Electronic Supplementary Information

Cu(II)-catalyzed enantioselective oxygen atom transfer from oxaziridine to oxindole derivatives with chiral phenanthroline

Yuki Naganawa,* Tomotaka Aoyama, and Hisao Nishiyama*

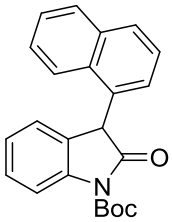
Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR-230 spectrometer. ^{1}H NMR spectra were measured at 25 ˚C on a Varian Mercury 300 (300 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, ddd = double-double-doublet, dt =double-triplet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured at 25 ˚C on a Varian Mercury 300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed carried out on a JASCO GULLIVER 1500 series using 4.6 mm x 25 cm Daicel Chiral Coulmns. High-resolution mass spectra (HRMS) were performed on a double-focusing magnetic sector mass spectrometer JEOL JMS-700. For thin layer chromatography (TLC) analysis throughout this work, TLC Silica gel 60 F_{254} were used. The products were purified by flash column chromatography on silica gel 60 N (Kanto, 60-210 μm).

In experiments requiring dry solvent, CH_2Cl_2, diethyl ether and isopropyl alcohol were purchased from Wako Pure Chemical Industries as “Dehydrated”. CPME was purchased from Sigma-Aldrich as “Dehydrated”. Toluene and THF were purchased from Kanto Chemical as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. BinThro ligands (*S*)-**1** were prepared according to our previous report.[S1] Oxindole derivatives **2**[S2] and Davis’ oxaziridine **3**[S3] were synthesized according to the literature, respectively.

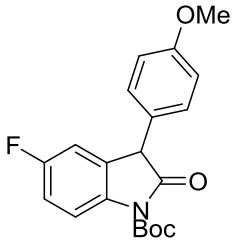
·Spectroscopic data and NMR spectra for new oxindole derivatives (2)

***N*-*t*-Butoxycarbonyl-3-(1-naphtyl)-2-oxindole (2g).**



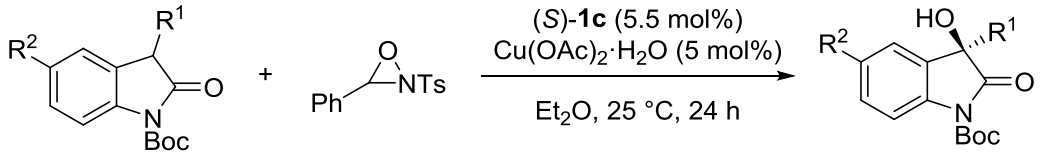
IR (KBr): 3050, 2976, 1784, 1598, 1511, 1480, 1394, 1352, 1299, 1143, 1092, 1048, 1023 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.33 (br, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.53 (br, 2H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.6 Hz, 3H), 5.64 (br, 1H), 1.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.4, 149.2, 134.0, 128.7, 128.4, 127.9, 126.5, 125.8, 125.2, 124.5, 123.7, 115.0, 84.4, 48.1, 28.2 (Six peaks were overlapped.); HRMS (FAB) Calcd for $C_{23}H_{21}NO_3$ ($[M]^+$) 359.1521. Found 359.1515.

***N*-*t*-Butoxycarbonyl-5-fluoro-3-(*p*-methoxyphenyl)-2-oxindole (2n).**

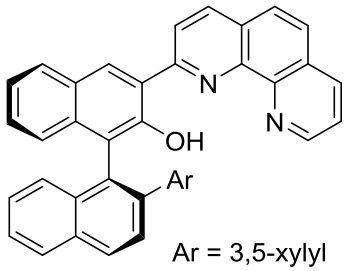


IR (KBr): 2982, 1774, 1717, 1608, 1510, 1485, 1371, 1346, 1296, 1249, 1146, 1093, 1036 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.89-7.93 (m, 1H), 7.05-7.11 (m, 3H), 6.87-6.90 (m, 3H), 4.66 (s, 1H), 3.80 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.4, 159.6 (d, *J* = 242 Hz), 159.1, 149.1, 136.1 (d, *J* = 2.3 Hz), 129.3 (d, *J* = 9.1 Hz), 129.2, 127.4, 116,2 (d, *J* = 7.4 Hz), 115.0 (d, *J* = 22.2 Hz), 114.3, 112.3 (d, *J* = 24.0 Hz), 84.5, 55.4, 51.9 (d, *J* = 1.7 Hz), 28.2; HRMS (FAB) Calcd for $C_{20}H_{20}FNO_4$ ($[M]^+$) 357.1376. Found 357.1376.

·General procedure for enantioselective C-H oxidation of oxindoles (2).



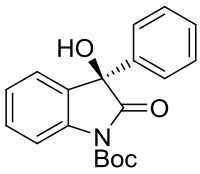
2 **3** (*R*)-**4**



(*S*)-**1c**

To a mixture of (*S*)-**1c** (3.0 mg, 5.5 μmol) and $Cu(OAc)_2 \cdot H_2O$ (1.0 mg, 5.0 μmol) in schlenk tube under Ar atmosphere, dry diethyl ether (1 mL) were added at 25 °C. After stiring for 1 h at 25 °C, oxindole **2** (0.1 mmol) was added portion-wise to the mixture. After stiring another 5 min, Davis' oxaziridine **3** (33.0 mg, 0.12 mmol) was added portion-wise to the mixture and stirred for 24 h at the same temperature. The catalyst was removed by passing through short column chromatography on silica gel (eluting chloroform) and the solvent was evapolated. The residue was purified by column chromatography (eluting hexane/EtOAc) to give the desired product (*R*)-**4**.

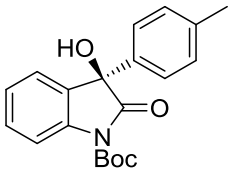
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-phenyl-2-oxindole (4a).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (d, *J* = 7.8 Hz, 1H), 7.17-7.49 (m, 8H), 3.37 (s, 1H), 1.64 (s, 9H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, retention time; 26.1 min (*R*) and 56.5 min (*S*)). [e.r. = 97.5/2.5][e.e. = 95.0%]

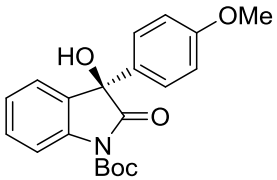
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(4-methylphenyl)-2-oxindole (4b).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.96 (d, *J* = 8.1 Hz, 1H), 7.18-7.43 (m, 7H), 3.37 (s, 1H), 2.36 (s, 3H), 1.67 (s, 9H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, retention time; 15.1 min (*R*) and 28.3 min (*S*)). [e.r. = 98.0/2.0][e.e. = 96.0%]

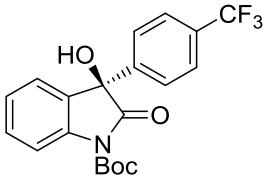
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(4-methoxyphenyl)-2-oxindole (4c).



IR (KBr): 3444, 2979, 1779, 1732, 1609, 1510, 1467, 1370, 1344, 1289, 1253, 1149, 1102, 1034 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, *J* = 8.1 Hz, 1H), 7.20-7.42 (m, 5H), 6.85 (dd, *J* = 2.1 Hz, 6.9 Hz, 2H), 3.78 (s, 3H), 3.36 (s, 1H), 1.62 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.6, 159.5, 148.8, 139.3, 131.5, 129.9, 128.0, 126.9, 125.0, 124.8, 115.2, 113.8, 84.8, 77.2, 55.4, 28.2; $[\alpha]_D^{26}$ = +17.1 (c = 0.98, $CHCl_3$); HRMS (FAB) Calcd for $C_{20}H_{21}NO_5$ ($[M+Na]^+$) 378.1317. Found 378.1317.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.8 mL/min, retention time; 30.5 min (*R*) and 53.8 min (*S*)). [e.r. = 96.5/3.5][e.e. = 93.0%]

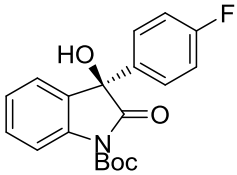
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(4-trifluoromethylphenyl)-2-oxindole (4d).



IR (KBr): 3821, 3448, 2983, 1793, 1737, 1609, 1468, 1413, 1372, 1327, 1253, 1150, 1069, 1018 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.96 (d, *J* = 8.4 Hz, 1H), 7.43-7.61 (m, 5H), 7.22-7.26 (m, 2H), 3.44 (s, 1H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 174.8, 148.6, 143.3, 139.4, 130.5 (q, *J* = 32.5 Hz), 130.4, 129.4, 125.9, 125.4 (q, *J* = 4.0 Hz), 125.4, 124.8, 123.6 (q, *J* = 270 Hz), 115.5, 85.2, 77.2, 28.2; $[\alpha]_D^{26}$ = +19.1 (c = 0.63, $CHCl_3$); HRMS (FAB) Calcd for $C_{20}H_{18}FNO_4$ ($[M+Na]^+$) 416.1086. Found 416.1103.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, retention time; 9.4 min (*R*) and 14.6 min (*S*)). [e.r. = 97.4/2.6][e.e. = 94.8%]

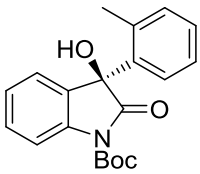
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy -3-(4-fluorophenyl) -2-oxindole (4e).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (d, *J* = 8.4 Hz, 1H), 7.22-7.44 (m, 5H), 7.20 (dt, *J* = 15 Hz, 0.9 Hz, 1H), 3.34 (s, 1H), 1.63 (s, 9H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, retention time; 13.8 min (*R*) and 24.1 min (*S*)). [e.r. = 97.5/2.5][e.e. = 95.0%]

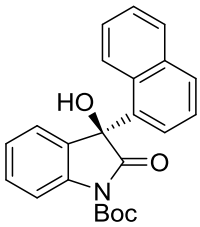
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(2-methylphenyl)-2-oxindole (4f).



IR (KBr): 3865, 3803, 3751, 3446, 3059, 2980, 2931, 1730, 1608, 1480, 1292, 1149, 1094, 1036 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.90-7.95 (m, 2H), 7.22-7.42 (m, 4H), 7.05-7.16 (m, 3H), 3.18 (s, 1H), 1.88 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.0, 148.8, 139.9, 137.3, 134.3, 131.4, 130.1, 128.7, 128.4, 125.9, 125.6, 125.1, 124.7, 115.2, 84.8, 77.3, 28.2, 19.8; $[\alpha]_D^{26}$ = +86.5 (c = 0.97, $CHCl_3$); HRMS (FAB) Calcd for $C_{20}H_{21}NO_4$ ($[M+H]^+$) 340.1549. Found 340.1560.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, retention time; 31.0 min (*R*) and 103.6 min (*S*)). [e.r. = 90.0/10.0][e.e. = 80.0%]

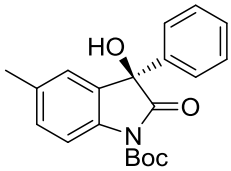
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(1-naphtyl)-2-oxindole (4g).



IR (KBr): 3444, 2980, 1733, 1607, 1511, 1479, 1287, 1155, 1101, 1002, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 6.9 Hz, 1H), 7.84-7.90 (m, 2H), 7.70 (d, 1H), 7.33-7.53 (m, 5H), 7.18-7.20 (m, 1H), 7.06-7.12 (m, 1H), 3.41 (s, 1H), 1.68 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.0, 149.0, 139.4, 134.3, 134.1, 130.3, 130.1, 129.8, 129.7, 128.9, 126.4, 125.4, 125.1, 124.8, 124.71, 124.68, 124.0, 115.6, 84.9, 78.3, 28.2; $[\alpha]_D^{26}$ = +93.0 (c = 1.0, $CHCl_3$); HRMS (FAB) Calcd for $C_{23}H_{21}NO_4$ ($[M]^+$) 375.1471. Found 375.1466.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, retention time; 40.0 min (*R*) and 98.0 min (*S*)). [e.r. =83.5/16.5][e.e. = 67.0%]

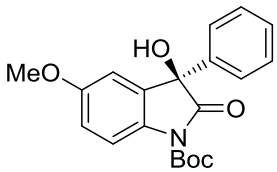
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-methyl-3-phenyl-2-oxindole (4h).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 1H), 7.30-7.35 (m, 5H), 7.11-7.21 (m, 2H), 7.11 (d, *J* = 0.6 Hz, 1H) 3.26 (s, 1H), 2.33 (s, 3H) 1.64 (s, 9H); The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.8 mL/min, retention time; 18.6 min (*R*) and 32.0 min (*S*)). [e.r. = 97.8/2.2][e.e. = 95.6%]

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-methoxy-3-phenyl-2-oxindole (4i).

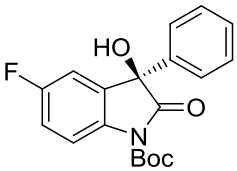


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.86 (d, *J* = 9.0 Hz, 1H), 7.26-7.36 (m, 5H), 6.93 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.85 (d, 2.7 Hz, 1H), 3.77 (s, 3H), 3.31 (br, 1H), 1.63 (s, 9H).; $[\alpha]_D^{25}$ = +31.6 (c

= 1.0, $CHCl_3$). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.8 mL/min, retention time; 30.0 min (*R*) and 54.0 min (*S*)). [e.r. = 96.9/3.1][e.e. = 93.8%]

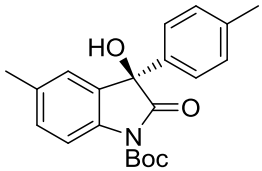
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-fluoro-3-phenyl-2-oxindole (4j).



IR (KBr): 3429, 2927, 1789, 1732, 1610, 1511, 1485, 1371, 1341, 1297, 1252, 1149, 1108, 1034, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (dd, *J* = 4.8 Hz, 9.0 Hz, 1H), 7.33 (m, 5H), 7.01-7.13 (m, 2H), 3.35 (s, 1H), 1.64 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.2, 159.9 (d, *J* = 243 Hz), 148.6, 139.0, 135.2 (d, *J* = 2.3 Hz), 131.6 (d, *J* = 8.0 Hz), 128.6, 125.9, 125.1, 116.8 (d, *J* = 4.0 Hz), 116.6 (d, *J* = 19.4 Hz), 112.3 (d, *J* = 2.4 Hz), 85.1, 77.6 (d, *J* = 1.7 Hz), 28.2; $[\alpha]_D^{23}$ = +69.6 (c = 0.71, $CHCl_3$). HRMS (FAB) Calcd for $C_{19}H_{18}FNO_4$ ($[M+Na]^+$) 366.1118. Found 366.1122.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.8 mL/min, retention time; 14.5 min (*R*) and 25.5 min (*S*)). [e.r. = 97.3/2.7][e.e. = 94.6%]

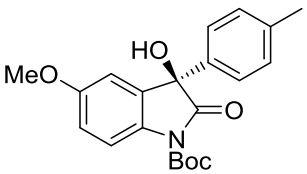
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-methyl-3-(4-methylphenyl)-2-oxindole (4k).



^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.80 (d, *J* = 8.4 Hz, 1H), 7.12-7.23 (m, 6H), 3.25 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.63 (s, 9H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate =1.0 mL/min, retention time; 16.5 min (*R*) and 27.0 min (*S*)). [e.r. =97.3/2.7][e.e. = 94.6%]

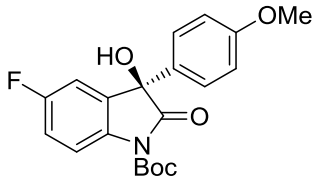
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-methoxy-3-(4-methylphenyl)-2-oxindole (4l).



IR (KBr): 3444, 2979, 1779, 1733, 1609, 1510, 1467, 1370, 1344, 1289, 1252, 1149, 1102, 1034, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.86 (d, *J* = 9.0 Hz, 1H), 7.23-7.26 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.92 (dd, *J* = 2.7 Hz, 8.7 Hz 1H), 6.86 (d, *J* = 2.7 Hz 1H), 3.77 (s, 3H), 3.18 (s, 1H), 2.33 (s, 3H), 1.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.6, 157.0, 148.8, 138.2, 136.5, 132.6, 131.1, 129.1, 125.2, 116.3, 115.4, 110.1, 84.5, 77.8, 55.7, 28.2, 21.3; $[\alpha]_D^{25}$ = -1.0 (c = 1.0, $CHCl_3$); HRMS (FAB) Calcd for $C_{21}H_{23}NO_5$ ($[M+Na]^+$) 392.1474. Found 392.1479.

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, retention time; 27.2 min (*R*) and 50.7 min (*S*)). [e.r. = 97.9/2.1][e.e. = 95.8%]

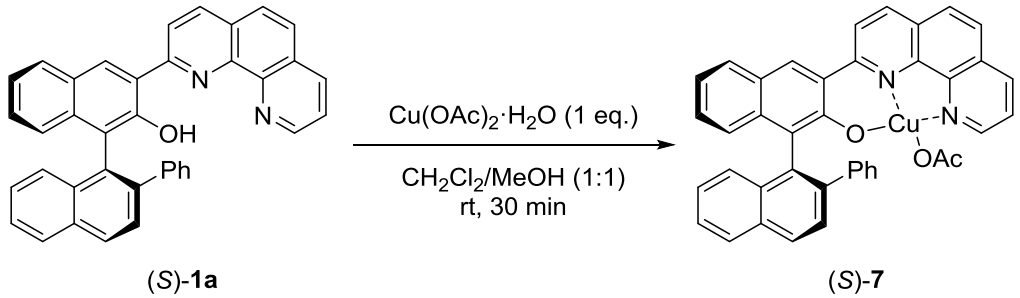
(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-5-fluoro-3-(4-methoxyphenyl)-2-oxindole (4m).



IR (KBr): 3821, 3448, 2983, 1793, 1737, 1609, 1468, 1413, 1372, 1327, 1254, 1150, 1069, 1018 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.90-7.95 (m, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.03-7.13 (m, 2H), 6.87 (dd, *J* = 6.9 Hz, 9.3 Hz, 2H), 3.79 (s, 3H), 3.33 (s, 1H), 1.63 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 175.3, 159.9 (d, *J* = 243 Hz), 159.6, 148.7, 135.2, 131.6 (d, *J* = 8.0 Hz), 131.0, 126.7, 116.8 (d, *J* = 7.4 Hz), 116.4, 114.0, 112.3 (d, *J* = 24.0 Hz), 85.0, 77.2 (d, *J* = 5.1 Hz), 55.4, 28.2; $[\alpha]_D^{27}$ = +21.0 (c = 0.84, $CHCl_3$); HRMS (FAB) Calcd for $C_{20}H_{20}FNO_5$ ($[M+Na]^+$) 396.1223. Found 396.1222.

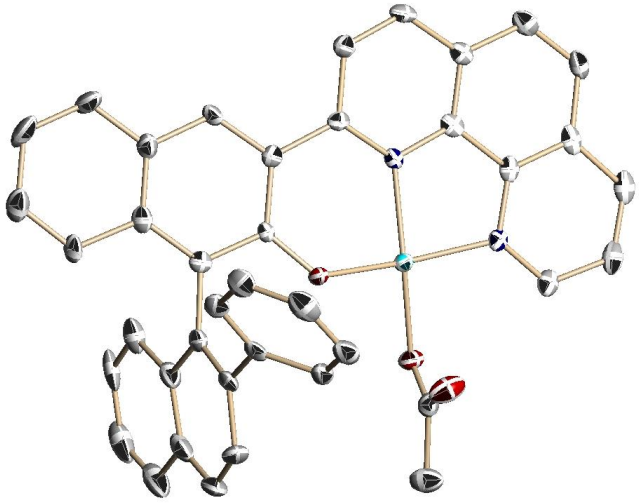
The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL AD-H, hexane/*i*PrOH = 95/5, flow rate = 0.5 mL/min, retention time; 25.1 min (*R*) and 41.5 min (*S*)). [e.r. = 97.24/2.76][e.e. = 94.48%]

·General procedure for the preparation of Cu complex (*S*)-7.



A yellow solution of BinThro (*S*)-**1a** (52.4 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was added to a pale blue solution of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.1 mmol) in MeOH (5 mL). The color of the mixture changed to dark red. Then, the mixture was concentrated to ca. 2 mL to form dark red solids, which were collected by filtration. The crude products were recrystallized with acetone to give dark red crystals (*S*)-**7** of 54.0 mg (84% yield).

X-ray crystallographic analysis of (*S*)-7.



A clear dark orange columun-like specimen of $C_{40}H_{26}CuN_2O_3$, approximate dimensions 0.100 mm x 0.400 mm x 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 23913 reflections to a maximum θ angle of 25.06° (0.84 Å resolution), of which 11568 were independent (average redundancy 2.067, completeness = 99.4%, R_{int} = 1.87%) and 10939 (94.56%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.2618(6) Å, b = 13.0327(5) Å, c = 17.7452(8) Å, β = 108.0781(12)°, volume = 3355.3(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum

transmission coefficients (based on crystal size) are 0.7700 and 0.9340.

The final anisotropic full-matrix least-squares refinement on F^2 with 876 variables converged at R1 = 5.77%, for the observed data and wR2 = 18.26% for all data. The goodness-of-fit was 1.507. The largest peak in the final difference electron density synthesis was 2.510 $e^-/Å^3$ and the largest hole was -0.539 $e^-/Å^3$ with an RMS deviation of 0.129 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.279 g/cm^3 and F(000), 1332 e^-.

Table 1. Sample and crystal data for Naganawa5420.

Identification code	Naganawa5420	
Chemical formula	$C_{40}H_{26}CuN_2O_3$	
Formula weight	646.17	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.400 x 0.400 mm	
Crystal habit	clear dark orange columun	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 15.2618(6) Å	α = 90°
	b = 13.0327(5) Å	β = 108.0781(12)°
	c = 17.7452(8) Å	γ = 90°
Volume	3355.3(2) $Å^3$	
Z	4	
Density (calculated)	1.279 g/cm^3	
Absorption coefficient	0.691 mm^{-1}	
F(000)	1332	

Table 2. Data collection and structure refinement for Naganawa5420.

Theta range for data collection	2.19 to 25.06°
Index ranges	-18<=h<=17, -15<=k<=15, -20<=l<=20
Reflections collected	23913

Independent reflections	11568 [R(int) = 0.0187]	
Max. and min. transmission	0.9340 and 0.7700	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11568 / 1 / 876	
Goodness-of-fit on F^2	1.507	
Δ/σ_{max}	0.008	
Final R indices	10939 data; $I>2\sigma(I)$	R1 = 0.0577, wR2 = 0.1798
	all data	R1 = 0.0603, wR2 = 0.1826
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	2.510 and -0.539 $eÅ^{-3}$	
R.M.S. deviation from mean	0.129 $eÅ^{-3}$	

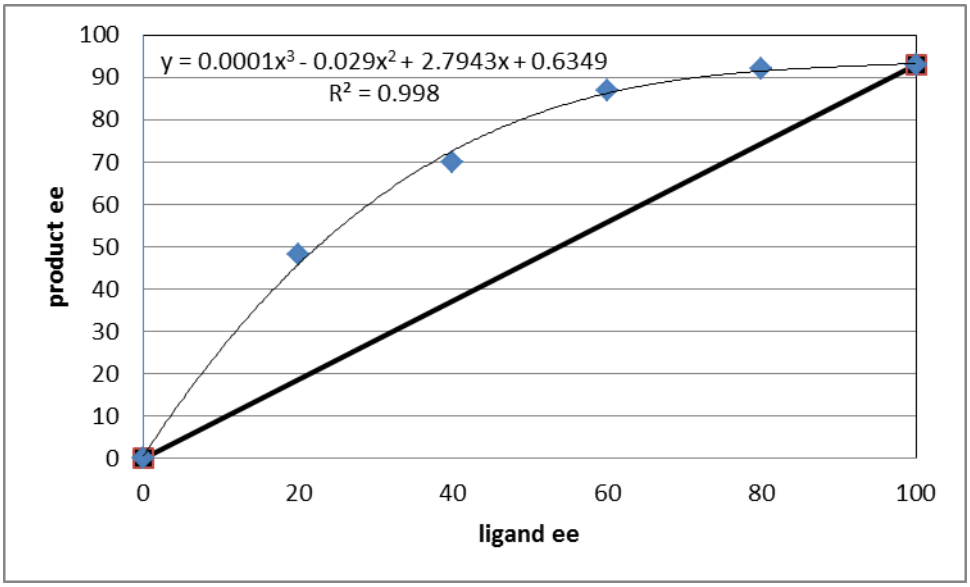


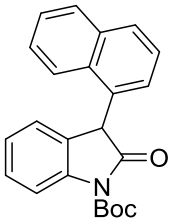
Figure S1. The relationship between ee of (*S*)-**2a** and ee of the product (*R*)-**1a**. (refer to Table 3)

·**References.**

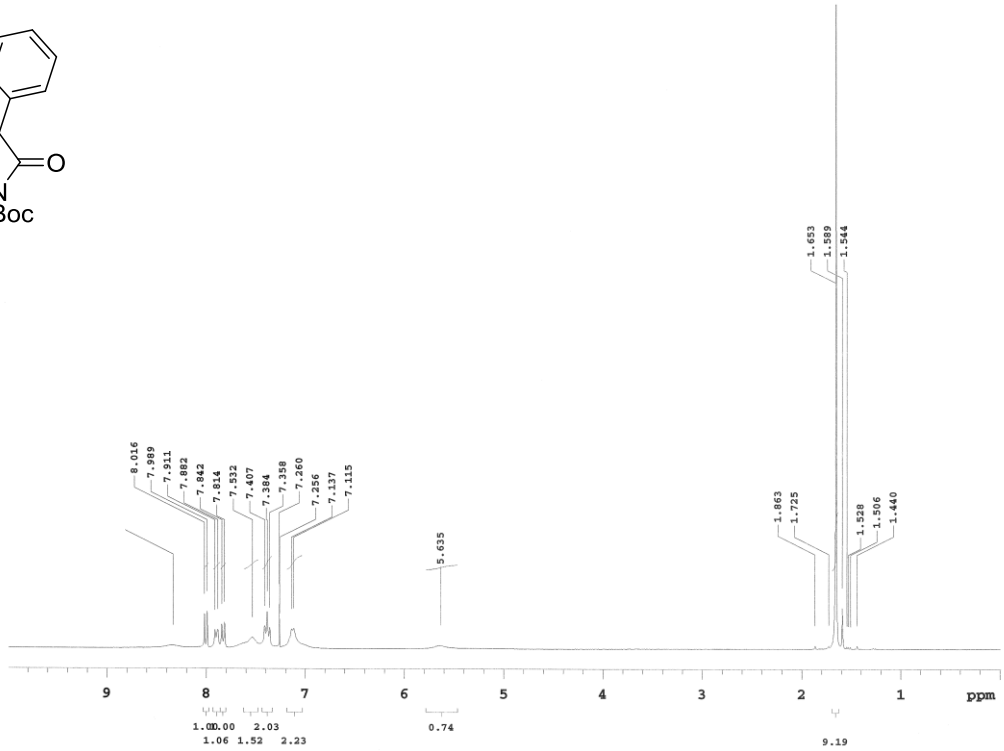
(S1) Y. Naganawa, T. Namba, T. Aoyama, K. Shoji, H. Nishiyama, H. *Chem. Commun*. **2014**, *50*, 13224.

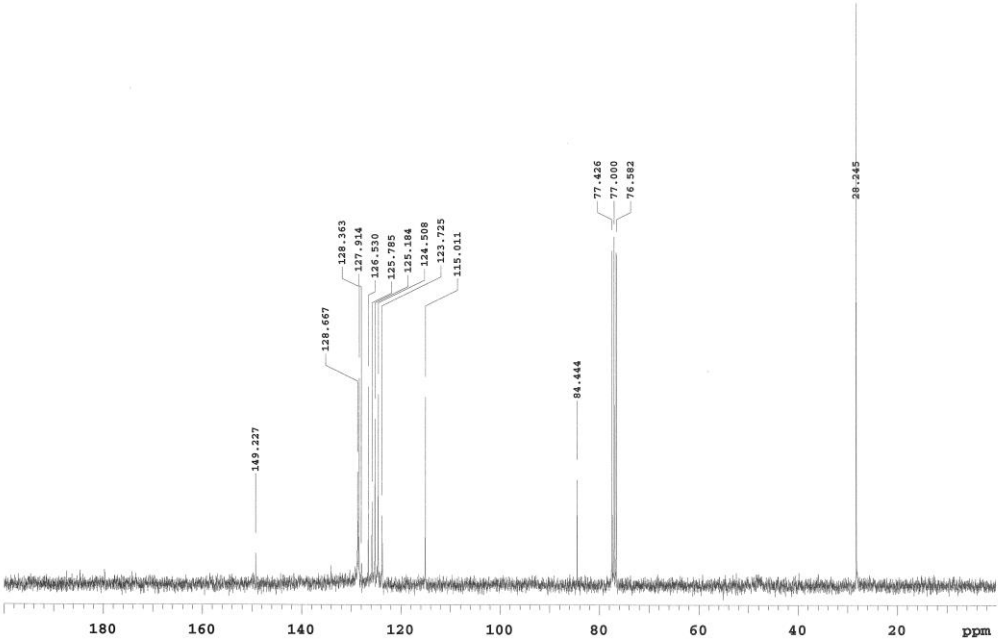
(S2) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru, S. Kanemasa, *J. Am. Chem. Soc*. **2006**, *128*, 16488.

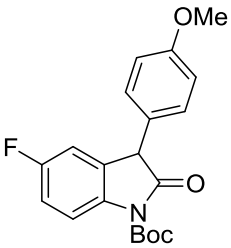
(S3) J. L. G. Ruano, J. Alemán, C. Fajardo, A. Parra, *Org. Lett*. **2005**, *7*, 5493.


O
N
Boc

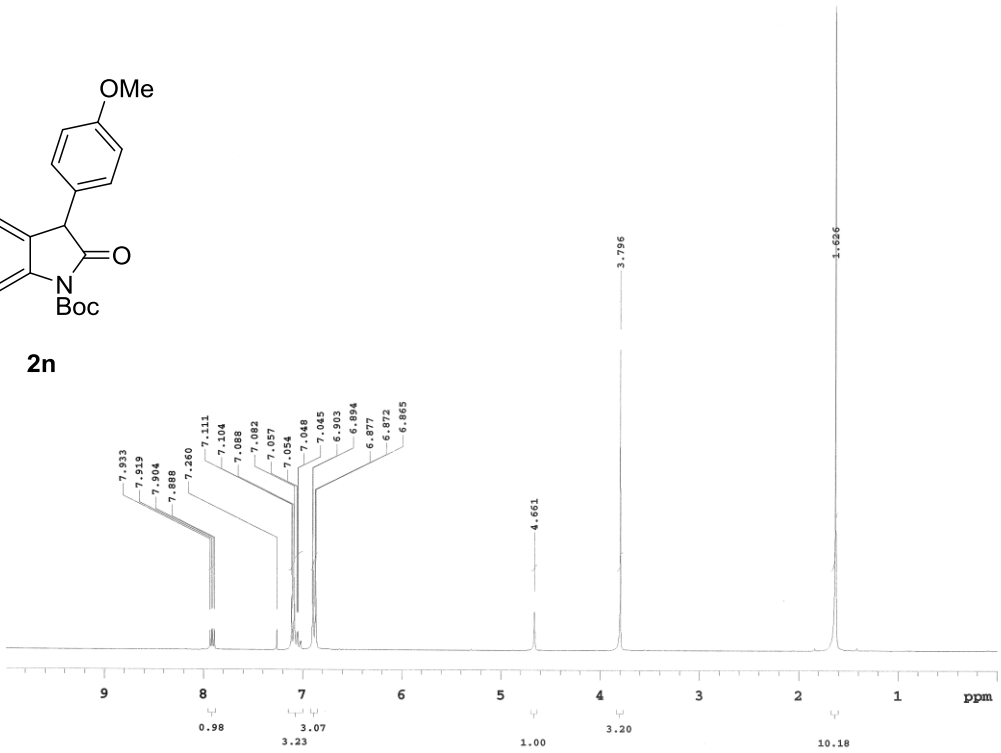
2g

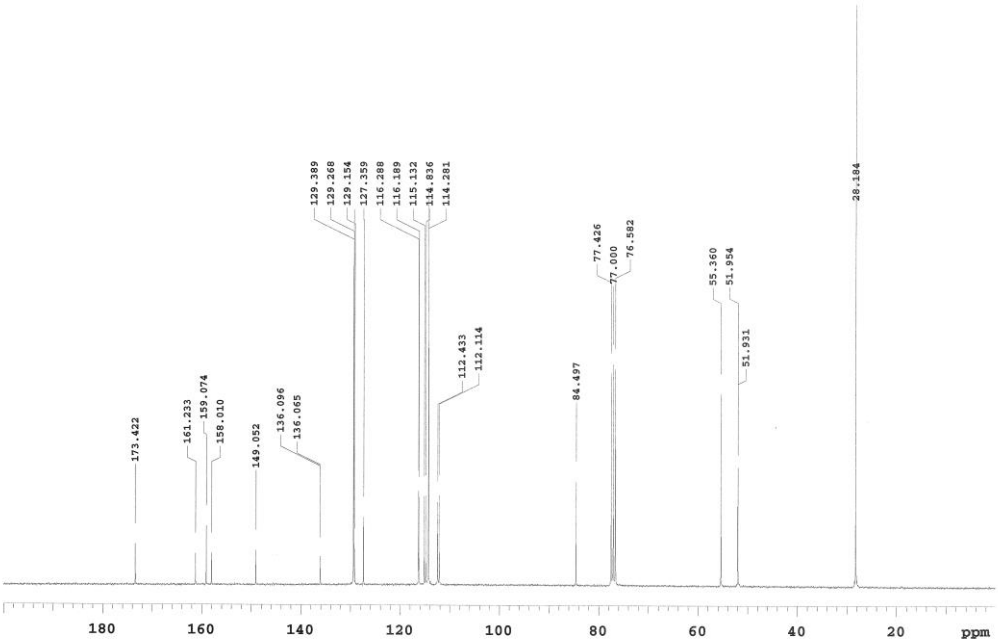

8.016
7.989
7.911
7.882
7.842
7.814
7.532
7.407
7.384
7.358
7.260
7.256
7.137
7.115
5.635
1.863
1.725
1.653
1.589
1.544
1.528
1.506
1.440
9
8
7
6
5
4
3
2
1
ppm
1.00 1.00 2.03
1.06 1.52 2.23
0.74
9.19

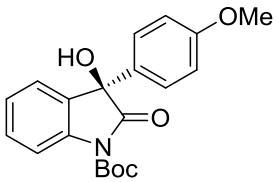

149.227
128.667
128.363
127.914
126.530
125.785
125.184
124.508
123.725
115.011
84.444
77.426
77.000
76.582
28.245
180
160
140
120
100
80
60
40
20
ppm


OMe
F
O
N
Boc

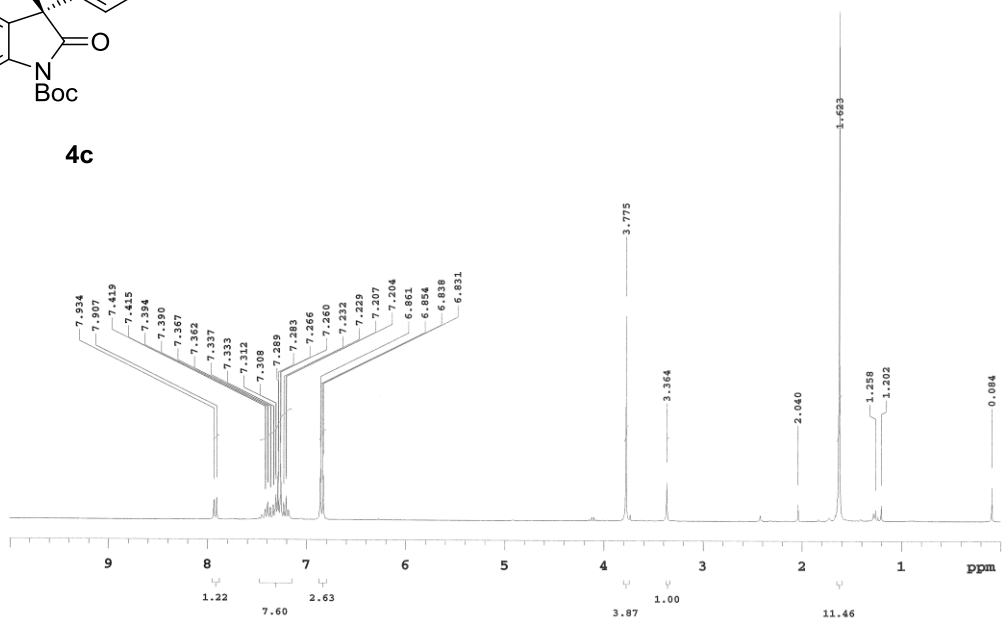
2n

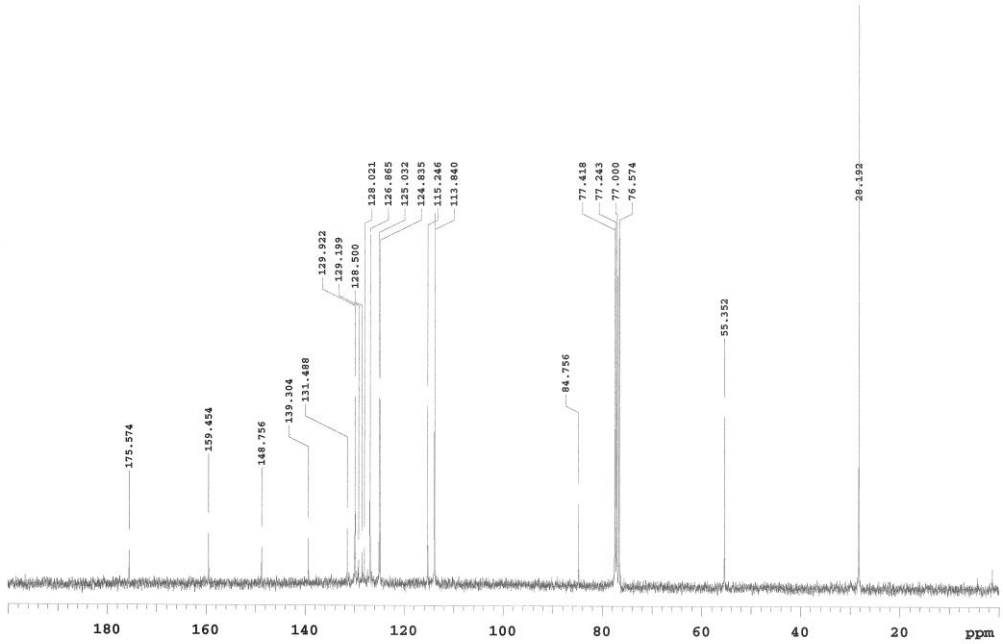

7.933
7.919
7.904
7.888
7.260
7.111
7.104
7.088
7.082
7.057
7.054
7.048
7.045
6.903
6.894
6.877
6.872
6.865
4.661
3.796
1.626
9
8
7
6
5
4
3
2
1
ppm
0.98
3.23
3.07
1.00
3.20
10.18

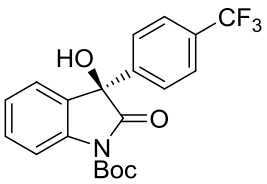

173.422
161.233
159.074
158.010
149.052
136.096
136.065
129.389
129.268
129.154
127.359
116.288
116.189
115.132
114.836
114.281
112.433
112.114
84.497
77.426
77.000
76.582
55.360
51.954
51.931
28.184
180
160
140
120
100
80
60
40
20
ppm


OMe
HO
O
N
Boc

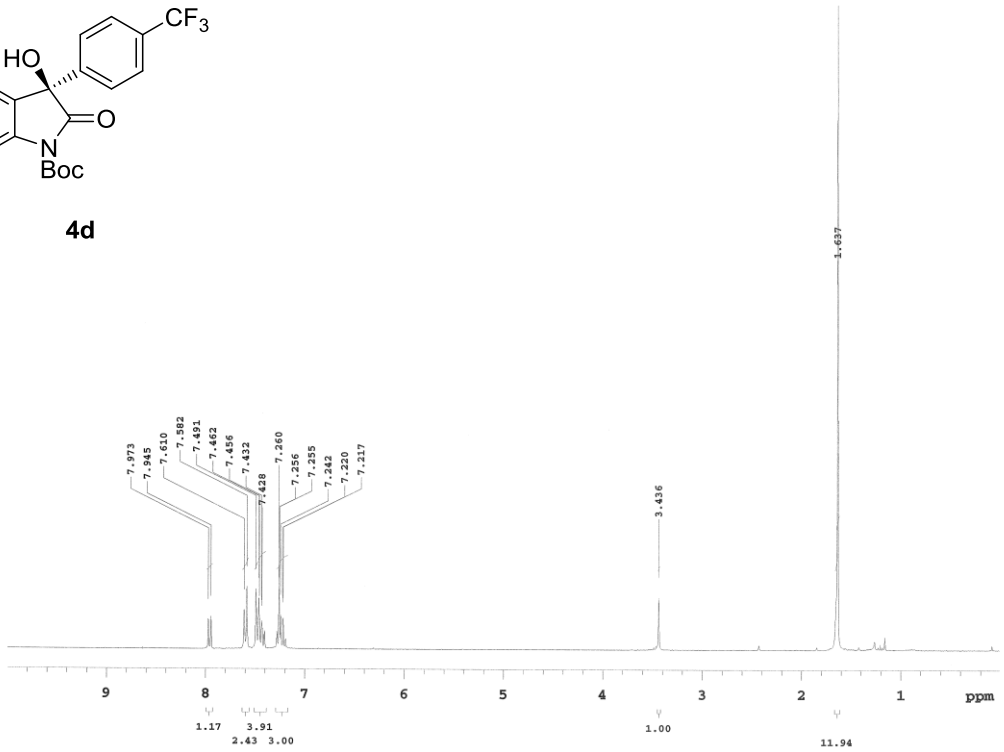
4c

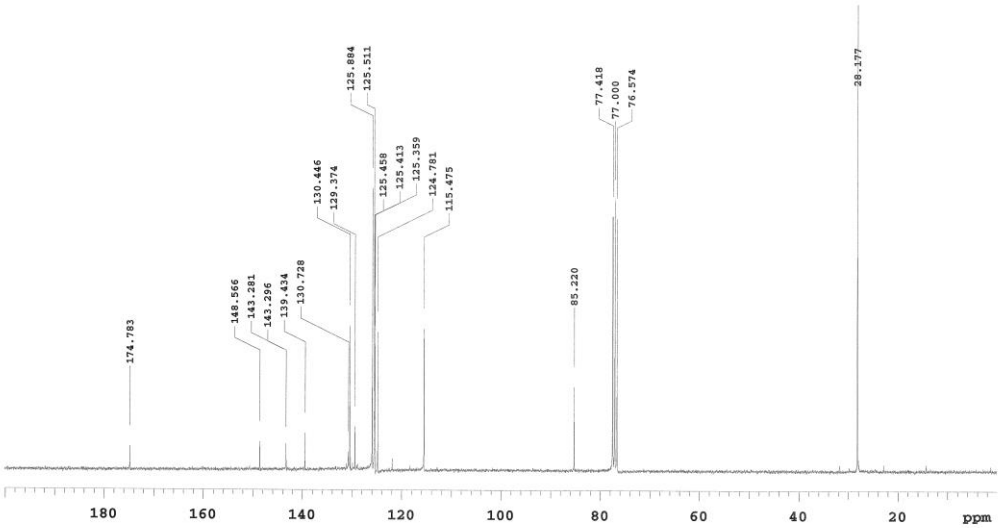

7.934
7.907
7.419
7.415
7.394
7.390
7.367
7.362
7.337
7.333
7.312
7.308
7.289
7.283
7.266
7.260
7.232
7.229
7.207
7.204
6.861
6.854
6.838
6.831
3.775
3.364
2.040
1.623
1.258
1.202
0.084
9
8
7
6
5
4
3
2
1
ppm
1.22
7.60
2.63
3.87
1.00
11.46

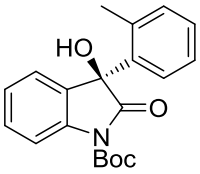

175.574
159.454
148.756
139.304
131.488
129.922
129.199
128.500
128.021
126.865
125.032
124.835
115.246
113.840
84.756
77.418
77.243
77.000
76.574
55.352
28.192
180
160
140
120
100
80
60
40
20
ppm


CF3
HO
O
N
Boc

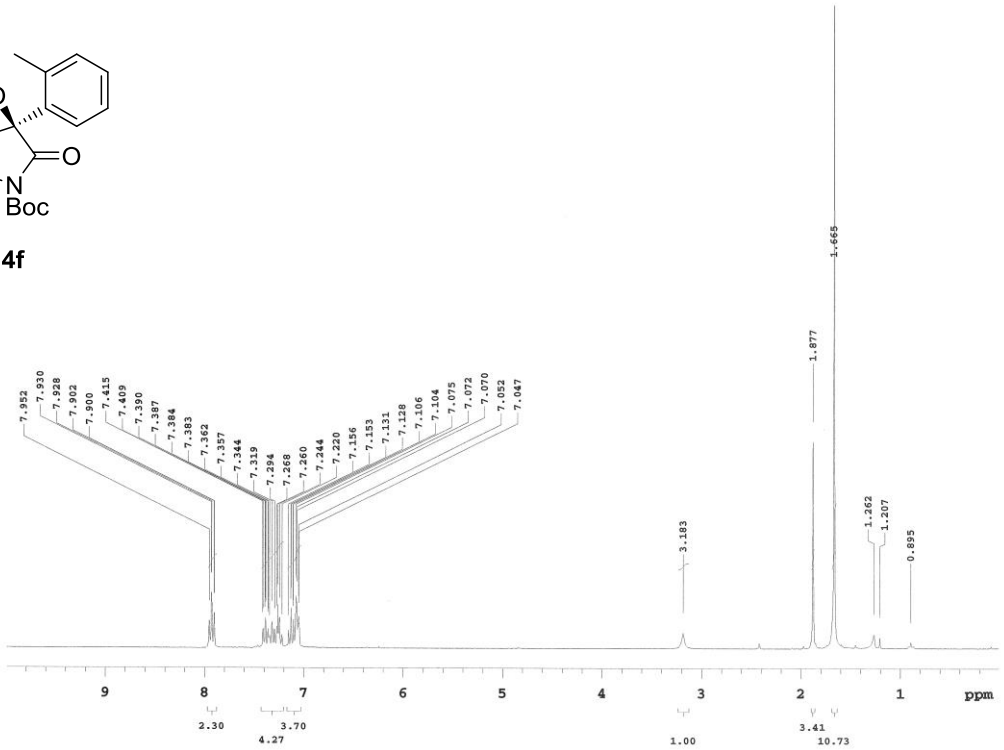
4d

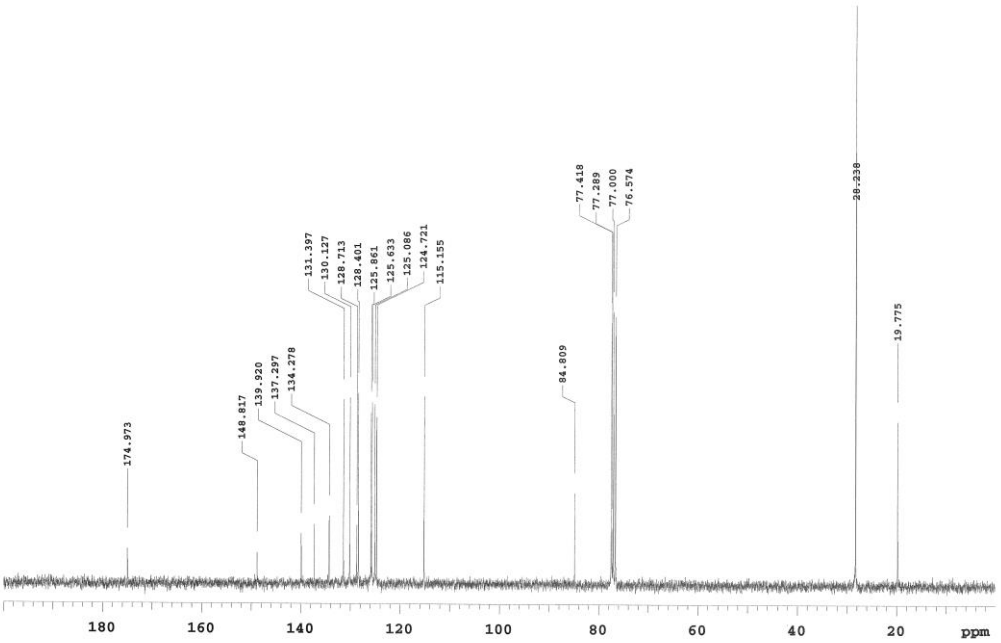

7.973
7.945
7.610
7.582
7.491
7.462
7.456
7.432
7.428
7.260
7.256
7.255
7.242
7.220
7.217
3.436
1.637
9
8
7
6
5
4
3
2
1
ppm
1.17
3.91
2.43
3.00
1.00
11.94

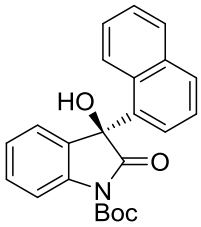

174.783
148.566
143.281
143.296
139.434
130.728
130.446
129.374
125.884
125.511
125.458
125.413
125.359
124.781
115.475
85.220
77.418
77.000
76.574
28.177
180
160
140
120
100
80
60
40
20
ppm


HO
O
N
Boc

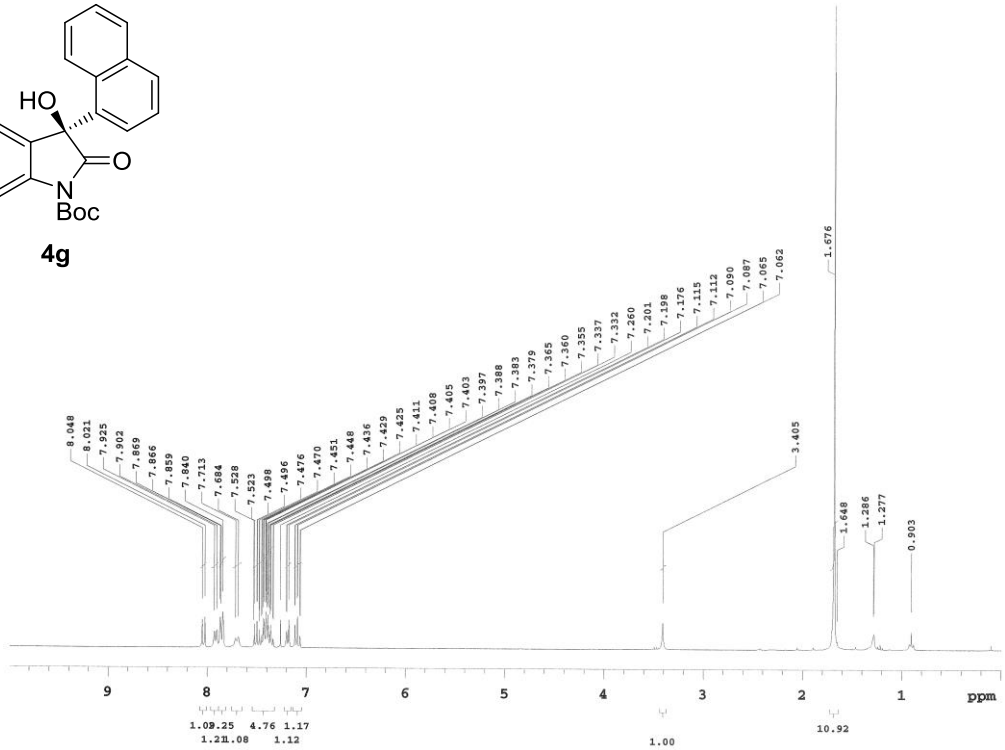
4f

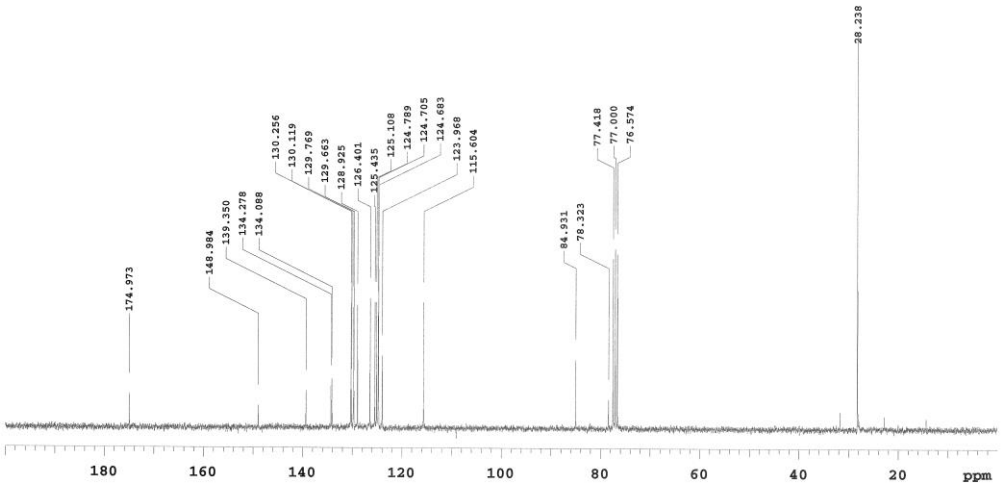

7.952
7.930
7.928
7.902
7.900
7.415
7.409
7.390
7.387
7.384
7.383
7.362
7.357
7.344
7.319
7.294
7.268
7.260
7.244
7.220
7.156
7.153
7.131
7.128
7.106
7.104
7.075
7.072
7.070
7.052
7.047
3.183
1.877
1.665
1.262
1.207
0.895
9
8
7
6
5
4
3
2
1
ppm
2.30
3.70
4.27
1.00
3.41
10.73

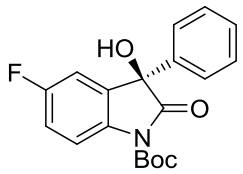

174.973
148.817
139.920
137.297
134.278
131.397
130.127
128.713
128.401
125.861
125.633
125.086
124.721
115.155
84.809
77.418
77.289
77.000
76.574
28.238
19.775
180
160
140
120
100
80
60
40
20
ppm


HO
O
N
Boc

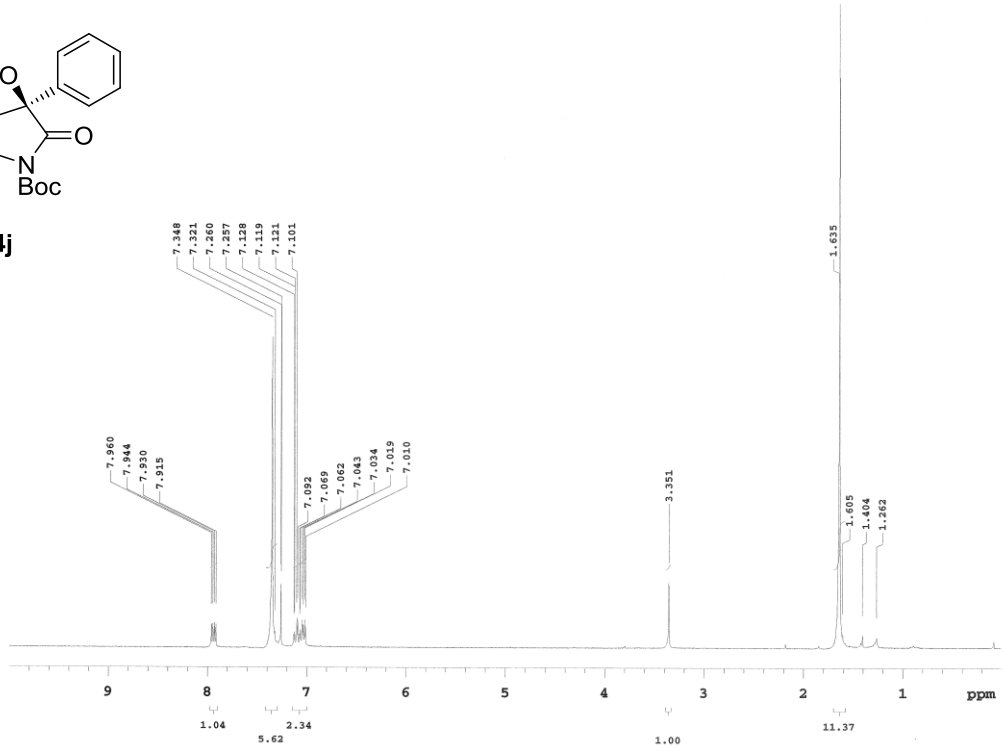
4g

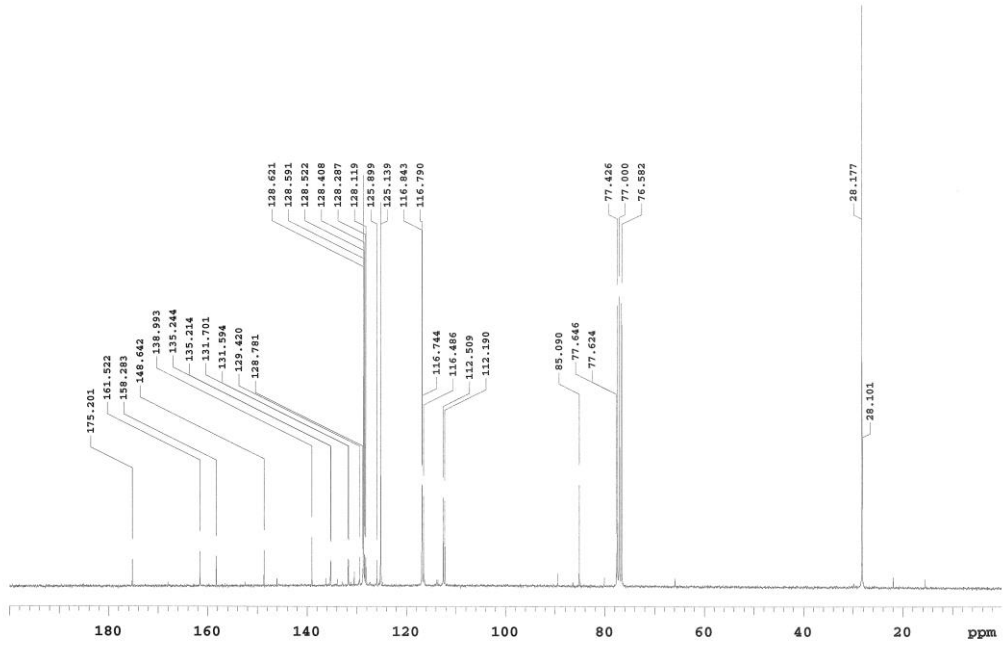

8.048
8.021
7.925
7.902
7.869
7.866
7.859
7.840
7.713
7.684
7.528
7.523
7.498
7.496
7.476
7.470
7.451
7.448
7.436
7.429
7.425
7.411
7.408
7.405
7.403
7.397
7.388
7.383
7.379
7.365
7.360
7.355
7.337
7.332
7.260
7.201
7.198
7.176
7.115
7.112
7.090
7.087
7.065
7.062
3.405
1.676
1.648
1.286
1.277
0.903
9
8
7
6
5
4
3
2
1
ppm
1.09
1.21
25
11.08
4.76
1.12
1.17
1.00
10.92

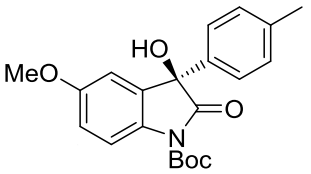

28.238
174.973
148.984
139.350
134.278
134.088
130.256
130.119
129.769
129.663
128.925
126.401
125.435
125.108
124.789
124.705
124.683
123.968
115.604
84.931
78.323
77.418
77.000
76.574
180
160
140
120
100
80
60
40
20
ppm


HO
F
O
N
Boc

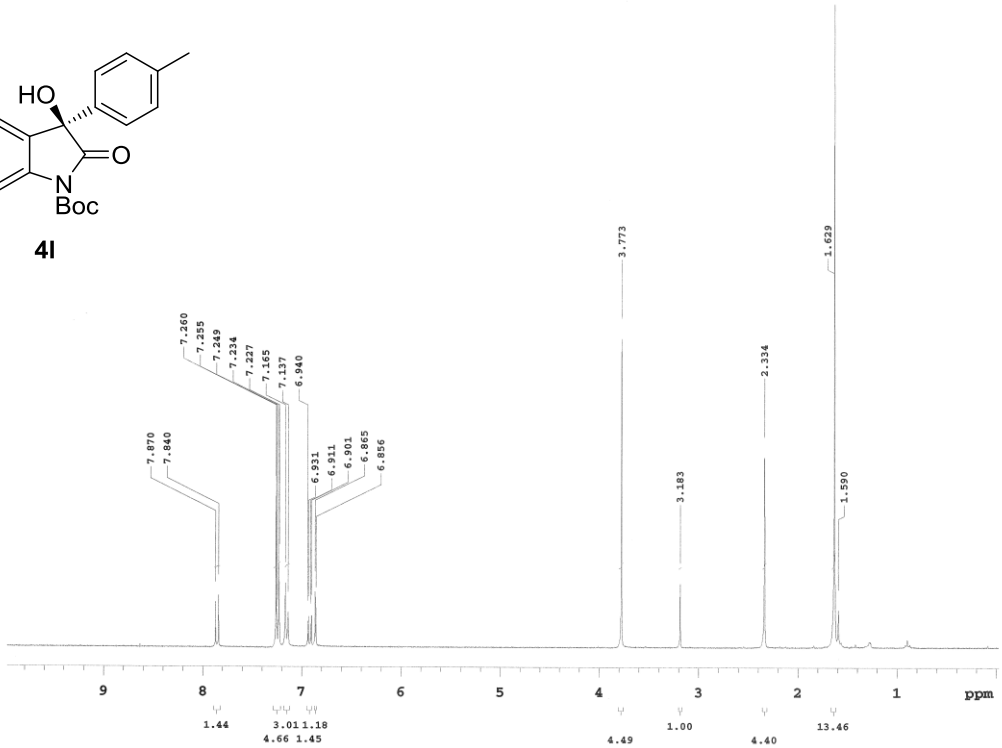
4j

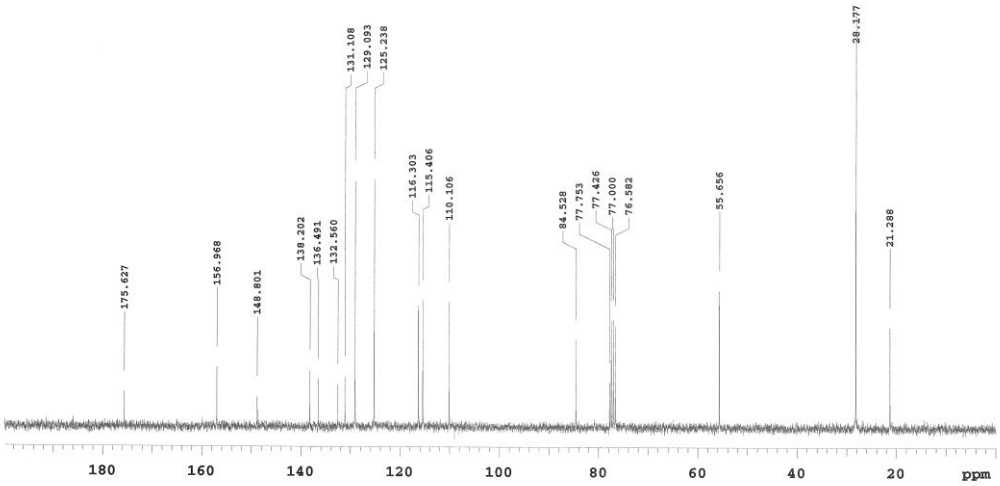

7.348
7.321
7.260
7.257
7.128
7.119
7.121
7.101
7.960
7.944
7.930
7.915
7.092
7.069
7.062
7.043
7.034
7.019
7.010
3.351
1.635
1.605
1.404
1.262
9
8
7
6
5
4
3
2
1
ppm
1.04
2.34
5.62
1.00
11.37

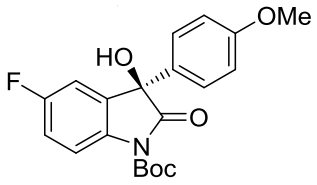

128.621
128.591
128.522
128.408
128.287
128.119
125.899
125.139
116.843
116.790
77.426
77.000
76.582
28.177
175.201
161.522
158.283
148.642
138.993
135.244
135.214
131.701
131.594
129.420
128.781
116.744
116.486
112.509
112.190
85.090
77.646
77.624
28.101
180
160
140
120
100
80
60
40
20
ppm


HO
MeO
O
N
Boc

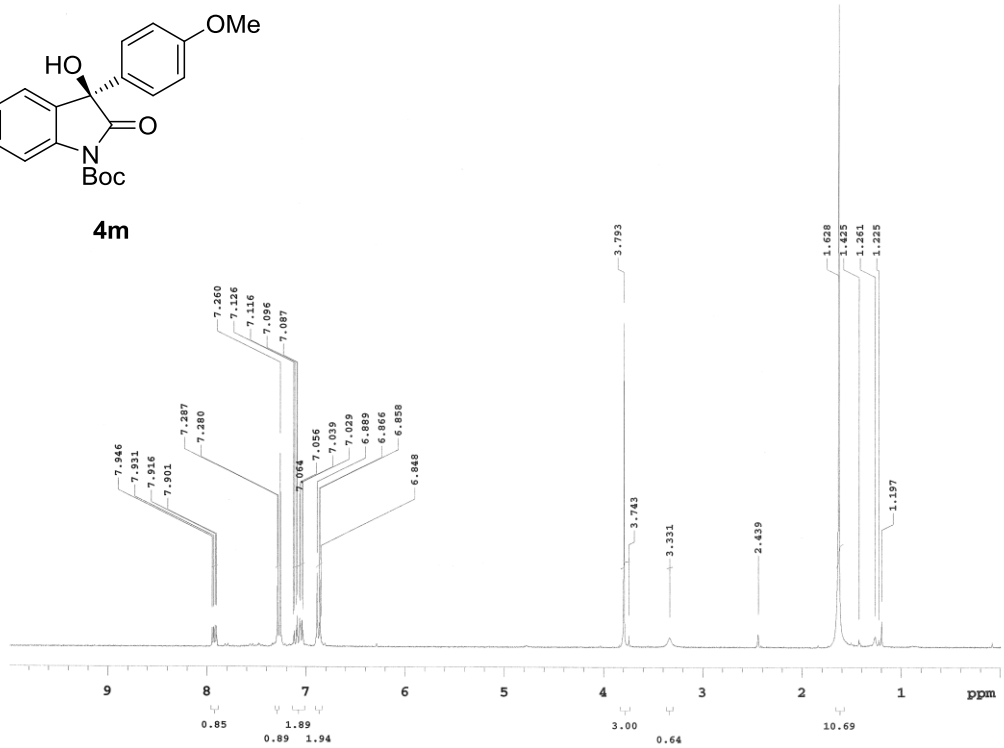
4l

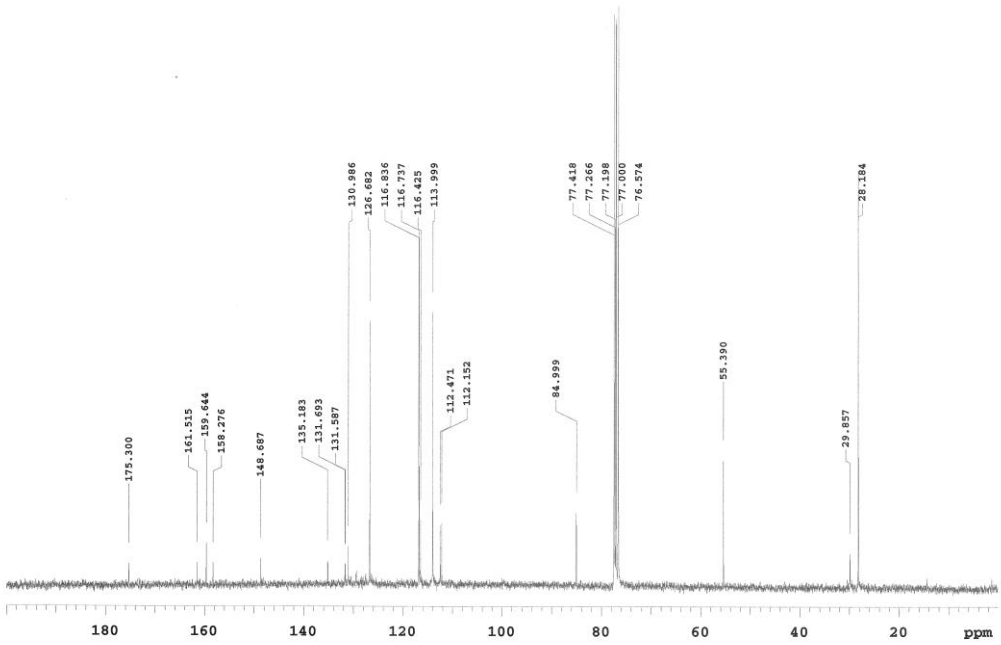

7.870
7.840
7.260
7.255
7.249
7.234
7.227
7.165
7.137
6.940
6.931
6.911
6.901
6.865
6.856
3.773
3.183
2.334
1.629
1.590
9
8
7
6
5
4
3
2
1
ppm
1.44
3.01
1.18
4.66
1.45
4.49
1.00
4.40
13.46


175.627
156.368
148.801
138.202
136.491
132.560
131.108
129.093
125.238
116.303
115.406
110.106
84.528
77.753
77.426
77.000
76.582
55.656
28.177
21.288
180
160
140
120
100
80
60
40
20
ppm

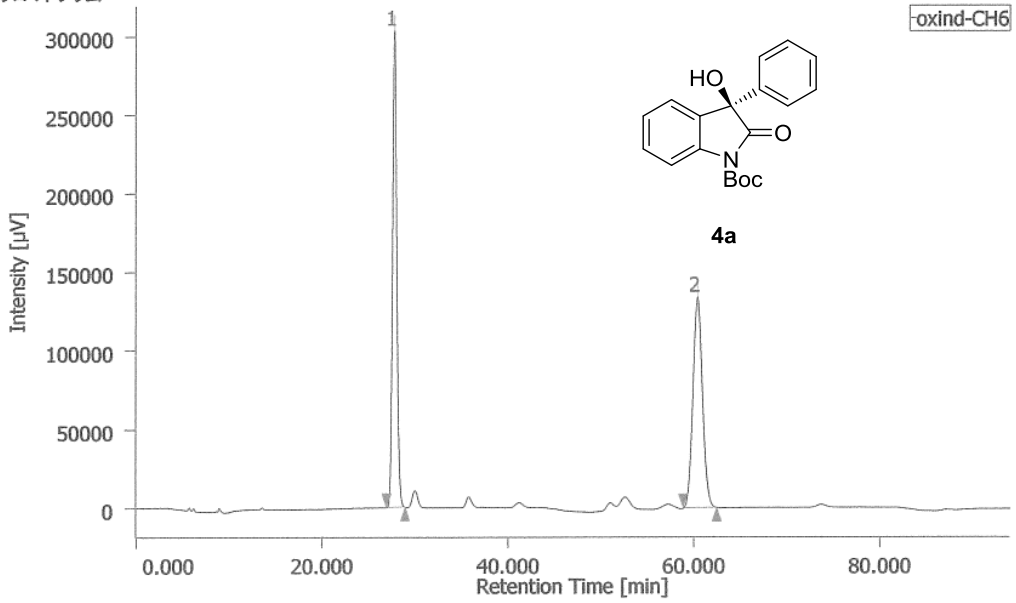

OMe
HO
F
O
N
Boc

4m


7.946
7.931
7.916
7.901
7.287
7.280
7.260
7.126
7.116
7.096
7.087
7.064
7.056
7.039
7.029
6.889
6.866
6.858
6.848
3.793
3.743
3.331
2.439
1.628
1.425
1.261
1.225
1.197
9
8
7
6
5
4
3
2
1
ppm
0.85
1.89
0.89
1.94
3.00
0.64
10.69


175.300
161.515
159.644
158.276
148.687
135.183
131.693
131.587
130.986
126.682
116.836
116.737
116.425
113.999
112.471
112.152
84.999
77.418
77.266
77.198
77.000
76.574
55.390
29.857
28.184
180
160
140
120
100
80
60
40
20
ppm

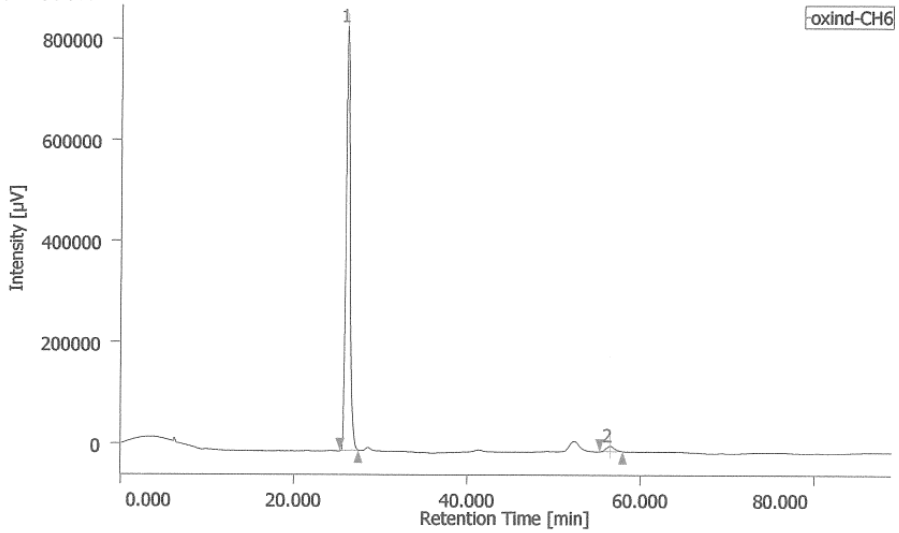
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	27.810	9875771	303755	50.713	69.363	17193
2	60.390	9597944	134168	49.287	30.637	16524

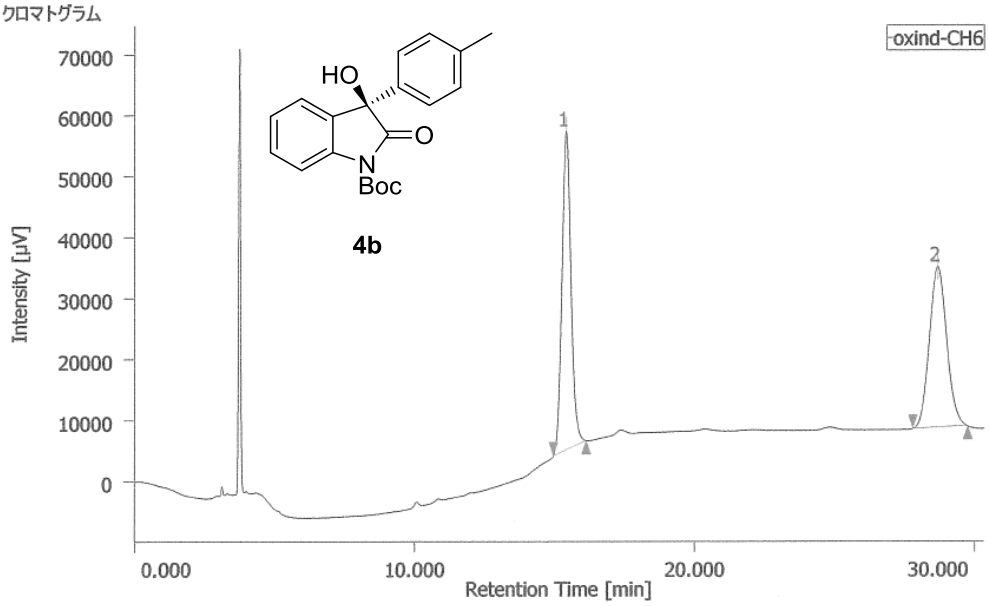
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	26.097	28173821	838718	97.500	98.738	14989
2	56.455	722418	10722	2.500	1.262	15850

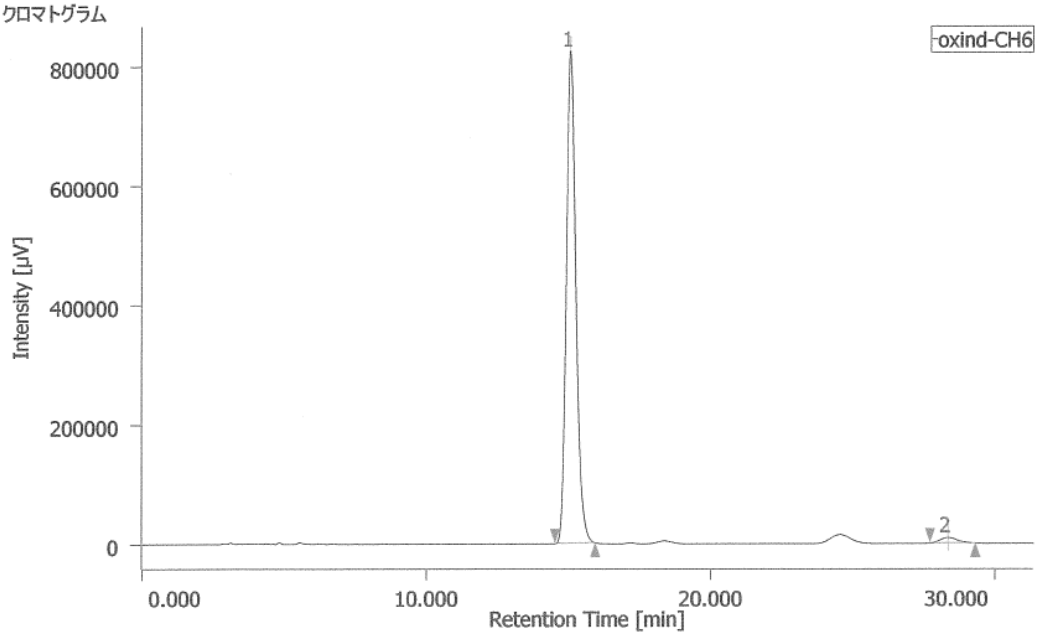
クロマトグラム



ピーク情報

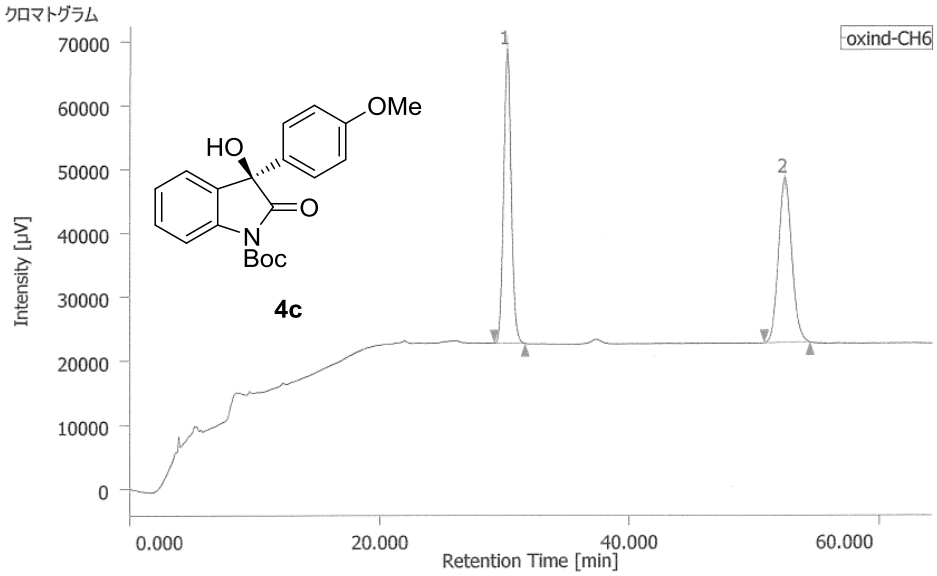
#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	15.408	1163028	52245	50.686	66.488	11425
2	28.668	1131566	26333	49.314	33.512	10317

クロマトグラム



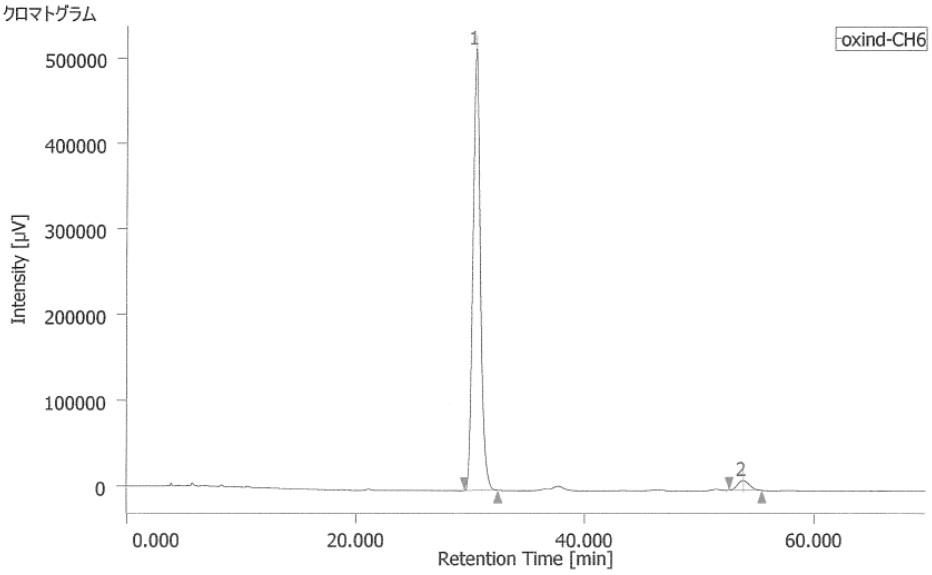
ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	15.067	19605027	824811	97.998	98.889	9700
2	28.328	400605	9270	2.002	1.111	9676



ピーク情報

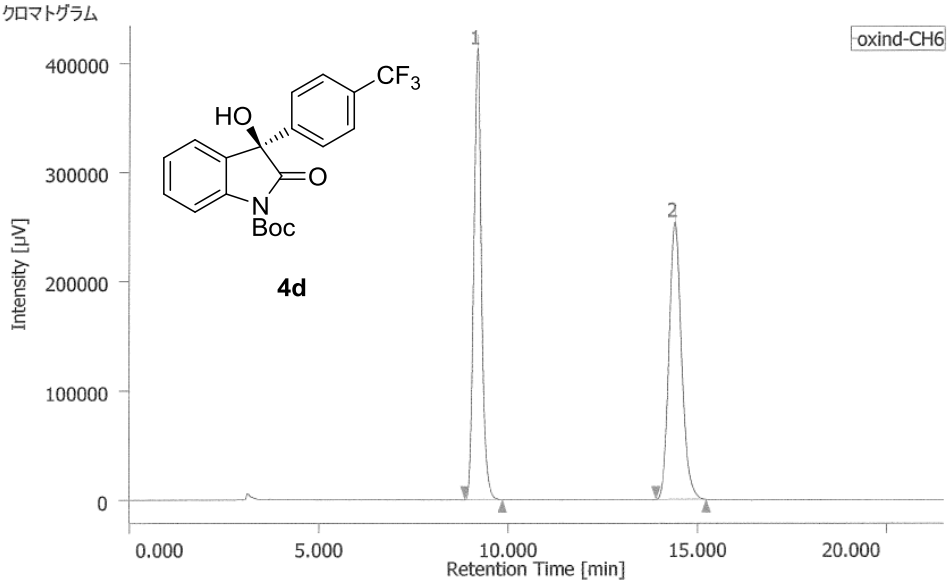
#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	30.173	1941992	46163	50.361	64.107	12254
2	52.418	1914148	25847	49.639	35.893	11783



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	30.463	23454450	516734	96.484	97.802	10968
2	53.845	854797	11611	3.516	2.198	11981

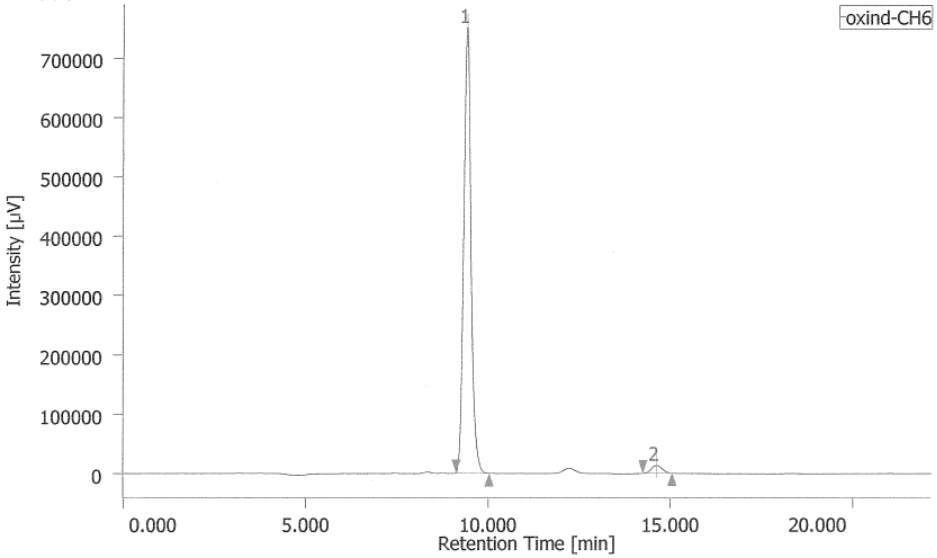
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	9.175	5837213	413525	49.991	61.881	10363
2	14.395	5839272	254734	50.009	38.119	9523

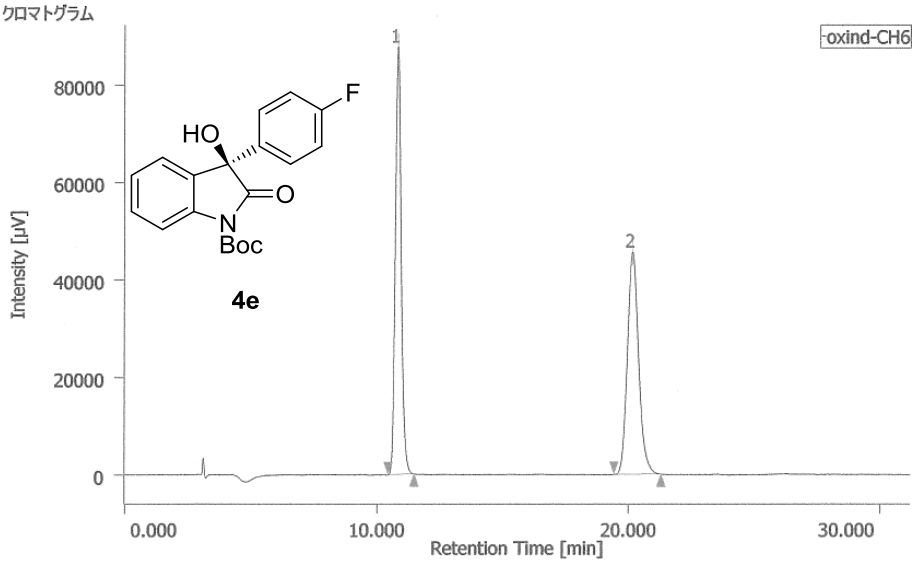
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	9.407	10480863	752510	97.401	98.256	11092
2	14.617	279634	13353	2.599	1.744	10796

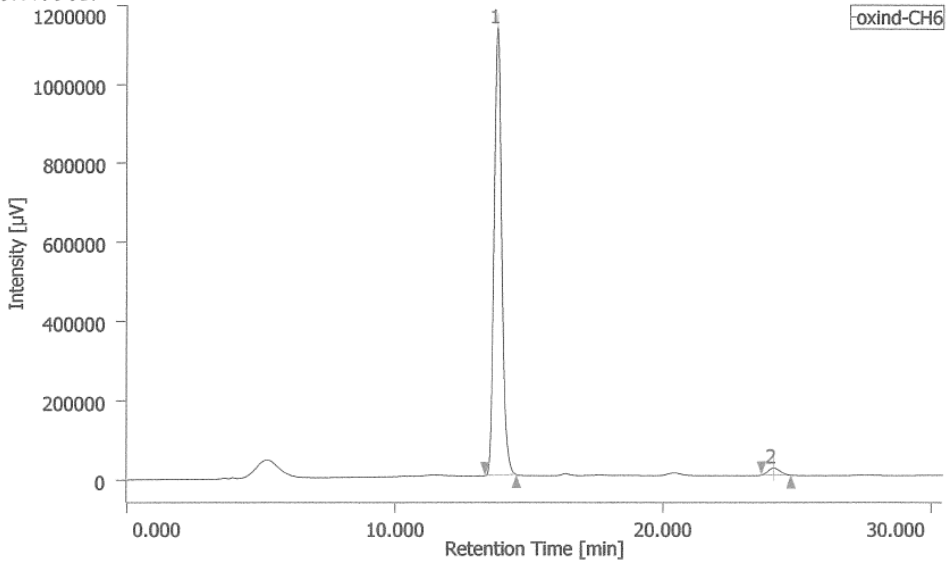
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	10.840	1413957	87877	49.944	65.828	11142
2	20.155	1417153	45618	50.056	34.172	10241

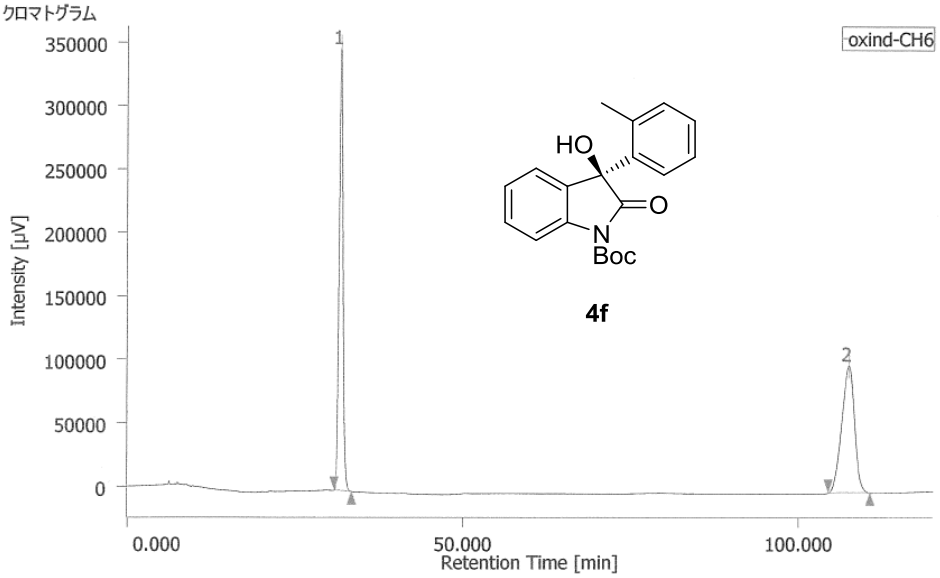
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	13.798	22120005	1132308	97.530	98.407	12179
2	24.118	560306	18326	2.470	1.593	13495

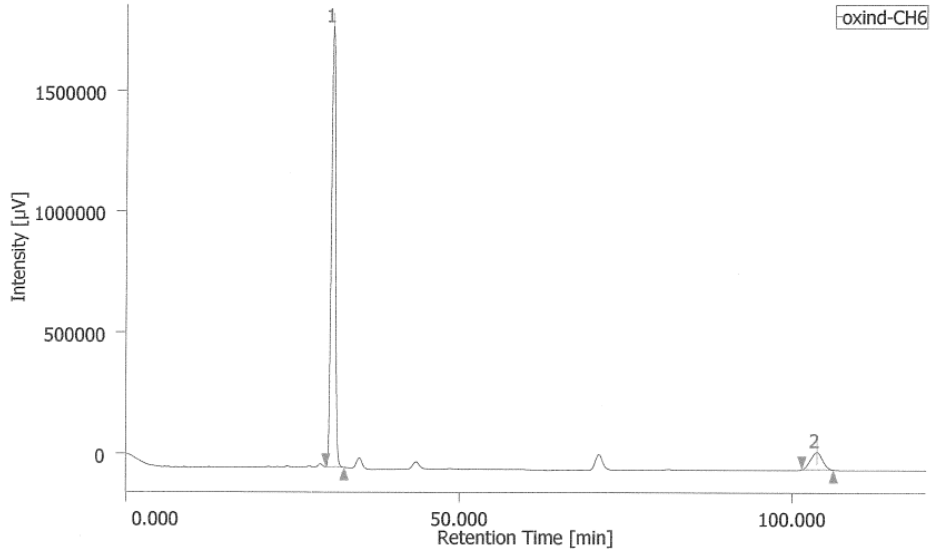
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	31.777	13589797	348724	50.354	77.684	15910
2	107.450	13398614	100177	49.646	22.316	14843

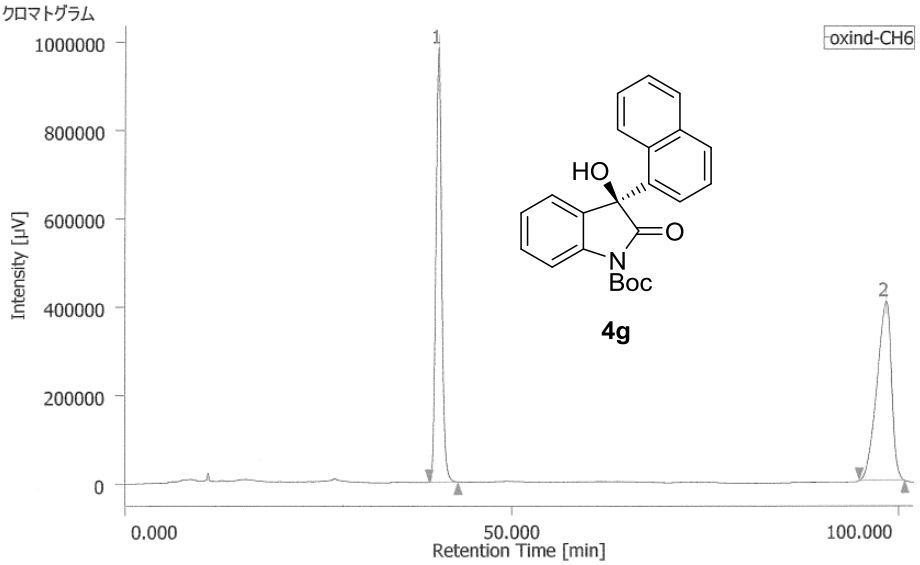
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	31.028	80474784	1819777	90.048	96.202	11082
2	103.642	8893538	71845	9.952	3.798	15469

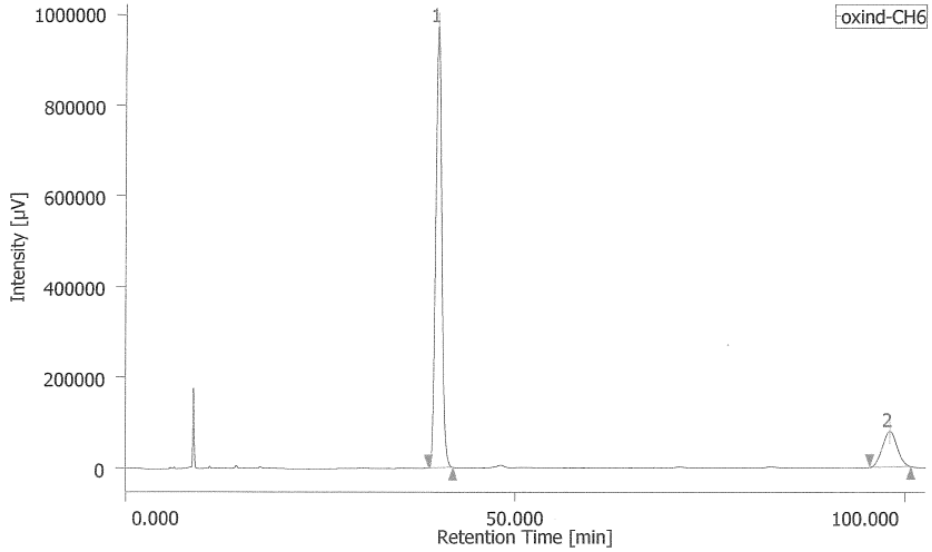
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	40.450	52530848	984454	49.550	70.774	13645
2	98.313	53485254	406522	50.450	29.226	12650

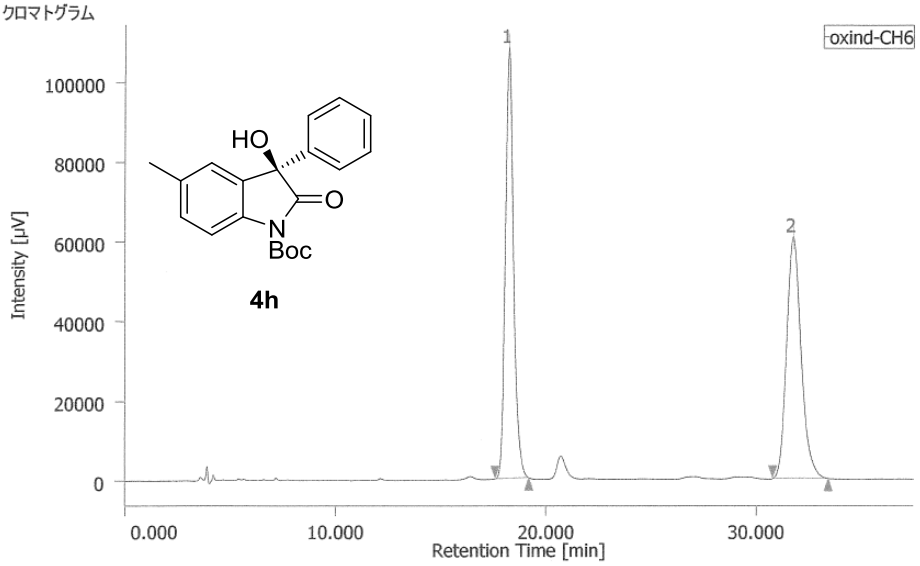
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	40.052	51990823	973956	83.479	92.525	13278
2	98.017	10289149	78679	16.521	7.475	12621

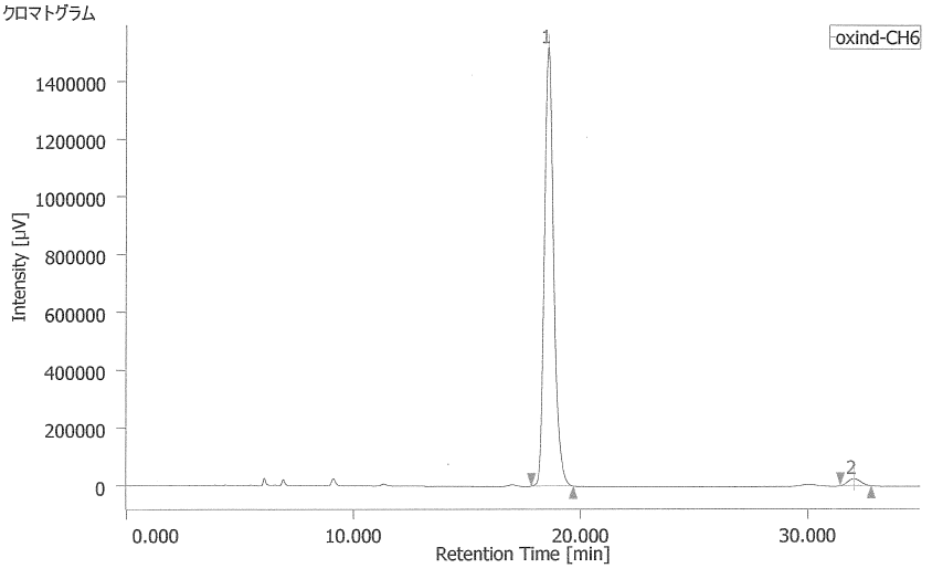
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	18.237	2944007	108428	50.230	64.090	11166
2	31.725	2917042	60753	49.770	35.910	10637

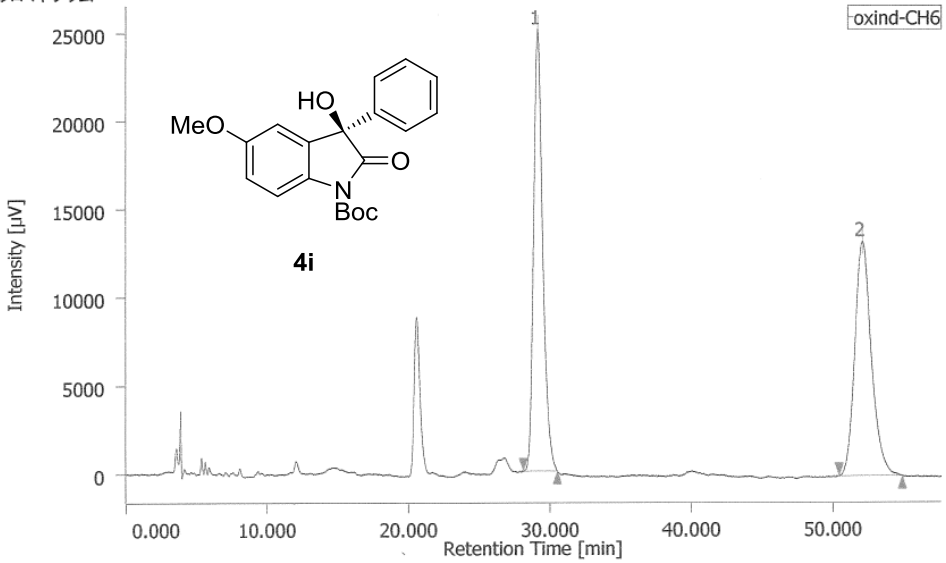
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	18.568	43622131	1522324	97.808	98.426	10242
2	32.013	977792	24343	2.192	1.574	13510

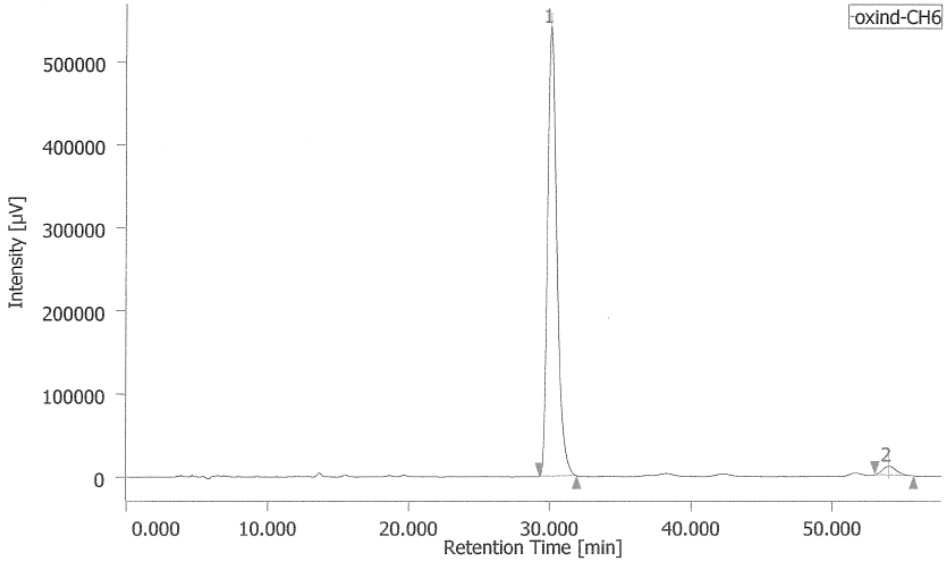
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	29.102	1129783	25129	50.847	65.352	10329
2	52.042	1092130	13323	49.153	34.648	9890

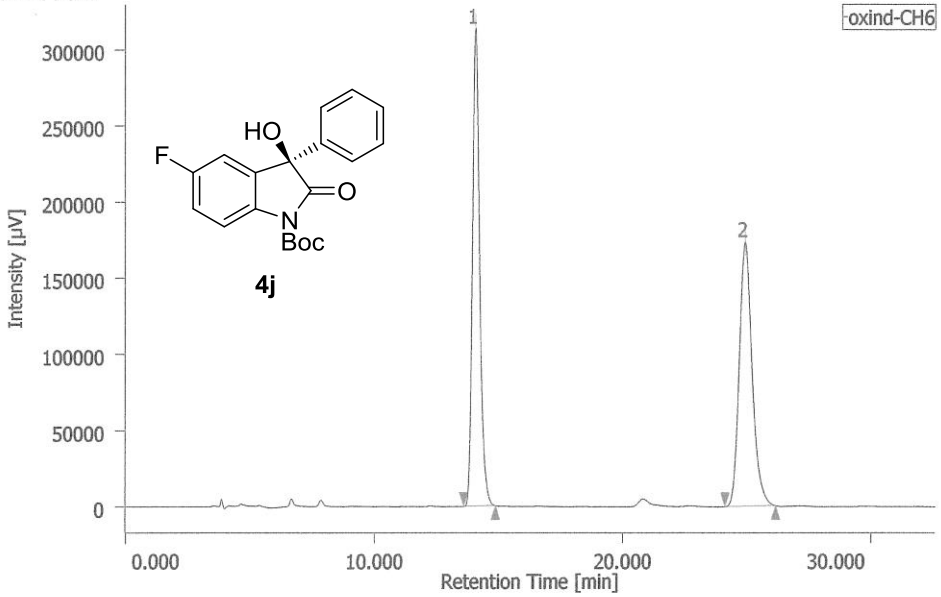
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	30.085	24941729	541600	96.902	97.987	10532
2	53.967	797299	11129	3.098	2.013	12565

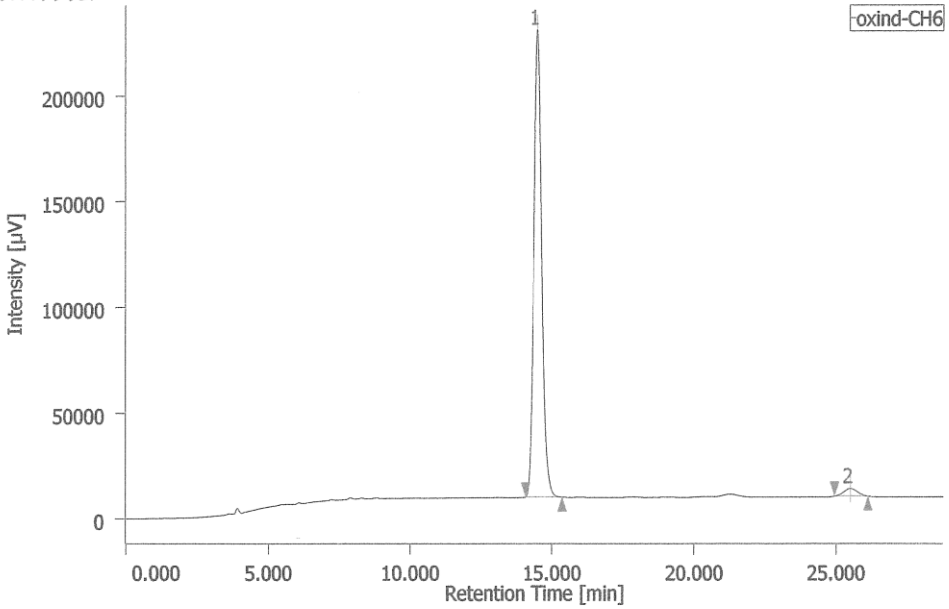
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	14.080	6359835	313747	50.211	64.407	11998
2	24.903	6306464	173383	49.789	35.593	11471

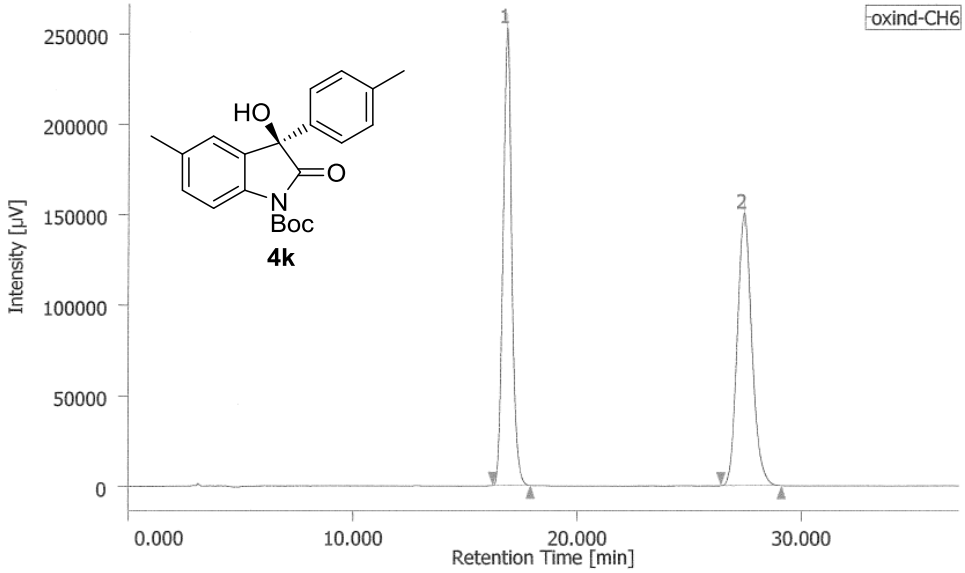
クロマトグラム



ピーク情報

#	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	NTP
1	14.485	4324876	221218	97.285	98.389	13245
2	25.493	120709	3623	2.715	1.611	12733

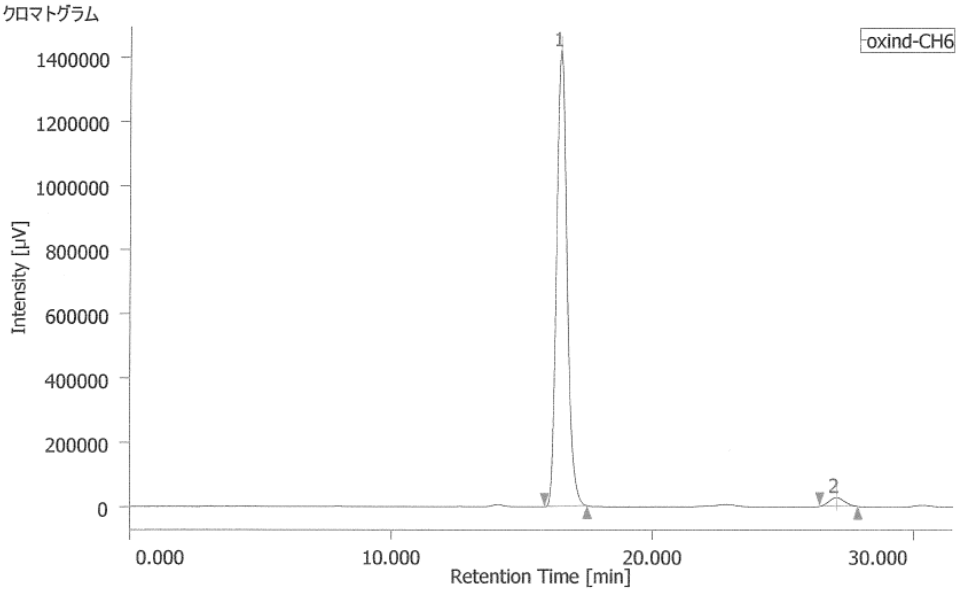
クロマトグラム



ピーク情報

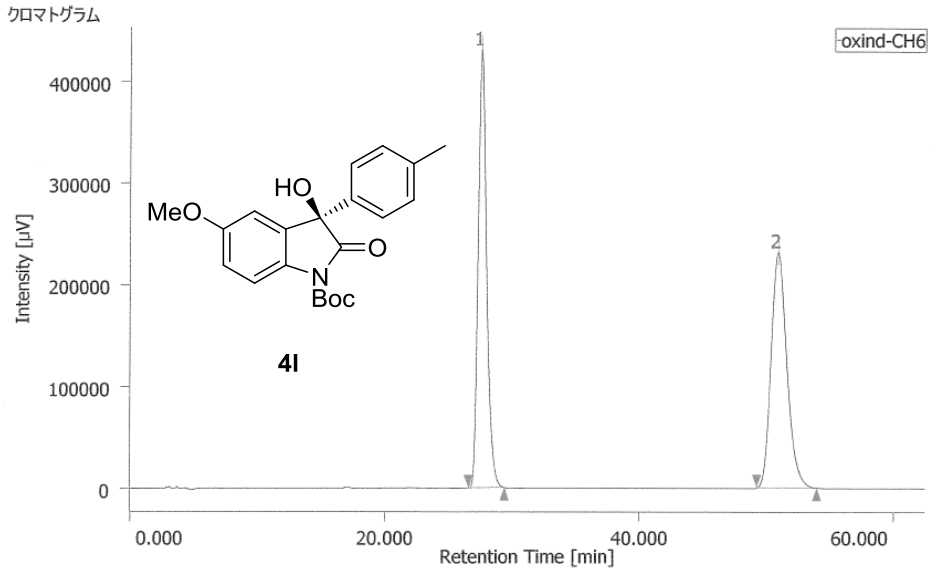
#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	16.833	6852715	253586	49.917	62.708	9399
2	27.400	6875404	150803	50.083	37.292	8658

クロマトグラム



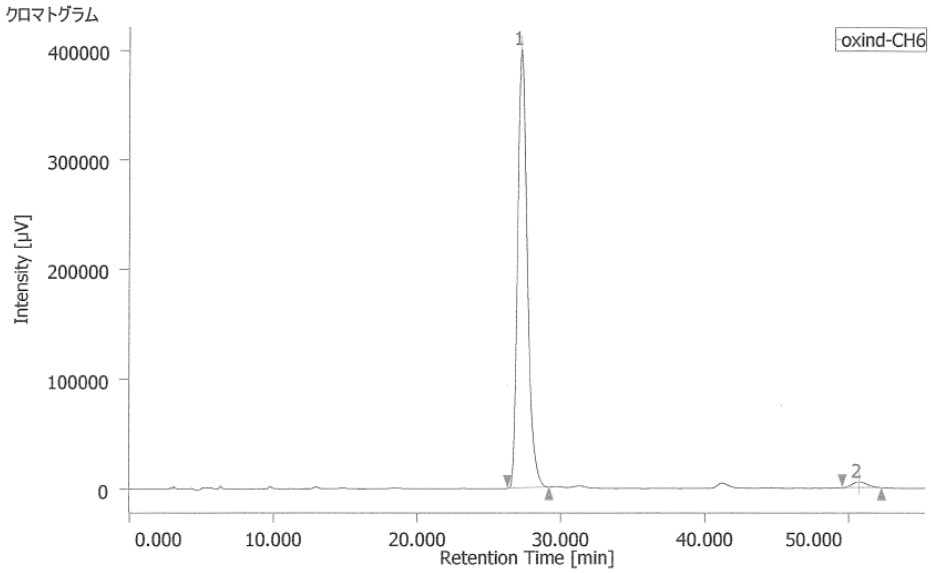
ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	16.465	39865810	1423247	97.256	98.096	8232
2	27.023	1124867	27624	2.744	1.904	9564



ピーク情報

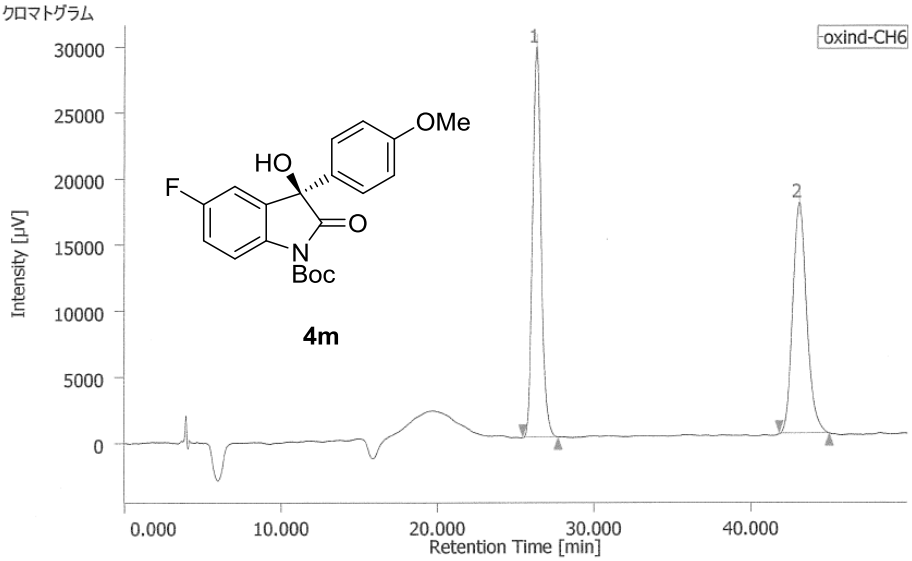
#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	27.548	20112283	431683	50.048	65.028	8454
2	50.863	20074002	232157	49.952	34.972	8276



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	27.230	18734285	400042	97.912	98.733	8252
2	50.698	399463	5133	2.088	1.267	9072

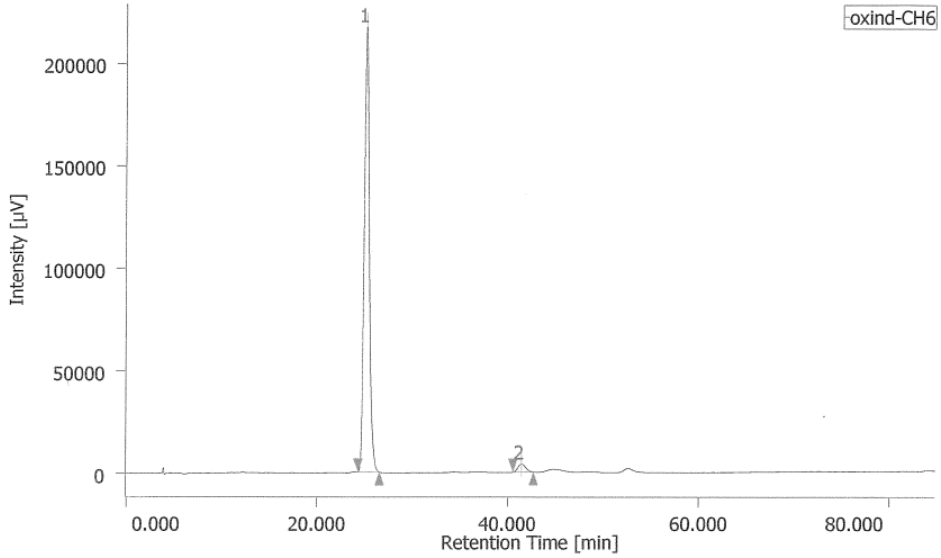
クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	26.297	1113458	29604	50.479	62.824	11933
2	43.088	1092320	17518	49.521	37.176	11467

クロマトグラム



ピーク情報

#	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	NTP
1	25.147	8052601	217439	97.241	98.207	11239
2	41.480	228490	3970	2.759	1.793	11569