Supplemetary data

Chemiluminescence in Molecular Recognition: Base-induced Decomposition of Optically Active Dioxetanes Bearing a Bisnaphthol Moiety with a Complex of Optically Active Crown Ether / Potassium *t*-Butoxide

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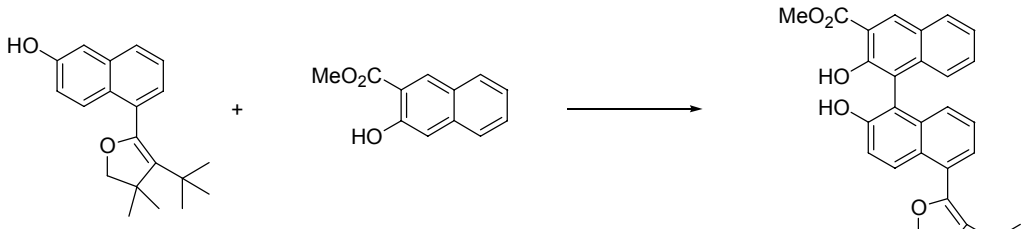
I. Synthesis of dioxetanes

Synthesis of 5'-(4-t-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2,2'-dihydroxy-1,1'-binaphthalene-3-carboxylic acid methyl ester (21)



20 **21**

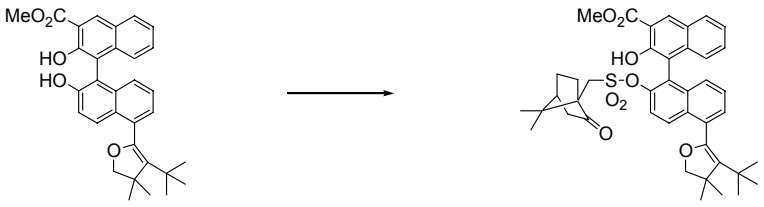
CuCl (871 mg, 8.80 mmol) was added to a solution of **20** (2.05 g, 6.92 mmol), 3-hydroxy-3-naphthoic acid methyl ester (4.08 g, 20.2 mmol) and pyridine(4.6 mL, 56.8 mmol) in MeOH(60 mL) at room temperature. The atmosphere was replaced with O_2 immediately and the solution was stirred for 4 h at room temperature. The reaction

mixture was poured into 1N HCl and extracted with CH_2Cl_2. The organic layer was washed with sat. aq. $NaHCO_3$ and sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with CH_2Cl_2 to afford **21** (3.24 g, 6.52 mmol, 94.3 %) as a yellow solid.

21: Pale yellow needles melted at 164.6-165.4 ^oC (from MeOH-CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ= 1.06 (s, 9H), 1.43 (s, 3H), 1.51 (s, 1.08H), 1.51 (s, 1.92H), 3.97-4.10 (m, 2H), 4.08 (s, 3H), 4.92 (s, 0.36H), 4.97 (s, 0.64H), 7.02-7.41 (m, 7H), 7.89-7.93 (m, 1H), 8.04 (d, *J* = 9.2 Hz, 0.36H), 8.05 (d, *J* = 9.2 Hz, 0.64H), 8.72 (s, 1H), 10.72 (s, 0.36H), 10.87 (s, 0.64H) ppm (mixture of diastereoisomers; 64 : 36);***1)** ^{13}C NMR (125 MHz, $CDCl_3$): δ= 27.4 and 27.4 (CH_3), 27.6 (CH_3), 32.0 and 32.1 (CH_3 x 3), 32.7 (C), 47.3 and 47.4 (C), 52.8 (CH_3), 83.3 (CH_2), 114.1 and 114.2 (C), 114.2 and 114.4 (C), 114.6 (C), 117.9 and 118.1 (CH), 124.4 and 124.5 (CH), 124.7 and 125.0 (CH), 125.2. and 125.3 (CH), 125.6 and 125.8 (CH), 125.7 and 125.8 (CH), 127.3 (C), 127.6 and 128.0 (C), 128.0 and 128.2 (C), 128.1 and 128.2 (CH), 129.7 and 129.8 (CH), 130.0 and 130.1 (CH), 133.6 and 133.6 (C), 133.8 and 133.9 (CH), 133.8 and 133.9 (C), 137.4 and 137.5 (C), 148.1 and 148.3 (C), 151.3 and 151.3 (C), 154.7 and 155.0 (C), 170.2 and 170.3(C) ppm; IR (KBr): ν= 3535, 3433, 3228, 2956, 2866, 1683, 1618 cm^{-1}; Mass: *m/z* (%) 497 (21) [M^++1,], 496 (59) [M^+], 482 (35), 481 (100), 406 (11), 393 (26), 224 (16); HRMS (ESI): 519.2196, calcd for $C_{32}H_{32}O_5Na$ [M + Na^+] 519.2147.

***1)** In a solution, atropisomerism around an axis joining a dihydrofuran and a naphthalene ring was observed. Similar phenomenon was observed for all compounds described below, though diasteroisomeric ratio varied with substitution pattern on binaphtyl moiety.

Synthesis of
5'-(4-t-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-2'-camphorsulfonyloxy-2-hydroxy-1,1'-binaphthalene-3-carboxylic acid methyl ester (3)



21 (***Ra***)-**3** and (***Sa***)-**3**

(1*S*)-(+)-camphorsulufonyl chloride (618 mg, 2.47 mmol) was added to a solution of

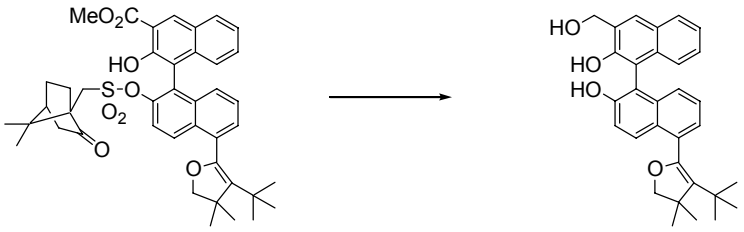
21 (1.01 g, 2.03 mmol) and triethylamine (1.41 mL, 10.1 mmol) in THF (10 mL) under a nitrogen atmosphere at room temperature and stirred for 1 h. To the solution, (1*S*)-(+)-comphorsulufonyl chloride (163 mg, 0.65 mmol) was further added and stirred for 1 h. The reaction mixture was poured into H_2O and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with AcOEt-hexane (1:3) to afford a mixture of **(*Ra*)-3** and **(*Sa*)-3**. The mixture was separated by the use of preparative high pressure column chromatography with CH_2Cl_2 to afford **(*Ra*)-3** (496 mg, 0.698 mmol, 34.4 %) and **(*Sa*)-3**. (357 mg, 0.503 mmol, 24.8 %).

(*Ra*)-3: Yellow plates melted at 148.5-149.2 ^oC (from MeOH-CH_2Cl_2); $[\alpha]_D^{25}$ –39.4 (c 0.336, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): δ= 0.60 (s, 1.8H), 0.63 (s, 1.2H), 0.89 (s, 1.8H), 0.91 (s, 1.2H), 1.06 (s, 3.6H), 1.07 (s, 5.4H), 1.20-1.34 (m, 2H), 1.44 (s, 3H), 1.51 (s, 1.2H), 1.52 (s, 1.8H), 1.78 (d, *J* = 18.3Hz, 1H), 1.81-1.98 (m, 2H), 2.08-2.28 (m, 2H), 2.72 (d, *J* = 14.9Hz, 0.6H), 2.82 (d, *J* = 14.9Hz, 0.4H), 2.93 (d, *J* = 14.9Hz, 0.4H), 2.99 (d, *J* = 14.9Hz, 0.6H), 3.98-4.08 (m, 2H), 4.06 (s, 1.2H), 4.07 (s, 1.8H), 7.01-7.13 (m, 1H), 7.25-7.47 (m, 5H), 7.79 (d, *J* = 9.2Hz, 0.4H), 7.80 (d, *J* = 9.6Hz, 0.6H), 7.87-7.93 (m, 1H), 8.15 (d, *J* = 9.2Hz, 0.4H), 8.16 (d, *J* = 9.6Hz, 0.6H), 8.71 (s, 0.6H), 8.72 (s, 0.4H), 10.67 (s, 0.4H), 10.79 (s, 0.6H) ppm (mixture of diastereoisomers; 60 : 40); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 19.4 (CH_3), 19.7 and 19.7 (CH_3), 24.9 and 24.9 (CH_2), 26.7 (CH_2), 27.3 and 27.4 (CH_3), 27.6 (CH_3), 32.1 and 32.2 (CH_3 x 3), 32.7 (C), 42.2 (CH_2), 42.7 (CH), 47.4 (C), 47.4 and 47.5 (C), 47.7 and 48.0 (CH_2), 52.8 (CH_3), 57.8 and 57.9 (C), 83.3 (CH_2), 113.9 and 114.0 (C), 115.9 and 115.9 (C), 121.9 and 121.9 (CH), 124.1 (CH), 124.4 and 124.5 (C), 124.6 and 124.9 (CH), 126.1 and 126.1 (CH), 126.7 and 126.7 (CH), 126.8 and 126.8 (C), 128.0 and 128.1 (CH), 128.3 and 128.4 (CH), 128.3 and 128.5 (C), 129.4 and 129.5 (CH), 129.7 and 129.8 (CH), 130.8 and 131.0 (C), 133.2 and 133.3 (C), 133.3 (CH), 134.0 and 134.0 (C), 136.8 and 136.9 (C), 145.9 (C), 147.3 and 147.4 (C), 153.7 (C), 170.2 (C), 213.2 and 213.3 (C) ppm; IR (KBr): ν= 3434, 3203, 2957, 1748, 1683, 1626, 1371, 1165 cm^{-1}; Mass: (m/z, %) 712 (20) [M^++2], 711 (49) [M^++1], 710 (100) [M^+], 697 (14), 696 (40), 695 (86), 664 (16), 663 (33), 607 (10), 497 (20), 496 (49), 495 (11), 482 (27), 481 (84), 480 (16), 466(18), 465(23), 406 (20), 393 (30); HRMS (ESI); 733.2811, calcd for $C_{42}H_{46}O_8SNa$ [M + Na^+] 733.2811.

(*Sa*)-3: yellow plates melted at 148.2-148.9 ^oC (from MeOH-CH_2Cl_2); $[\alpha]_D^{25}$ +49.6 (c 0.335, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ= 0.44 (s, 1.8H), 0.50 (s, 1.2H), 0.77 (s, 1.8H), 0.81 (s, 1.2H), 1.06 (s, 3.6H), 1.07 (s, 5.4H), 1.20-1.40 (m, 2H), 1.44 (s, 3H), 1.51

(s, 1.2H), 1.51 (s, 1.8H), 1.73-1.95 (m, 3H), 2.09-2.28 (m, 3H), 3.18 (d, *J* = 14.9Hz, 0.6H), 3.28 (d, *J* = 14.9Hz, 0.4H), 3.97-4.07 (m, 2H), 4.05 (s, 1.2H), 4.06 (s, 1.8H), 7.01-7.12 (m, 1H), 7.22-7.47 (m, 5H), 7.78 (d, *J* = 9.2Hz, 1H), 7.86-7.92 (m, 1H), 8.16 (d, *J* = 9.2Hz, 1H), 8.70 (s, 1H), 10.66 (s, 0.4H), 10.81 (s, 0.6H) ppm (mixture of diastereoisomers; 60 : 40); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 19.1 and 19.1 (CH_3), 19.4 and 19.5 (CH_3), 24.7 and 24.8 (CH_2), 26.6 (CH_2), 27.3 and 27.3 (CH_3), 27.5 (CH_3), 32.0 and 32.1 (CH_3 x 3), 32.7 (C), 42.1 (CH_2), 42.7 and 42.8 (CH), 47.3 (C), 47.3 and 47.4 (C), 48.2 and 48.3 (CH_2), 52.8 (CH_3), 57.7 and 57.7 (C), 83.3 (CH_2), 114.1 and 114.1 (C), 115.9 and 116.0 (C), 121.7 and 122.1 (CH), 124.1 and 124.1 (CH), 124.5 and 124.5 (C), 124.9 and 125.1 (CH), 126.2 and 126.2 (CH), 126.7 and 126.8 (CH), 126.8 (C), 128.0 and 128.1 (CH), 128.3 and 128.4 (CH), 128.3 and 128.6 (C), 129.5 and 129.6 (CH), 129.7 (CH), 130.9 and 131.1 (C), 133.3 and 133.3 (CH), 133.4 and 133.4 (C), 134.0 and 134.1 (C), 137.0 and 137.0 (C), 145.9 and 146.0 (C), 147.4 and 147.5 (C), 154.1 and 154.1 (C), 170.1 and 170.2 (C), 213.2 and 213.5 (C) ppm; IR(KBr): ν= 3433, 3204, 2957, 1748, 1684, 1628, 1369, 1164 cm^{-1}; Mass: (m/z, %) 712 (17) [M^++2], 711 (46) [M^++1], 710 (100) [M^+], 697 (14), 696 (40), 695 (86), 664 (18), 663 (41), 607 (13), 497 (20), 496 (49), 495 (11), 482 (33), 481 (84), 480 (14), 466(17), 465(21), 406 (20), 393 (29); HRMS (ESI); 711.2963, calcd for $C_{42}H_{47}O_8S$ [M + H^+] 711.2992.

Synthesis of 5'-(4-t-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)-3-hydroxymethyl-1,1'-binaphthalene-2,2'-diol (22)



(***Ra***)-3 or (***Sa***)-3 (***Sa***)-22 or (***Ra***)-22

(*Ra*)-3 (1.817g, 2.56 mmol) in THF (20 mL) was added dropwise to a solution of $LiAlH_4$ (357 mg, 9.41 mmol) in THF (10 mL) for 40 min under a nitrogen atmosphere at 0□ and stirred at room temperature for overnight. The reaction mixture was poured into 1N HCl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with AcOEt-hexane (1:2) to afford **(*Sa*)-22** (1.083 g, 2.31 mmol, 90.4 %) as a colorless solid.

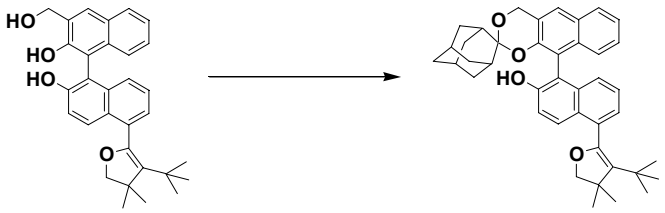
(*Sa*)-22: colorless amorphous solid; $[\alpha]_D^{25}$ –35.0 (c 0.335, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.05 (s, 9H), 1.41 (s, 1.65H), 1.43 (s, 1.35H), 1.48 (s, 1.65H), 1.51 (s, 1.35H), 3.84 (d, *J* = 8.1Hz, 0.55H), 3.91 (d, *J* = 8.1Hz, 0.55H), 3.99 (d, *J* = 8.1Hz, 0.45H), 4.05 (d, *J* = 8.1Hz, 0.45H), 4.70-4.90 (m, 2H), 5.33 (broad s, 1H), 6.00-6.45 (m, 1H), 7.00-7.10 (m, 2H), 7.16-7.37 (m, 5H), 7.77-7.84 (m, 2H), 8.05 (d, *J* = 9.0Hz, 0.55H), 8.07 (d, *J* = 9.0Hz, 0.45H) ppm (mixture of diastereoisomers; 55 : 45); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 27.4 (CH_3), 27.6 and 27.7 (CH_3), 32.1 and 32.2 (CH_3 x 3), 32.7 (C), 47.4 and 47.4 (C), 62.6 and 62.8 (CH_2), 83.1 and 83.3 (CH_2), 111.5 (C), 111.7 and 112.2 (C), 118.1 (CH), 118.1 (C), 124.1 (CH), 124.2 and 124.4 (CH), 124.9 and 125.0 (CH), 126.2 and 126.3 (CH), 126.4 and 126.5 (CH), 127.1 (CH), 128.0 (C), 128.1 and 128.2 (CH), 128.2 and 128.4 (C), 128.9 (CH), 128.9 (C), 129.0 (CH), 133.0 and 133.2 (C), 133.5 and 133.6 (C), 133.9 and 134.0 (C), 147.5 and 147.8 (C), 151.1 and 151.4 (C), 152.4 and 152.5 (C) ppm; IR (KBr): ν= 3507, 3396, 2956, 1617 cm^{-1}; Mass: (m/z, %) 469 (22) [M^++1], 468 (61) [M^+], 466 (12), 454 (35), 453 (100), 451 (23), 437 (11), 420 (10), 403 (12), 379 (25) ; HRMS (ESI): 491.2240, calcd for $C_{31}H_{32}O_4Na$ [M + Na^+] 491.2198.

(Ra)-22 was synthesized from (Sa)-3 similarly to the case of (Sa)-22

(*Ra*)-22: colorless amorphous solid; $[\alpha]_D^{25}$ +34.9 (c 0.335, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.05 (s, 4.95H), 1.06 (s, 4.05H), 1.40 (s, 1.65H), 1.43 (s, 1.35H), 1.47 (s, 1.65H), 1.51 (s, 1.35H), 2.73 (broad s, 1H), 3.81 (d, *J* = 8.1Hz, 0.55H), 3.88 (d, *J* = 8.1Hz, 0.55H), 3.99 (d, *J* = 8.1Hz, 0.45H), 4.04 (d, *J* = 8.1Hz, 0.45H), 4.65-4.85 (m, 2H), 5.40 (s, 0.55H), 5.48 (s, 0.45H), 6.11 (s, 0.45H), 6.22 (s, 0.55H), 7.00-7.10 (m, 2H), 7.15-7.35 (m, 5H), 7.75-7.82 (m, 2H), 8.04 (d, *J* = 9.0Hz, 0.55H), 8.06 (d, *J* = 9.0Hz, 0.45H) ppm (mixture of diastereoisomers; 55 : 45); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 27.3 and 27.4 (CH_3), 27.6 and 27.7 (CH_3), 32.0 and 32.1 (CH_3 x 3), 32.7 (C), 47.4 and 47.4 (C), 62.5 and 62.7 (CH_2), 83.1 and 83.3 (CH_2), 111.6 (C), 111.8 and 112.2 (C), 118.1 (CH), 118.1 (C), 124.0 (CH), 124.1 and 124.4 (CH), 124.9 and 125.0 (CH), 126.2 and 126.2 (CH), 126.3 and 126.4 (CH), 127.1 (CH), 127.9 (C), 128.1 and 128.2 (CH), 128.2 and 128.3 (C), 128.8 and 128.9 (CH), 128.9 (C), 128.9 (CH), 133.0 and 133.2 (C), 133.5 and 133.6 (C), 133.8 and 133.9 (C), 147.5 and 147.8 (C), 151.1 and 151.4 (C), 152.4 and 152.5 (C) ppm; IR (KBr): ν= 3525, 3396, 2956, 1617 cm^{-1}; Mass: (m/z, %) 469 (22) [M^++1], 468 (61) [M^+], 454 (34), 453 (100), 451 (20), 403 (11), 379 (23) ; HRMS (ESI): 491.2238, calcd for $C_{31}H_{32}O_4Na$ [M + Na^+] 491.2198.

Synthesis of 1-[2,2-(adamantane-2,2-diyl)-1,3-dioxa-1,2,3,4-tetrahydroanthracen-

10-yl]-5-(4-t-butyl-3,3-dimethyl-2,3-dihydrofuran-5-yl)naphthalen-2-ol (2)



(*Sa*)-22 or (*Ra*)-22 (*Sa*)-2 or (*Ra*)-2

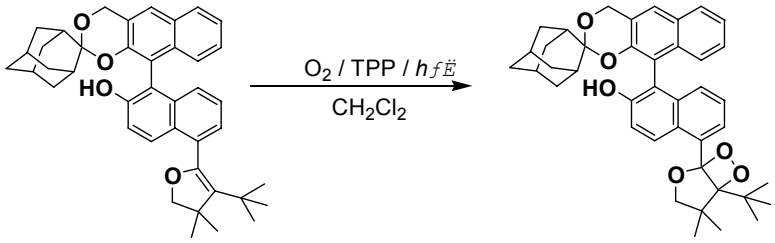
PPTS (57 mg, 0.227 mmol) was added to a solution of **(*Sa*)-22** (537 mg, 1.15 mmol) and 2-adamantanone (197 mg, 1.31 mmol) in benzene (6 mL) and stirred at 75 ^{o}C for 3 h, then refluxed for 3 h. To the reaction mixture, 2-adamantanone (96 mg, 0.639 mmol) was further added and refluxed for 4.5 h. The reaction mixture was poured into sat. aq. $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with AcOEt-hexane (1:25 ~ 1:10) to afford **(*Sa*)-2** (625 mg, 1.04 mmol, 90.8 %) as a colorless solid.

(*Sa*)-2: Colorless amorphous solid; $[\alpha]_D^{25}$ –36.8 (c 0.335, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 0.98 (s, 7.2H), 1.04 (s, 1.8H), 0.96-1.63 (m, 10H), 1.43 (s, 3H), 1.51 (s, 3H), 1.74 (broad s, 1H), 1.88-2.14 (m, 4H), 3.98-4.08 (m, 0.4H), 4.01 (d, *J* = 8.0Hz, 0.8H), 4.07 (d, *J* = 8.0Hz, 0.8H), 4.92 (s, 0.8H), 5.03-5.14 (m, 2.2H), 7.04 (d, *J* = 8.5Hz, 0.8H), 7.07 (d, *J* = 8.5Hz, 0.2H), 7.10-7.37 (m, 5H), 7.61 (s, 0.2H), 7.62 (s, 0.8H), 7.78 (d, *J* = 8.2Hz, 0.2H), 7.79 (d, *J* = 8.2Hz, 0.8H), 8.01 (d, *J* = 9.2Hz, 1H) ppm (mixture of diastereoisomers; 80 : 20); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 26.5 (CH), 26.8 (CH), 27.3 (CH_3), 27.8 (CH_3), 31.7 (CH_3 x 3), 32.6 (C), 32.8 (CH_2), 32.9 (CH_2), 33.3 (CH_2), 33.5 (CH_2), 33.5 (CH), 35.3 (CH), 37.0 (CH_2), 47.3 (C), 59.8 (CH_2), 83.4 (CH_2), 102.6 (C), 114.4 (C), 114.9 (C), 117.7 (CH), 122.2 (C), 124.3 (CH), 124.6 (CH), 124.7 (CH), 125.4 (CH), 125.4 (CH), 125.8 (CH), 126.7 (CH), 127.6 (C), 127.7 (CH), 127.7 (CH), 127.9 (C), 128.6 (C), 133.3 (C), 133.5 (C), 133.8 (C), 148.3 (C), 148.3 (C), 151.3 (C) ppm; IR (KBr): ν= 3430, 2911, 2858, 1616, 1128, 1084, 1048, 1004 cm^{-1}; Mass: (m/z, %) 600 (24) [M$^+$], 451 (37), 450 (100), 436 (15), 435 (44), 403 (10); HRMS (ESI): 623.3174, calcd for $C_{41}H_{44}O_4Na$ [M + Na$^+$] 623.3137.

(Ra)-2 was synthesized from (Ra)-22 similarly to the case of (Sa)-2

(*Ra*)-2: Colorless amorphous solid; $[\alpha]_D^{25}$ +36.8 (c 0.336, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.98 (s, 7.2H), 1.04 (s, 1.8H), 0.96-1.63 (m, 10H), 1.43 (s, 3H), 1.51 (s, 3H), 1.74 (broad s, 1H), 1.88-2.14 (m, 4H), 3.98-4.08 (m, 0.4H), 4.01 (d, *J* = 8.1Hz, 0.8H), 4.07 (d, *J* = 8.1Hz, 0.8H), 4.95 (s, 0.8H), 5.03-5.14 (m, 2,2H), 7.04 (d, *J* = 8.5Hz, 0.8H), 7.07 (d, *J* = 8.5Hz, 0.2H), 7.10-7.37 (m, 5H), 7.61 (s, 1H), 7.78 (d, *J* = 8.2Hz, 0.2H), 7.79 (d, *J* = 8.2Hz, 0.8H), 8.01 (d, *J* = 9.0Hz, 1H) ppm (mixture of diastereoisomers; 80 : 20); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 26.5 (CH), 26.8 (CH), 27.4 (CH_3), 27.9 (CH_3), 31.8 (CH_3 x 3), 32.7 (C), 32.8 (CH_2), 32.9 (CH_2), 33.3 (CH_2), 33.5 (CH_2), 33.6 (CH), 35.3 (CH), 37.0 (CH_2), 47.4 (C), 59.8 (CH_2), 83.4 (CH_2), 102.5 (C), 114.3 (C), 114.8 (C), 117.6 (CH), 122.1 (C), 124.2 (CH), 124.6 (CH), 124.6 (CH), 125.3 (CH), 125.3 (CH), 125.7 (CH), 126.6 (CH), 127.5 (C), 127.6 (CH), 127.6 (CH), 127.8 (C), 128.5 (C), 133.2 (C), 133.4 (C), 133.7 (C), 148.1 (C x 2), 151.2 (C) ppm; IR (KBr): ν= 3504, 3429, 2911, 2857, 1615, 1128, 1084, 1048, 1004 cm^{-1}; Mass: (m/z, %) 600 (26) [M^+], 451 (37), 450 (100), 436 (16), 435 (43); HRMS (ESI); 623.3175, calcd for $C_{41}H_{44}O_4Na$ [M + Na^+] 623.3137.

Synthesis of 1-[2,2-(adamantane-2,2-diyl)-1,3-dioxa-1,2,3,4-tetrahydroanthracen-10-yl]-5-(5-t-butyl-4,4-dimethyl-2,6,7-trioxabicyclo[3.2.0]heptan-1-yl)naphthalen-2-ol (1)



A solution of **(*Sa*)-2** (210 mg, 0.350 mmol) and tetraphenylporphine (TPP) (1.2 mg) in CH_2Cl_2 (20 mL) was irradiated externally with 940 W Na lamp under an oxygen atmosphere at 0 □ for 6 h. The photolysate was concentrated *in vacuo*. The residue was chromatographed on silica gel with hexane-Et_2O (4:1) to afford **(*Sa,1S,5S*)-1** (48.4 mg, 0.0805 mmol, 21.8 %) and **(*Sa,1R,5R*)-1** (145.9 mg, 0.231 mmol, 66.0 %) as a colorless solid, respectively.

(*Sa,1S,5S*)-1: colorless amorphous solid; $[\alpha]_D^{25}$ +19.2 (c 0.335, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.93 (s, 9H), 1.07-1.78 (m, 16H), 1.92-2.12 (m, 4H), 4.05-4.18 (m, 1H),

4.74 (d, J = 8.3 Hz, 1H), 4.97 (s, 1H), 5.12 (s, 2H), 7.07 (broad d, J = 8.3 Hz, 1H), 7.15-7.38 (m, 5H), 7.66 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.89-8.11 (m, 1H), 8.60-8.90 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 20.0 (broad CH_3), 26.1 (broad CH_3), 26.5 (CH), 26.8 (CH), 26.9 (CH_3 x 3), 32.9 (CH_2), 33.0 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 34.2 (CH), 34.6 (CH), 36.9 (C), 37.0 (CH_2), 45.7 (C), 59.7 (CH_2), 80.5 (CH_2), 102.7 (C), 106.0 (broad C), 114.7 (C), 115.0 (broad C), 117.2 (broad CH), 117.6 (broad C), 122.2 (C), 124.1 (CH), 124.4 (CH), 124.7 (broad CH), 124.8 (CH), 126.7 (CH), 126.8 (broad C), 127.2 (broad CH), 127.7 (CH), 127.9 (CH), 128.0 (broad CH), 128.6 (C), 131.1 (broad C), 133.2 (C), 134.7 (C), 148.2 (C), 150.8 (C) ppm; IR (KBr): ν= 3502, 2915, 2856, 1611, 1128, 1084, 1037, 999 cm^{-1}; Mass: (m/z, %, 20eV) 633 (15) [M^++1], 632 (34) [M^+], 483 (35), 482 (100), 426 (11), 325 (25), 324 (11); HRMS (ESI): 655.2988, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

(*Sa,1R,5R*)-1: Colorless amorphous solid; $[\alpha]_D^{25}$ –95.3 (c 0.339, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.87 (s, 9H), 1.03 (broad d, J = 12.5 Hz, 1H), 1.15 (broad d, J = 12.5 Hz, 1H), 1.25-1.35 (m, 2H), 1.32 (s, 3H), 1.47-1.60 (m, 5H), 1.68 (s, 3H), 1.76 (broad s, 1H), 1.90-2.09 (m, 4H), 4.14 (d, J = 8.3 Hz, 1H), 4.74 (d, J = 8.3 Hz, 1H), 4.93 (s, 1H), 5.06 (d, J = 15.1Hz, 1H), 5.14 (d, J = 15.1 Hz, 1H), 7.16-7.38 (m, 6H), 7.64 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 8.04 (broad d, J = 6.3 Hz, 1H), 8.67 (broad d, J = 9.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 20.3 (CH_3), 26.3 (CH_3), 26.5 (CH), 26.7 (CH_3 x 3), 26.8 (CH), 32.9 (CH_2 x 2), 33.3 (CH_2), 33.5 (CH_2), 33.6 (CH), 35.2 (CH), 36.8 (C), 37.0 (CH_2), 45.7 (C), 59.7 (CH_2), 80.6 (CH_2), 102.5 (C), 105.7 (C), 114.7 (C), 115.1 (C), 117.2 (CH), 117.5 (broad C), 122.1 (C), 124.2 (CH), 124.4 (CH), 124.7 (CH), 124.8 (CH), 126.5 (C), 126.7 (CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.5 (C), 131.0 (C), 133.1 (C), 134.7 (C), 148.3 (C), 150.8 (C) ppm; IR (KBr): ν= 3540, 3450, 2910, 2858, 1623, 1126, 1082, 1038, 999 cm^{-1}; Mass: (m/z, %, 20eV) 633 (17) [M^++1], 632 (40) [M^+], 483 (35), 482 (100), 426 (10), 325 (22); HRMS (ESI): 655.2993, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

Optically pure (Ra,1R,5R)-1 and (Ra,1S,5S)-1 were synthesized from (Ra)-2 similarly to the case of (Sa,1S,5S)-1 and (Sa,1R,5R)-1.

(*Ra,1R,5R*)-1: Colorless amorphous solid; $[\alpha]_D^{25}$ –19.2 (c 0.335, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.93 (s, 9H), 1.07-1.78 (m, 16H), 1.92-2.12 (m, 4H), 4.05-4.18 (m, 1H), 4.74 (d, J = 8.5 Hz, 1H), 4.99 (s, 1H), 5.12 (s, 2H), 7.07 (broad d, J = 8.3 Hz, 1H), 7.15-7.38 (m, 5H), 7.65 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.89-8.11 (m, 1H), 8.60-8.90 (m,

1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 19.9 (broad CH_3), 26.1 (broad CH_3), 26.5 (CH), 26.9 (CH), 26.9 (CH_3 x 3), 32.9 (CH_2), 33.0 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 34.2 (CH), 34.7 (CH), 36.9 (C), 37.0 (CH_2), 45.7 (C), 59.7 (CH_2), 80.5 (CH_2), 102.8 (C), 106.0 (broad C), 114.7 (C), 115.0 (broad C), 117.2 (broad CH), 117.6 (broad C), 122.2 (C), 124.2 (CH), 124.4 (CH), 124.7 (broad CH), 124.8 (CH), 126.7 (CH), 126.9 (broad C), 127.2 (broad CH), 127.8 (CH), 127.9 (CH), 128.0 (broad CH), 128.6 (C), 131.1 (broad C), 133.2 (C), 134.7 (C), 148.3 (C), 150.8 (C) ppm; IR (KBr): ν= 3429, 2915, 2856, 1621, 1128, 1084, 1037, 1000 cm^{-1}; Mass: (m/z, %, 20eV) 633 (16) [M^++1], 632 (36) [M^+], 483 (36), 482 (100), 426 (8), 325 (22), 324 (10), 150 (39); HRMS (ESI): 655.2998, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

(*Ra,1S,5S*)-1: Colorless amorphous solid; $[\alpha]_D^{25}$ +95.2 (c 0.335, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 0.87 (s, 9H), 1.02 (broad d, *J* = 12.5 Hz, 1H), 1.15 (broad d, *J* = 12.5 Hz, 1H), 1.25-1.35 (m, 2H), 1.32 (s, 3H), 1.47-1.60 (m, 5H), 1.68 (s, 3H), 1.76 (broad s, 1H), 1.90-2.09 (m, 4H), 4.14 (d, *J* = 8.3 Hz, 1H), 4.74 (d, *J* = 8.3 Hz, 1H), 4.97 (s, 1H), 5.02 (d, *J* = 15.3 Hz, 1H), 5.10 (d, *J* = 15.3 Hz, 1H), 7.16-7.38 (m, 6H), 7.60 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 8.03 (broad d, *J* = 5.9 Hz, 1H), 8.67 (broad d, *J* = 9.3 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ= 20.3 (CH_3), 26.4 (CH_3), 26.6 (CH), 26.7 (CH_3 x 3), 26.8 (CH), 32.9 (CH_2 x 2), 33.3 (CH_2), 33.5 (CH_2), 33.6 (CH), 35.2 (CH), 36.8 (C), 37.0 (CH_2), 45.7 (C), 59.7 (CH_2), 80.6 (CH_2), 102.5 (C), 105.8 (C), 114.7 (C), 115.1 (C), 117.2 (CH), 117.5 (broad C), 122.1 (C), 124.2 (CH), 124.4 (CH), 124.7 (CH), 124.8 (CH), 126.6 (C), 126.7 (CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.5 (C), 131.0 (C), 133.1 (C), 134.7 (C), 148.3 (C), 150.8 (C) ppm; IR (KBr): ν=3429, 2914, 2856, 1621, 1128, 1083, 1038, 990 cm^{-1}; Mass: (m/z, %, 20eV) 633 (14) [M^++1], 632 (30) [M^+], 483 (35), 482 (100), 426 (11), 325 (33), 324 (13), 150 (39); HRMS (ESI): 655.2990, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

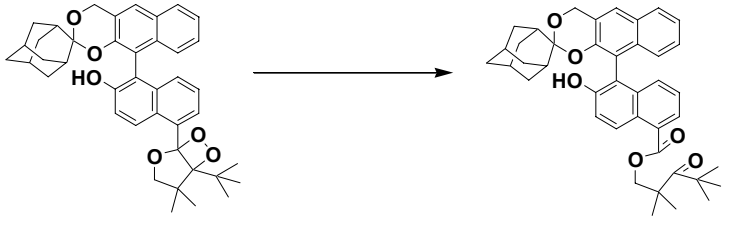
Synthesis of racemic-1 was carried out by the use of racemic-2 as a starting material similarly to the synthesis of optically pure isomers of 1.

Racemic 1 [(*Sa,1S,5S*) + (*Ra,1R,5R*)]: Colorless amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.93 (s, 9H), 1.07-1.78 (m, 16H), 1.92-2.12 (m, 4H), 4.05-4.18 (m, 1H), 4.74 (d, *J* = 8.3 Hz, 1H), 4.96 (s, 1H), 5.13 (s, 2H), 7.07 (broad d, *J* = 8.3 Hz, 1H), 7.15-7.38 (m, 5H), 7.67 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.89-8.11 (m, 1H), 8.60-8.90 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 20.0 (broad CH_3), 26.1 (broad CH_3), 26.5 (CH), 26.9 (CH), 26.9 (CH_3 x 3), 32.9 (CH_2), 33.0 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 34.2 (CH), 34.7 (CH),

36.9 (C), 37.0 (CH_2), 45.7 (C), 59.8 (CH_2), 80.5 (CH_2), 102.8 (C), 106.0 (broad C), 114.7 (C), 115.0 (broad C), 117.2 (broad CH), 117.2 (broad C), 122.2 (C), 124.1 (CH), 124.4 (CH), 124.7 (broad CH), 124.8 (CH), 126.7 (CH), 126.8 (broad C), 127.2 (broad CH), 127.8 (CH), 127.9 (CH), 128.0 (broad CH), 128.6 (C), 131.1 (broad C), 133.2 (C), 134.7 (C), 148.2 (C), 150.8 (C) ppm; IR (KBr): ν= 3441, 2914, 2857, 1610, 1129, 1081, 1036, 1000 cm^{-1}; Mass: (m/z, %, 20eV) 633 (15) [M^++1], 632 (30) [M^+], 483 (37), 482 (100), 426 (13), 342 (17), 326 (23), 325 (80), 324 (22); HRMS (ESI): 655.2995, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

Racemic 1 [(*Sa,1R,5R*) + (*Ra,1S,5S*)]: colorless needles melted at 154.6-155.2 °C (dec) (from hexane-CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.87 (s, 9H), 1.04 (broad d, *J* = 12.5 Hz, 1H), 1.16 (broad d, *J* = 12.5 Hz, 1H), 1.25-1.35 (m, 2H), 1.33 (s, 3H), 1.47-1.60 (m, 5H), 1.69 (s, 3H), 1.77 (broad s, 1H), 1.90-2.12 (m, 4H), 4.14 (d, *J* = 8.3 Hz, 1H), 4.74 (d, *J* = 8.3 Hz, 1H), 4.90 (s, 1H), 5.08 (d, *J* = 15.4Hz, 1H), 5.15 (d, *J* = 15.4 Hz, 1H), 7.16-7.38 (m, 6H), 7.66 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 8.04 (broad d, *J* = 6.3 Hz, 1H), 8.68 (broad d, *J* = 9.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 20.3 (CH_3), 26.4 (CH_3), 26.6 (CH), 26.7 (CH_3 x 3), 26.8 (CH), 32.9 (CH_2 x 2), 33.3 (CH_2), 33.5 (CH_2), 33.6 (CH), 35.4 (CH), 36.8 (C), 37.0 (CH_2), 45.7 (C), 59.8 (CH_2), 80.6 (CH_2), 102.6 (C), 105.8 (C), 114.6 (C), 115.1 (C), 117.2 (CH), 117.5 (broad C), 122.1 (C), 124.3 (CH), 124.4 (CH), 124.8 (CH), 124.9 (CH), 126.6 (C), 126.8 (CH), 127.1 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.5 (C), 131.0 (C), 133.1 (C), 134.7 (C), 148.3 (C), 150.8 (C) ppm; IR (KBr): ν= 3434, 2915, 2857, 1622, 1127, 1083, 1038, 1000 cm^{-1}; Mass: (m/z, %, 20eV) 633 (17) [M^++1], 632 (40) [M^+], 483 (35), 482 (100), 426 (14), 342 (15), 326 (22), 325 (83), 324 (20); HRMS (ESI): 655.3046, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

Synthesis of 5-[2,2-(adamantane-2,2-diyl)-1,3-dioxa-1,2,3,4-tetrahydroanthracen-10-yl]-6-hydroxynaphthalen-1-carboxylic acid 2,2,4,4-tetramethyl-3-oxopentyl ester (neutral form of 4)---chemiluminescent decomposition of a mixture of [(Sa,1R,5R)-1 and (Sa,1S,5S)-1] obtained from (Sa)-2



(*Sa*,1*R*,5*R*)-1, (*Sa*,1*S*,5*S*)-1 or (*Ra*,1*S*,5*S*)-1 and (*Ra*,1*R*,5*R*)-1

neutral form of (*Sa*)-4 or (*Ra*)-4

TBAF (1.0 M in THF, 0.55 ml, 0.55 mmol) in dry DMSO (2.0 mL), was added to a solution of a mixture **(*Sa,1R,5R*)-1** and **(*Sa,1S,5S*)-1** (27:73 mixture, 70mg, 0.111 mmol) in dry DMSO (3.0 mL) and stirred at room temperature for 5 min: bright cinnabar light was observed during the addition of TBAF. The reaction mixture was poured into aq. sat. NH_4Cl and extracted with AcOEt. The organic layer was washed with sat. aq. NaCl and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on silica gel with CH_2Cl_2-hexane (1:2) and CH_2Cl_2 to afford neutral form of **(*Sa*)-4** (69 mg, 0.109 mmol, 98.6 %) as a colorless solid.

Neutral form of (*Sa*)-4: colorless columns melted at 186.2-186.7 ^oC (from hexane-AcOEt); $[\alpha]_D^{25}$ –37.6 (c 0.336, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ= 1.06 (broad d, *J* = 12.5Hz, 1H), 1.19 (broad dd, *J* = 12.5 and 2.6Hz, 1H), 1.29 (s, 9H), 1.44 (s, 6H), 1.38-1.64 (m, 7H), 1.77 (broad s, 1H), 1.92-2.02 (m, 3H), 2.12 (broad s, 1H), 4.48 (d, *J* = 10.7Hz, 1H), 4.53 (d, *J* = 10.7Hz, 1H), 5.03 (s, 1H), 5.12 (s, 2H), 7.12 (d, *J* = 8.3 Hz, 1H), 7.18 (dd, *J* = 8.3 and 7.1Hz, 1H), 7.22-7.37 (m, 3H), 7.44 (d, *J* = 9.5Hz, 1H), 7.67 (s, 1H), 7.81 (d, *J* = 8.1Hz, 1H), 7.88 (dd, *J* = 7.1 and 1.2Hz, 1H), 8.94 (d, *J* = 9.5Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 23.8 (CH_3), 23.9 (CH_3), 26.6 (CH), 26.8 (CH), 28.2 (CH_3 x 3), 32.9 (CH_2), 33.0 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 34.4 (CH), 34.5 (CH), 37.0 (CH_2), 45.9 (C), 49.2 (C), 59.7 (CH_2), 72.3 (CH_2), 102.7 (C), 114.4 (C), 114.8 (C), 119.0 (CH), 122.1 (C), 124.2 (CH), 124.4 (CH), 124.8 (CH), 124.8 (CH), 126.7 (CH), 126.8 (C), 127.1 (C), 127.2 (CH), 127.5 (CH), 127.7 (CH), 128.5 (C), 130.2 (CH), 133.2 (C), 134.3 (C), 148.2 (C), 151.4 (C), 167.5 (C), 215.9 (C) ppm; IR(KBr): ν= 3443, 2911, 2857, 1713, 1686, 1613 cm^{-1}; Mass: (m/z, %) 633 (11) [M^++1], 632 (25) [M^+], 483 (36), 482 (100), 426 (17), 342 (15), 326 (21), 325 (81), 324 (19); HRMS (ESI): 655.2989, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

Neutral form of (*Ra*)-4 was synthesized from a mixture of [(*Ra,1S,5S*)-1 and (*Ra,1R,5R*)-1] similarly to the case of neutral form of (*Sa*)-4.

neutral form of (*Ra*)-4: colorless columnss melted at 186.3-186.8 ^oC (from hexane-AcOEt); $[\alpha]_D^{25}$ +37.6 (c 0.335, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ= 1.06 (broad d, *J* = 12.5Hz, 1H), 1.19 (broad d, *J* = 12.5Hz, 1H), 1.29 (s, 9H), 1.44 (s, 6H), 1.38-1.64 (m, 7H), 1.77 (broad s, 1H), 1.92-2.02 (m, 3H), 2.13 (broad s, 1H), 4.48 (d, *J* = 10.5Hz, 1H), 4.53 (d, *J* = 10.5Hz, 1H), 5.02 (s, 1H), 5.12 (s, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.15-7.38 (m, 4H), 7.44 (d, *J* = 9.3Hz, 1H), 7.67 (s, 1H), 7.81 (d, *J* = 8.1Hz, 1H), 7.88 (dd, *J* = 7.1 and 1.2Hz, 1H), 8.94 (d, *J* = 9.3Hz, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$) δ= 23.8

(CH_3), 23.9 (CH_3), 26.6 (CH), 26.8 (CH), 28.2 (CH_3 x 3), 32.9 (CH_2), 33.0 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 34.4 (CH), 34.5 (CH), 37.0 (CH_2), 45.9 (C), 49.2 (C), 59.7 (CH_2), 72.3 (CH_2), 102.7 (C), 114.4 (C), 114.8 (C), 118.9 (CH), 122.1 (C), 124.2 (CH), 124.4 (CH), 124.8 (CH), 124.8 (CH), 126.7 (CH), 126.8 (C), 127.1 (C), 127.2 (CH), 127.5 (CH), 127.7 (CH), 128.5 (C), 130.2 (CH), 133.1 (C), 134.3 (C), 148.2 (C), 151.4 (C), 167.5 (C), 215.9 (C) ppm; IR (KBr): ν= 3427, 2911, 2857, 1713, 1685, 1612 cm^{-1}Mass (m/z, %) 633 (12) [M^++1], 632 (26) [M^+], 483 (34), 482 (100), 426 (19), 342 (17), 326 (25), 325 (89), 324 (24); HRMS (ESI): 655.2997, calcd for $C_{41}H_{44}O_6Na$ [M + Na^+] 655.3036.

II. Analysis of optically active compounds synthesized here by HPLC using chiral column

Apparatus: HPLC analysis was carried out by the use of Shimazu Liquid Chromatograph LC-10Ai. As a chiral column, CHIRALCEL AD-RH (Daicel, column size: 0.46 cmID x 15cm) or CHIRALCEL OJ-RH (Daicel, column size: 0.46 cmID x 15cm) was used. Conditions for analysis are summarized in the following **Table 2**.

Table 2. HPLC conditions and retention time of optically active compounds bearing an atropisomeric binapthyl moiety[a)]

Compound	Column	Eluent	Retention time / min
(*Ra*)-and (*Sa*)-**22**	AD-RH	CH_3CN/H_2O (65/35)	(*Ra*): 7.0, (*Sa*): 9.3
(*Ra*)-and (*Sa*)-**2**	AD-RH	CH_3CN/H_2O (80/20)	(*Ra*): 12.9, (*Sa*): 17.7
(*Ra,*1*S,*5*S*)- and (*Sa,*1*R,*5*R*)-**1**	AD-RH	CH_3CN/H_2O (80/20)	(*Ra,1S,1S*): 13.3, (*Sa,1R,1R*): 18.4
(*Ra,*1*R,*5*R*)- and (*Sa,*1*S,*5*S*)-**1**	OJ-RH	CH_3CN/H_2O (65/35)	(*Ra,1R,1R*): 32.7, (*Sa,1S,1S*): 35.4
(*Ra*)-and (*Sa*)-**4**	OJ-RH	CH_3CN/H_2O (65/35)	(*Ra*): 26.4, (*Sa*): 28.2

a) Flow rate: 0.5 mL / min, Oven temperature: 35 °C.

III. Synthesis of (*Ra,Ra*)-bis(binaphtho)-22-crown-6 ether [(*Ra,Ra*)-5] and (*Sa,Sa*)-bis(binaphtho)-22-crown-6 ether [(*Sa,Sa*)-5]

These optically active crown ethers were synthesized from optically active 1,1'-bisnaphthol and diethylene glycol ditosylate in accordance with a procedure reported.[6] $[\alpha]_D^{25}$ was +207 for (*Ra,Ra*)-**5** (*c* 0.830, CH_2Cl_2), while $[\alpha]_D^{25}$ was -207 for (*Sa,Sa*)-**5** (*c* 0.837, CH_2Cl_2) {Lit.[10] $[\alpha]_{578}^{25}$ +221, $[\alpha]_{546}^{25}$ +262 for (*Ra,Ra*)-**5** (*c* 0.87, CH_2Cl_2), while $[\alpha]_{578}^{25}$ -220 $[\alpha]_{546}^{25}$ -262 for (*Sa,Sa*)-**5** (*c* 0.87, CH_2Cl_2)}

IV. Chemiluminescence Measurement

Apparatus: Chemiluminescences were measured by Hamamatsu Photonics PMA-11 (detection limit: 200-900nm) and/or JASCO FP-750 spectrometer (detection limit:200-700 nm).

Measurement:

(**In TBAF / DMSO system**) Freshly prepared solution of TBAF in DMSO (1.0×10^{-2} mol dm^{-3}, 2mL) was transferred to a quartz cell (10x10x50 mm) and the latter placed in the spectrometer, which was thermostated with stirring at 25 °C. After 3-5 min, a solution of the dioxetane in DMSO (1.0×10^{-5} mol dm^{-3}, 1 mL), which was thermostated at the same temperature as that of the above solution, was added with a syringe with immediate starting of measurement. The intensity of the light emission time-course was recorded and processed according to first-order kinetics. The total light emission was estimated by comparing it with that of 3-adamantylidene-4-(3-*tert*-butyldimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane, whose chemiluminescent efficiency Φ^{CL} has been reported to be 0.29 in TBAF / DMSO[5] and was used here as a standard.

(**In [K□(18-crown-6)]$^{+}$·*t*BuO^{-} / benzene-THF system**) Chemiluminescence measurement was carried out similarly to the case of TBAF / DMSO system except that freshly prepared [K□(18-crown-6)]$^{+}$·*t*BuO^{-} solution in benzene-THF (1:1) (1.0×10^{-1} mol dm^{-3}, 2mL) as a base and a dioxetane solution in benzene-THF (1:1) (1.0×10^{-4} mol dm^{-3}, 1mL).

(**In [K□(5)]$^{+}$·*t*BuO^{-} / benzene-THF system**) Chemiluminescence measurement was carried out similarly to the case of TBAF / DMSO system except that freshly prepared {K□[(*Ra,Ra*)-**5**]}$^{+}$·*t*BuO^{-} or {K□[(*Sa,Sa*)-**5**]}$^{+}$·*t*BuO^{-} solution in benzene-THF (1:1) (1.0×10^{-2} mol dm^{-3}, 2mL) as a base and a dioxetane solution in benzene-THF (1:1) (1.0×10^{-4} mol dm^{-3}, 1mL).

V. X-ray Single Crystallographic Analysis

X-ray diffraction data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated MoKα (λ=0.71070 □) radiation. Data were processed using CrystalClear*[1]. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 10470 observed reflections and 527 variable parameters (for (*Ra*)-**3**) and on 10769 observed reflections and 529 variable parameters (for (*Sa*)-**3**). All calculations were performed using the CrystalStructure crystallographic software

package*[2,3]. On the other hand, for the case of racemate **1** [(*Ra*,1*S*,5*S*) + (*Sa*,1*R*,5*R*)], the structure was solved by direct methods (SHELX97). *[4] The final cycle of full-matrix least-squares refinement on F^2 was based on 8933 observed reflections and 552 variable parameters.

Crystal data for (*Ra*)-**3**: $C_{42}H_{46}O_8S \square 0.6CH_3OH$ (M_r = 730.11), pale yellow prism, 0.50 ×0.40×0.30 mm, triclinic, space group *P1* (#1), *a* = 8.804(9)□, *b* = 10.30(2)□, *c* = 11.281(10)□, α= 99.78(4)°, β= 98.06(4)°, γ= 99.60(4)°, *V* = 978.5(22)□^{3}, *Z* = 1, ρ_{calcd} = 1.239 g cm^{-3}, *T* = 213 K, $2\theta_{max}$ = 55.0°, *F*(000) = 388.80, reflections collected/unique 10589 / 4331 (R_{int} = 0.019), μ(MoKα) = 1.36 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.8716 – 1.0000. The data were corrected for Lorentz and polarization effects. Final *R* indices *R*1 = 0.066 [$I > 2\sigma(I)$], *wR*2 = 0.193 (all data), GOF on F^2 = 1.003, and residual electron density 1.85 / -1.60 e□$^{-3}$□The Flack parameter is 0.1(7) *[5].

Crystal data for (*Sa*)-**3**: $C_{42}H_{46}O_8S \square CH_3OH$ (M_r = 742.92), pale yellow prism, 0.2×0.2 ×0.2 mm, triclinic, space group *P1* (#1), *a* = 8.992(6)□, *b* = 10.317(7)□, *c* = 11.138(7)□, α= 101.179(12)°, β= 96.22(1)°, γ= 100.522(12)°, *V* = 985.5(11) □^{3}, *Z* = 1, ρ_{calcd} = 1.252 g cm^{-3}, *T* = 233 K, $2\theta_{max}$ = 55.0°, *F*(000) = 396.00, reflections collected/unique 10769 / 4419 (R_{int} = 0.031), μ(MoKα) = 1.37 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.8480 – 1.0000. The data were corrected for Lorentz and polarization effects. Final *R* indices *R*1 = 0.065 [$I > 2\sigma(I)$], *wR*2 = 0.147 (all data), GOF on F^2 = 1.252, and residual electron density 1.71 / -1.01 e□$^{-3}$□The Flack parameter is –0.2(2).

Crystal data for Racemate 1 [(*Ra*,1*S*,5*S*) + (*Sa*,1*R*,5*R*)]: $C_{41}H_{44}O_6 \square CH_2Cl_2 \square C_6H_6$($M_r$ = 795.84), colorless prism, 0.25×0.07×0.05 mm, triclinic, space group *P-1* (#2), *a* = 10.94(2)□, *b* = 13.81(6)□, *c* = 14.37(4)□, α= 107.52(8)°, β= 95.20(7)°, γ= 93.93(7)°, *V* = 2052.0(12) □^{3}, *Z* = 2, ρ_{calcd} = 1.288 g cm^{-3}, *T* = 173 K, $2\theta_{max}$ = 55.0°, *F*(000) = 844.00, reflections collected/unique 22640 / 8934 (R_{int} = 0.049), μ(MoKα) = 2.08 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.8651 – 1.0000. The data were corrected for Lorentz and polarization effects. Final *R* indices *R*1 = 0.078 [$I > 2\sigma(I)$], *wR*2 = 0.196 (all data), GOF on F^2 = 1.000, and residual electron density 0.56 / -0.52 e□$^{-3}$□

CCDC-242157 [(*Ra*)-**3**], CCDC-242158 [(*Sa*)-**3**], and CCDC-242975 (**Racemate 1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK;

fax(+44)1223-336-033; or deposit@ccdc.cam.au.uk).

*1; Rigaku Corporation, 1999.
*2; CrystalStructure 3.5.1: Crystal Structure Analysis Package, Rigaku and Rigaku / MSC(2000-2003). 9009 New Trails Dr. The Woodlands TX 77381 USA.
*3; CRYSTALS Issue 10: Watkin, D. J., Prout, C. K. Carruthers, J. R. & Betteridge, P. W. Chemical Crystallography Laboratory, Oxford, UK. (1996)
*4; Sheldrick, G. M. University of Gottingen: Gottingen, Germany, 1997.
*5; Flack, H. D. Acta Cryst. A39, 876-881 (1983).

ORTEP views for (*Ra*)-**3,** (*Sa*)-**3,** and racemate **1** [(*Ra*,1*S*,5*S*) + (*Sa*,1*R*,5*R*)] are shown in the following **Figure**.

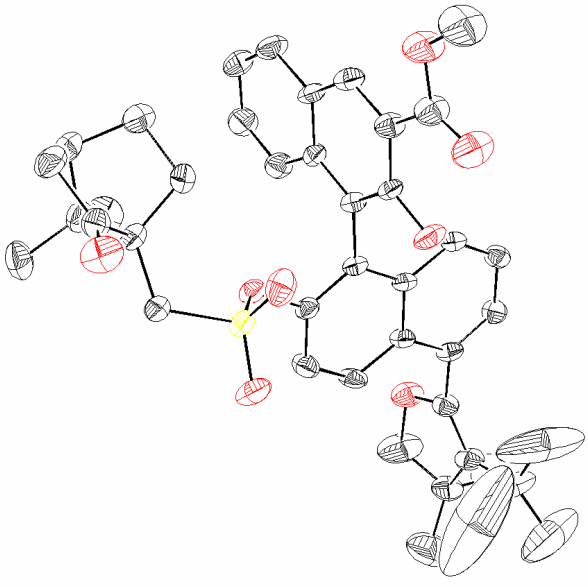


Figure. ORTEP view for (*Ra*)-3 and (*Sa*)-3

(*Ra*)-3

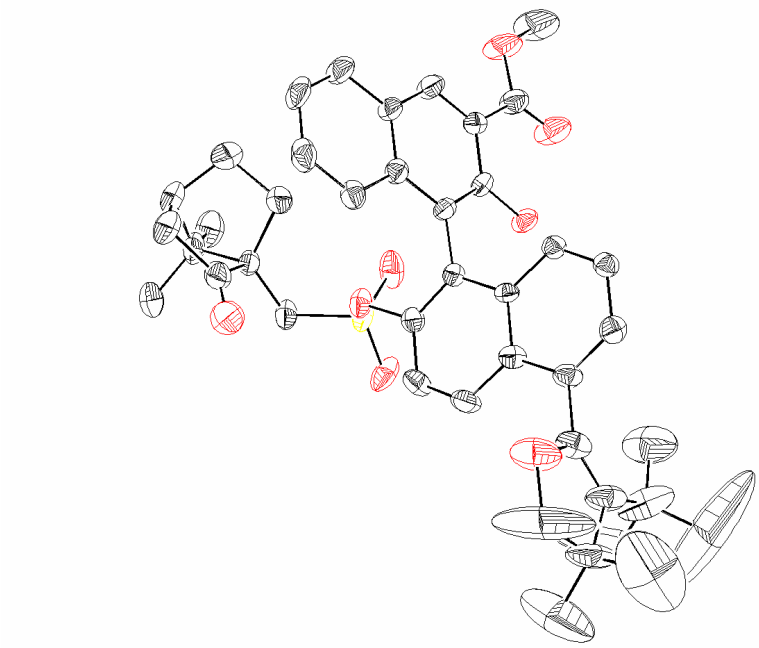
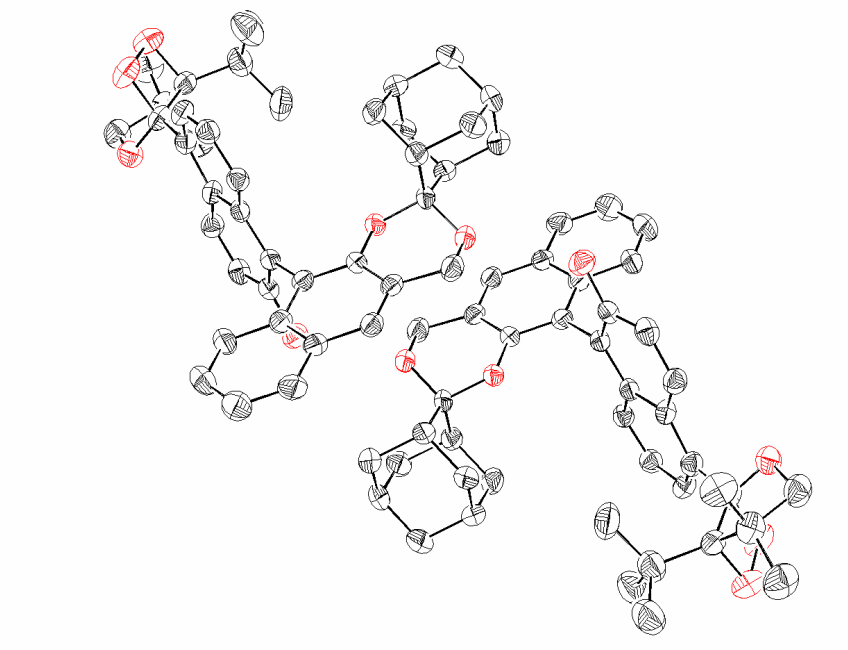


Figure. ORTEP view for racemate 1 [(*Ra*,1*S*,5*S*) + (*Sa*,1*R*,5*R*)]



Scheme 1. Synthetic Scheme of Optically Active Dioxetanes (**1**)