7(1)
C(16)	38(1)	34(1)	21(1)	–1(1)	4(1)	4(1)
C(17)	29(1)	22(1)	22(1)	–2(1)	2(1)	0(1)
C(18)	29(1)	23(1)	20(1)	2(1)	2(1)	1(1)
C(19)	31(1)	39(1)	34(1)	–1(1)	–3(1)	11(1)
C(20)	36(1)	32(1)	28(1)	7(1)	6(1)	9(1)
I(1)	35(1)	32(1)	36(1)	–7(1)	6(1)	–4(1)
O(1)	34(1)	43(1)	19(1)	1(1)	3(1)	6(1)
O(2)	30(1)	45(1)	24(1)	4(1)	1(1)	10(1)
O(3)	31(1)	26(1)	25(1)	5(1)	2(1)	1(1)
O(4)	31(1)	53(1)	66(1)	23(1)	–3(1)	2(1)
C(21)	55(2)	37(1)	39(1)	16(1)	10(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **21**.

	x	y	z	U(eq)
H(3)	8514	1696	–30	36
H(4)	7996	–350	79	45
H(5)	7467	250	985	50
H(6)	7458	2926	1733	47
H(8A)	7823	5507	2335	47
H(8B)	7761	6482	1377	47
H(9A)	8535	5862	2405	42
H(9B)	8328	7753	2203	42
H(10)	8366	7306	628	33
H(14)	10191	2178	–141	38
H(15)	9904	3184	–1538	42
H(16)	9248	4421	–1716	37
H(18)	8531	4275	–735	29
H(19A)	10461	2432	1291	53
H(19B)	10279	489	1151	53
H(19C)	10349	1314	2145	53
H(21A)	8260	9702	–1808	65
H(21B)	8606	8673	–2284	65
H(21C)	8723	9675	–1347	65

Table 6. Torsion angles [°] for **21**.

C(10)-C(1)-C(2)-C(7)	9.8(3)
C(11)-C(1)-C(2)-C(7)	–112.1(2)
C(18)-C(1)-C(2)-C(7)	136.23(19)
C(10)-C(1)-C(2)-C(3)	–172.37(17)
C(11)-C(1)-C(2)-C(3)	65.8(2)
C(18)-C(1)-C(2)-C(3)	–45.9(2)
C(7)-C(2)-C(3)-C(4)	–0.9(3)
C(1)-C(2)-C(3)-C(4)	–178.90(19)
C(2)-C(3)-C(4)-C(5)	1.6(3)
C(3)-C(4)-C(5)-C(6)	–0.9(3)
C(4)-C(5)-C(6)-C(7)	–0.5(4)
C(5)-C(6)-C(7)-C(2)	1.2(3)
C(5)-C(6)-C(7)-C(8)	–178.1(2)
C(3)-C(2)-C(7)-C(6)	–0.5(3)
C(1)-C(2)-C(7)-C(6)	177.40(19)
C(3)-C(2)-C(7)-C(8)	178.83(19)
C(1)-C(2)-C(7)-C(8)	–3.3(3)
C(6)-C(7)-C(8)-C(9)	–155.0(2)
C(2)-C(7)-C(8)-C(9)	25.7(3)

C(7)-C(8)-C(9)-C(10)	–53.4(3)
C(8)-C(9)-C(10)-C(1)	62.7(2)
C(8)-C(9)-C(10)-I(1)	–170.12(15)
C(2)-C(1)-C(10)-C(9)	–39.6(2)
C(11)-C(1)-C(10)-C(9)	78.7(2)
C(18)-C(1)-C(10)-C(9)	–164.21(17)
C(2)-C(1)-C(10)-I(1)	–163.41(12)
C(11)-C(1)-C(10)-I(1)	–45.10(19)
C(18)-C(1)-C(10)-I(1)	71.98(18)
C(2)-C(1)-C(11)-O(1)	62.7(2)
C(10)-C(1)-C(11)-O(1)	–58.4(3)
C(18)-C(1)-C(11)-O(1)	178.77(19)
C(2)-C(1)-C(11)-C(12)	–115.30(17)
C(10)-C(1)-C(11)-C(12)	123.58(17)
C(18)-C(1)-C(11)-C(12)	0.8(2)
O(1)-C(11)-C(12)-C(17)	–179.1(2)
C(1)-C(11)-C(12)-C(17)	–1.2(2)
O(1)-C(11)-C(12)-C(13)	2.7(4)
C(1)-C(11)-C(12)-C(13)	–179.4(2)
C(17)-C(12)-C(13)-O(2)	–179.98(18)
C(11)-C(12)-C(13)-O(2)	–2.0(3)
C(17)-C(12)-C(13)-C(14)	–1.0(3)
C(11)-C(12)-C(13)-C(14)	177.0(2)
O(2)-C(13)-C(14)-C(15)	179.6(2)
C(12)-C(13)-C(14)-C(15)	0.7(3)
C(13)-C(14)-C(15)-C(16)	0.3(4)
C(14)-C(15)-C(16)-C(17)	–0.9(3)
C(15)-C(16)-C(17)-C(12)	0.5(3)
C(15)-C(16)-C(17)-C(18)	–178.5(2)
C(13)-C(12)-C(17)-C(16)	0.4(3)
C(11)-C(12)-C(17)-C(16)	–177.99(19)
C(13)-C(12)-C(17)-C(18)	179.56(18)
C(11)-C(12)-C(17)-C(18)	1.2(2)
C(16)-C(17)-C(18)-O(3)	54.9(3)
C(12)-C(17)-C(18)-O(3)	–124.19(17)
C(16)-C(17)-C(18)-C(1)	178.5(2)
C(12)-C(17)-C(18)-C(1)	–0.6(2)
C(2)-C(1)-C(18)-O(3)	–129.69(17)
C(10)-C(1)-C(18)-O(3)	–4.7(2)
C(11)-C(1)-C(18)-O(3)	117.12(17)
C(2)-C(1)-C(18)-C(17)	113.05(17)
C(10)-C(1)-C(18)-C(17)	–121.95(17)
C(11)-C(1)-C(18)-C(17)	–0.1(2)
C(14)-C(13)-O(2)-C(19)	–2.1(3)
C(12)-C(13)-O(2)-C(19)	176.81(19)
O(4)-C(20)-O(3)-C(18)	–12.0(3)
C(21)-C(20)-O(3)-C(18)	167.77(17)
C(17)-C(18)-O(3)-C(20)	–146.14(17)
C(1)-C(18)-O(3)-C(20)	96.8(2)

References and Notes

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