Electronic Supplementary Material (ESI) for ChemComm.

Preparation of enantioenriched helical- and axial-chiral molecules by dynamic asymmetric induction

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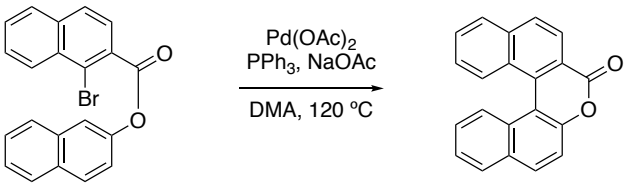
1. General Experimental:

All reactions were carried out in heat-gun-dried glassware under an argon atmosphere unless otherwise noted. Dry tetrahydrofuran (THF), 1,4-dioxane, CH_2Cl_2, CH_3CN, MeOH, EtOH, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), and AcOEt were purchased from Kanto Chemical Co., Inc. and used without further purification. **OCS1**,[1] **OCS2**,[2] **OCS3**,[3] **OCS4**,[4] and **OCS5**[5] were provided by Daicel corporation. ^{1}H NMR spectra were recorded on Varian Mercury spectrometer (300 MHz) or JEOL JNM-ECA600 (600 MHz) and ^{13}C NMR spectra were recorded on Varian Mercury spectrometer (75 MHz) or JEOL JNM-ECA600 (151 MHz) at ambient temperature using $CDCl_3$ as a solvent: $CHCl_3$ (^{1}H, δ 7.26), $CDCl_3$ (^{13}C, δ 77.1) were used as internal references. The peak multiplicities were given as followed: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Specific rotations were measured on a digital polarimeter (JASCO DIP-370). Circular dichroism (CD) spectra were measured on a spectrophotometer (JASCO J-720W). Infrared spectra (IR) were recorded on a Fourier transfer infrared spectrophotometer (Perkin Elmer SpectrumOne) as neat liquid on NaCl plates and as crystals used a diffuse reflector. High performance liquid chromatography (HPLC) were performed on circular dichroism chiral detector (JASCO CD-2095 or CD-4095), photodiode array detector (JASCO MD-2018 or MD-4010) and column oven (JASCO CO-2067 or CO-4060) equipped with a JASCO PU-2089 using Daicel CHIRALCEL OD-3 column (0.46 cm × 5.0 cm), CHIRALPAK AD-3 column (0.46 cm × 5.0 cm), CHIRALPAK AS-H column (0.46 cm × 25 cm), CHIRALPAK AS-3 column (0.46 cm × 5.0 cm), CHIRALPAK IB column (0.46 cm × 25 cm), and CHIRALPAK IE (0.46 cm × 25 cm). Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F_{254} (Merck 5715) plates and developed plates were visualized by UV (254 nm) and by heating on a hot plate after staining with a 4% solution of phosphomolybdic acid in ethanol or a 2.5% solution of *p*-anisaldehyde in ethanol. Column chromatography were performed using Kanto spherical silica gel 60N (neutral, 63-210 μm) or Fuji Silysia silica gel FL100D (neutral, 100 μm). X-ray crystallographic data were collected using a Rigaku AFC HyPix-6000 using Mo*K*α radiation (λ = 0.71073 Å) to a maximum 2θ range for data collection 4.812° to 60.972°. HRMS analyses were recorded on a JEOL JMS-700 at the Analytical Center in IMCE, Kyushu University.

Chemicals Unless otherwise noted, all reagents were purchased and used as delivered.

2. Detailed Reaction Procedures and Analytical Data:

lactone **2a**



s1 **2a**

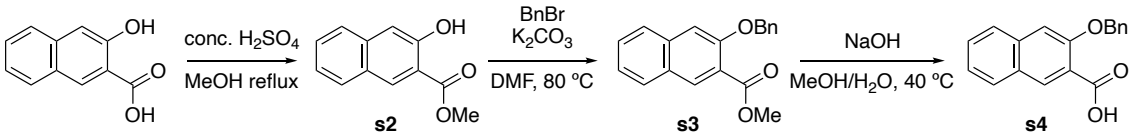
The compound **2a** was prepared according to the literature procedure with slight modification.[6]

To a solution of **s1** (377 mg, 1.00 mmol) in DMA (20 mL) was added PPh_3 (262 mg, 1.00 mmol), NaOAc (328 mg, 4.00 mmol) and $Pd(OAc)_2$ (89.8 mg, 0.400 mmol) at ambient temperature, then the mixture was degassed (3 times of freeze-pump-thaw). After stirred at 120 °C for 24 h, the mixture was cooled to ambient temperature and filtered through a pad of silica gel using AcOEt as eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 4:1) to afford a mixture of **2a** and its regioisomer. The mixture was suspended to *n*-C_6H_{14}/*i*-PrOH = 1:1 and the filtration afforded 160 mg (54%) of **2a** as colorless crystals. The spectroscopic data were in good agreement with the reported values.[6]

Analytical HPLC [column: CHIRALPAK AS-H (0.46 cm × 25 cm), eluent: *n*-C_6H_{14}/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, detection: UV 254 nm, temperature: 10 °C]: t_1 = 10.5 min for (*M*)-isomer, t_2 = 13.3 min for (*P*)-isomer.

Analytical HPLC [column: CHIRALPAK AS-3 (0.46 cm × 5.0 cm), eluent: *n*-C_6H_{14}/EtOH = 90:10, flow rate: 0.5 mL/min, detection: UV 254 nm, temperature: 10 °C]: t_1 = 5.1 min for (*M*)-isomer, t_2 = 7.4 min for (*P*)-isomer.

naphthoic acid **s4**



To a solution of 3-hydroxy-2-naphthoic acid (10.0 g, 53.1 mmol) in MeOH (250 mL) was added conc. H_2SO_4 (25 mL) at 0 °C. After stirred under reflux for 24 h, the mixture was cooled to ambient temperature. The mixture was poured into 28-30 % aq. NH_3 at 0 °C, and then the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to afford crude **s2**. To a solution of the crude **s2** in DMF (25 mL) was added K_2CO_3 (10.1 g, 73.1 mmol) and BnBr (9.30 ml, 77.8 mmol) at ambient temperature. After stirred at 80 °C for 20 h, the mixture was cooled to ambient temperature. H_2O was added to the mixture, and then the aqueous phase was extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to afford crude product **s3**. To a solution of the crude **s3** in MeOH (200 mL) / H_2O (80 mL) was added NaOH (4.24 g, 106 mmol) at ambient temperature. The mixture was stirred at 40 °C for 12 h, and then cooled to ambient temperature. The mixture was washed with Et_2O, and the aqueous phase was acidified with 35-37% aq. HCl, and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to afford 14.8 g (up to 99% in 3 steps) of **s4** as a yellow solid. The analytical data of the naphthoic acid **s4** were collected after purification by recrystallization from $CHCl_3$/*n*-C_6H_{14} providing colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.0 (br, 1H), 8.82 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.60 (ddd, *J* = 8.4, 7.5, 1.2 Hz, 1H), 7.52-7.41 (m, 7H), 5.39 (s, 2H).

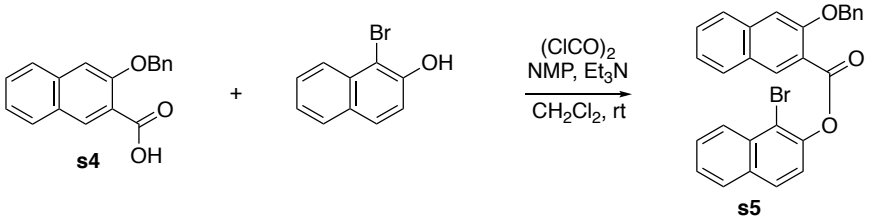
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 153.6, 136.6, 136.5, 134.4, 129.6, 129.4, 129.3, 128.6, 128.2, 126.7, 125.7, 108.7, 72.4 (two aromatic carbon's peaks are overlapping).

IR (reflection, cm^{-1}): 3228, 3058, 1953, 1727, 1632, 1502, 980, 710.

HRMS (EI, positive): Exact mass calcd. for $C_{18}H_{14}O_3$ $[M]^+$ requires *m*/*z*: 278.0943, found *m*/*z*: 278.0946.

Mp: 134.7-135.0 °C

ester **s5**



To a solution of **s4** (1.29 g, 4.64 mmol) in CH_2Cl_2 (20 mL) was added oxalyl chloride (519 μL, 6.05 mmol) and 1-methyl-2-pyrrolidone (NMP) (1 mL) at 0 °C. After stirred at ambient temperature for 1 h, Et_3N (2.70 mL, 19.4 mmol) and 1-bromo-2-naphthol (864 mg, 3.87 mmol) were added to the mixture. After stirred at that temperature for 14 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/CH_2Cl_2 = 3:2) to afford 1.71 g (76%) of **s5** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.90-7.87 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.67-7.51 (m, 5H), 7.47-7.29 (m, 6H), 5.35 (s, 2H).

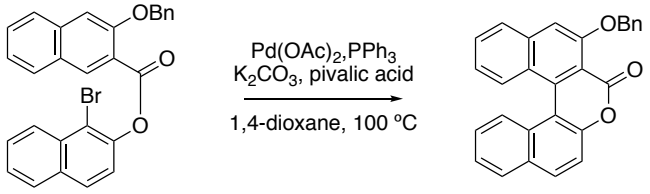
^{13}C NMR (75 MHz, $CDCl_3$): δ 163.5, 155.2, 146.8, 136.7, 134.3, 132.9, 132.6, 129.1, 129.03, 128.95, 128.7, 128.5, 128.3, 127.9, 127.8, 127.1, 126.7, 126.4, 124.8, 122.4, 120.7, 115.5, 108.8, 70.7. (two aromatic carbon's peaks are overlapping)

IR (reflection, cm^{-1}): 3057, 2889, 2349, 1741, 1627, 1127, 1047, 822.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{19}BrO_3$ $[M]^+$ requires *m*/*z*: 482.0518, found *m*/*z*: 482.0519.

Mp: 139.7-140.1 °C

lactone **s6**



s5 **s6**

To a solution of **s5** (483 mg, 1.00 mmol) in 1,4-dioxane (20 mL) was added PPh_3 (118 mg, 0.450 mmol), dried K_2CO_3 (415 mg, 3.00 mmol), pivalic acid (30.6 mg, 0.300 mmol) and $Pd(OAc)_2$ (33.7 mg, 0.150 mmol) at ambient temperature, then the mixture was degassed (3 times of freeze-pump-thaw). After stirred at 100 °C for 20 h, the mixture was cooled to ambient temperature and filtered through a pad of silica gel using AcOEt as eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 15:1) to afford 281 mg (70%) of **s6** as yellow crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 9.3 Hz, 1H), 7.91 (dd, *J* = 8.4, 8.4 Hz, 2H), 7.79 (dd, *J* = 9.6, 9.6 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.59-7.55 (m, 2H), 7.50-7.41 (m, 4H), 7.36-7.31 (m, 2H), 7.23-7.17 (m, 1H), 5.50 (d, *J* = 13.8 Hz, 1H), 5.44 (d, *J* = 13.8 Hz, 1H).

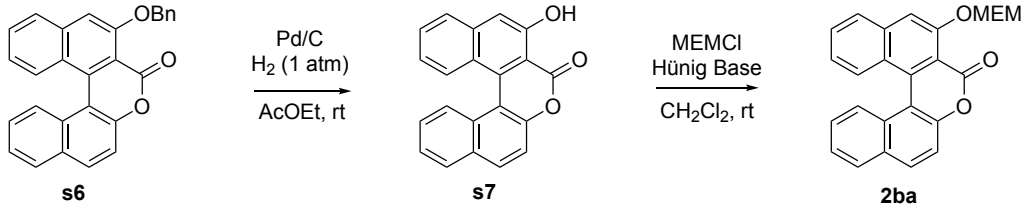
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 155.5, 150.6, 138.6, 137.6, 136.7, 132.1, 131.0, 130.2, 129.8, 129.3, 128.8, 128.5, 127.9, 127.10, 127.07, 126.9, 126.0, 125.3, 124.2, 123.4, 117.0, 114.3, 112.7, 109.7, 71.2.

IR (reflection, cm^{-1}): 3459, 3070, 2941, 1740, 1552, 1291, 1018, 821.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{18}O_3$ $[M]^+$ requires *m*/*z*: 402.1256, found *m*/*z*: 402.1257.

Mp: 208.7-209.2 °C

lactone **2ba**



s6 **s7** **2ba**

To a solution of **s6** (140 mg, 0.348 mmol) in AcOEt (20 mL) was added 10% palladium on active charcoal (370 mg, 0.348 mmol) at ambient temperature. The mixture was stirred for 14 h under atmospheric pressure of hydrogen at that temperature. The mixture was filtered through a pad of Celite using AcOEt as eluent, and the filtrate was concentrated under reduced pressure to afford **s7**. To a solution of crude **s7** in CH_2Cl_2 (5 mL) was added Hünig base (566 μL, 3.28 mmol) and 2-methoxyethoxymethyl chloride (MEMCl) (374 μL, 3.28 mmol) at ambient temperature. After stirred at that temperature for 20 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (toluene/AcOEt = 15:1) to afford 131 mg (94% in 2 steps) of **2ba** as yellow crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, J = 9.0 Hz, 1H), 7.93-7.85 (m, 3H), 7.77-7.74 (m, 2H), 7.62-7.57 (m, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.50-7.44 (m, 1H), 7.35-7.30 (m, 1H), 7.26-7.20 (m, 1H), 5.63 (d, J = 6.9 Hz, 1H), 5.60 (d, J = 6.9 Hz, 1H), 4.05-4.01 (m, 2H), 3.65-3.62 (m, 2H), 3.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 154.0, 150.3, 138.3, 137.5, 132.1, 131.0, 130.1, 129.3, 129.1, 128.5, 127.4, 127.0, 126.0, 125.3, 124.7, 123.8, 116.9, 114.4, 113.0, 112.7, 94.8, 71.6, 68.3, 59.1.

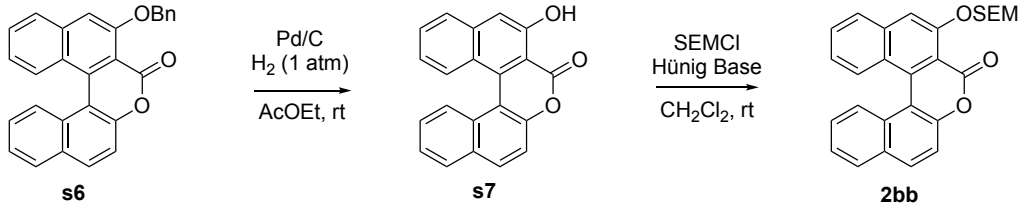
IR (reflection, cm^{-1}): 2923, 1736, 1621, 1331, 1209, 1009, 752.

HRMS (EI, positive): Exact mass calcd. for $C_{25}H_{20}O_5$ $[M]^+$ requires m/z: 400.1311, found m/z: 400.1310.

Mp: 97.7-98.3 °C

Analytical HPLC [column: CHIRALPAK AD-3 (0.46 cm × 5.0 cm), eluent: n-C_6H_{14}/i-PrOH = 80:20, flow rate: 1.0 mL/min, detection: UV 240 nm, temperature: 10 °C]: t_1 = 3.0 min for (P)-isomer, t_2 = 5.8 min for (M)-isomer.

lactone **2bb**



s6 **s7** **2bb**

To a solution of lactone **s6** (50.0 mg, 0.124 mmol) in AcOEt (6 mL) was added 10% palladium on active charcoal (132 mg, 0.124 mmol) at ambient temperature. The mixture was stirred for 1 h under atmospheric pressure of hydrogen at that temperature. The mixture was filtered through a pad of Celite using AcOEt as eluent, and the filtrate was concentrated under reduced pressure to afford **s7**. To a solution of crude **s7** in CH_2Cl_2 (10 mL) was added Hünig base (210 μL, 1.21 mmol) and 2-(trimethylsilyl)ethoxymethyl chloride (SEMCl) (110 μL, 0.622 mmol) at ambient temperature. After stirred at that temperature for 5 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 9:1) to afford 43.7 mg (80% in 2 steps) of lactone **2bb** as a yellow amorphous.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 9.0 Hz, 1H), 7.93-7.84 (m, 3H), 7.78-7.72 (m, 2H), 7.62-7.55 (m, 2H), 7.47 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.7, 8.7, 1.5 Hz, 1H), 7.22 (ddd, *J* = 8.4, 8.4, 1.5 Hz, 1H), 5.59 (d, *J* = 6.9 Hz, 1H), 5.56 (d, *J* = 6.9 Hz, 1H), 4.03-3.88 (m, 2H), 1.07-1.01 (m, 2H), 0.021 (s, 9H).

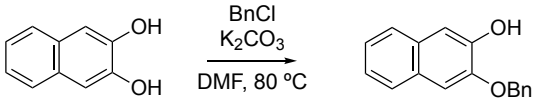
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 154.3, 150.4, 138.3, 137.6, 132.0, 131.0, 130.2, 129.7, 129.2, 128.5, 127.4, 127.0, 126.0, 125.3, 124.6, 123.7, 116.9, 114.4, 112.8, 94.4, 67.1, 18.3, –1.3. (one aromatic carbon's peak is overlapping).

IR (reflection, cm^{-1}): 2923, 1736, 1620, 1554, 1332, 1009, 751.

HRMS (EI, positive): Exact mass calcd. for $C_{27}H_{26}O_4Si$ $[M]^+$ requires *m*/*z*: 442.1600, found *m*/*z*: 442.1600.

Analytical HPLC [column: CHIRALCEL OD-3 (0.46 cm × 5.0 cm), eluent: *n*-C_6H_{14}/*i*-PrOH = 50:50, flow rate: 0.5 mL/min, detection: UV 240 nm, temperature: 15 °C]: t_1 = 4.1 min for (*M*)-isomer, t_2 = 21.8 min for (*P*)-isomer.

naphthol **s8**



s8

To a solution of 2,3-dihydroxynaphthalene (4.81 g, 30.0 mmol) in DMF (30 mL) was added K_2CO_3 (4.15 g, 30.0 mmol) at ambient temperature. The mixture was stirred at 50 °C for 30 min then BnCl (3.45 ml, 30.0 mmol) was added to the mixture. After stirred at 80 °C for 12 h, the reaction was quenched with H_2O and extracted with Et_2O. The combined organic phase was poured into 10 M aq. NaOH. The desired product **s8** and 2,3-dihydroxynaphthalene were extracted with 10 M aq. NaOH as a sodium salt. The combined aq. NaOH phase was acidified with 35-37% aq. HCl, and then the aqueous phase was extract with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 15:1) to afford 4.40 g (59%) of **s8** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69-7.63 (m, 2H), 7.54-7.30 (m, 8H), 7.22 (s, 1H), 5.98 (s, 1H), 5.24 (s, 2H).

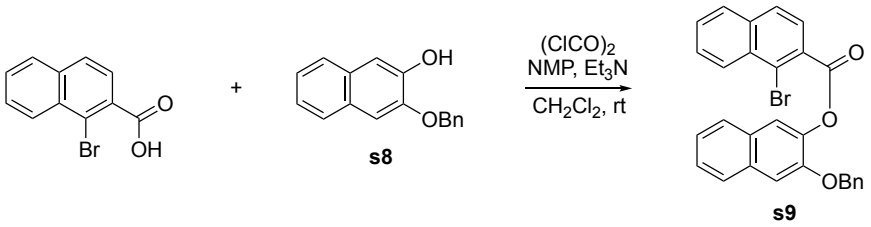
^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 145.8, 136.0, 129.8, 129.0, 128.9, 128.6, 128.0, 126.6, 126.4, 124.5, 124.0, 109.7, 107.1, 71.1.

IR (reflection, cm^{-1}): 3533, 3061, 2883, 1961, 1693, 1638, 1590, 1454, 1162, 942.

HRMS (EI, positive): Exact mass calcd. for $C_{17}H_{14}O_2$ $[M]^+$ requires *m*/*z*: 250.0994, found *m*/*z*: 250.0994.

Mp: 91.3-92.2 °C

ester **s9**



s9

To a solution of 1-bromo-2-naphthoic acid (500 mg, 1.99 mmol) in CH_2Cl_2 (10 mL) was added oxalyl chloride (267 μL, 3.11 mmol) and 1-methyl-2-pyrrolidone (1 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h then Et_3N (1.39 mL, 9.97 mmol) and **s8** (498 mg, 1.99 mmol) were added to the mixture. After stirred at that temperature for 14 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/CH_2Cl_2 = 3:2) to afford 894 mg (93%) of **s9** as colorless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8.1 Hz, 1H), 7.88-7.76 (m, 6H), 7.71-7.61 (m, 2H), 7.49-7.31 (m, 8H), 5.27 (s, 2H).

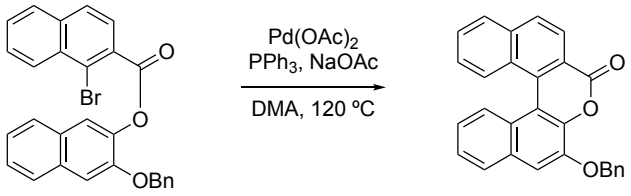
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 149.4, 140.6, 136.4, 135.5, 132.8, 132.4, 130.6, 128.8, 128.6, 128.4, 128.3, 128.22 128.15, 127.83, 127.75, 127.5, 126.7, 126.4, 126.3, 124.6, 123.4, 120.7, 108.8, 70.8. (one aromatic carbon's peak is overlapping)

IR (reflection, cm^{-1}): 3065, 2942, 1943, 1755, 1361, 1228, 991, 752.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{19}BrO_3$ $[M]^+$ requires *m*/*z*: 482.0518, found *m*/*z*: 482.0523.

Mp: 127.7-128.4 °C

lactone **s10**



s9 **s10**

To a solution of **s9** (483 mg, 1.00 mmol) in DMA (20 mL) was added PPh_3 (262 mg, 1.00 mmol), dried NaOAc (328 mg, 4.00 mmol) and $Pd(OAc)_2$ (89.8 mg, 0.400 mmol) at ambient temperature, then the mixture was degassed (3 times of freeze-pump-thaw). After stirred at 120 °C for 24 h, the mixture was cooled to ambient temperature and filtered through a pad of silica gel using AcOEt as eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel chromatography (*n*-C_6H_{14}/toluene = 1:4) to afford 257 mg (64%) of **s10** as yellow crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.7 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.68 (ddd, *J* = 6.9, 6.9, 0.9 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.47-7.35 (m, 6H), 7.22 (ddd, *J* = 8.1, 6.6, 1.2 Hz, 1H), 5.42 (s, 2H).

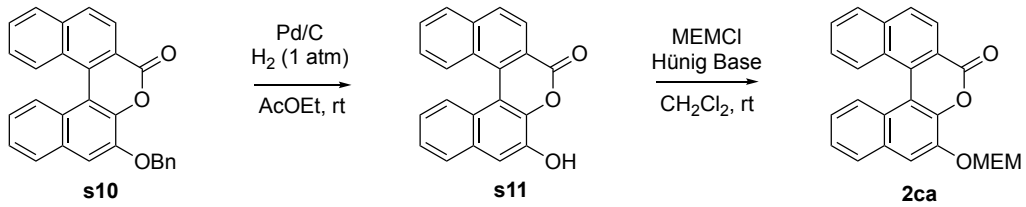
^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 146.3, 142.9, 136.7, 136.4, 134.9, 131.0, 129.7, 129.3, 129.1, 128.8, 128.6, 128.4, 128.2, 127.4, 127.3, 127.1, 125.8, 125.5, 124.9, 124.2, 123.5, 121.7, 114.3, 111.2, 71.1.

IR (reflection, cm^{-1}): 3059, 1729, 1592, 1470, 1065, 802, 759, 694.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{18}O_3$ $[M]^+$ requires *m*/*z*: 402.1256, found *m*/*z*: 402.1255.

Mp: 84.0-84.6 °C

lactone **2ca**



s10 **s11** **2ca**

To a solution of **s10** (136 mg, 0.338 mmol) in AcOEt (20 mL) was added 10% palladium on active charcoal (353 mg, 0.332 mmol) at ambient temperature. The mixture was stirred for 3 h under atmospheric pressure of hydrogen at that temperature. The mixture was filtered through a pad of Celite using AcOEt as eluent, and the filtrate was concentrated under reduced pressure to afford **s11**. To a solution of crude **s11** in CH_2Cl_2 (5 mL) was added Hünig base (290 μL, 1.66 mmol) and MEMCl (190 μL, 1.66 mmol) at ambient temperature. After stirred at that temperature for 4 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (toluene/AcOEt = 15:1) to afford 114 mg (84% in 2 steps) of **2ca** as yellow crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.86-7.80 (m, 3H), 7.68 (ddd, *J* = 7.8, 7.8, 0.9 Hz, 1H), 7.49-7.38 (m, 2H), 7.27-7.22 (m, 1H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.57 (d, *J* = 7.2 Hz, 1H), 4.03-4.00 (m, 2H), 3.65-3.62 (m, 2H), 3.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4, 144.8, 143.0, 136.8, 135.0, 131.1, 129.7, 129.3, 129.2, 128.7 128.4, 127.7, 127.0, 125.9, 125.6, 125.5, 124.2, 124.0, 121.6, 114.4, 114.2, 94.7, 71.6, 68.3, 59.1.

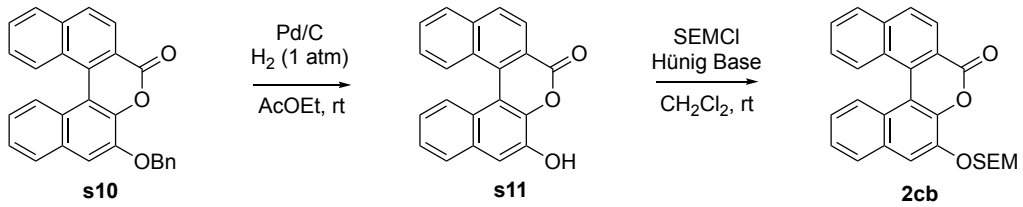
IR (reflection, cm^{-1}): 3449, 2922, 1730, 1592, 1404, 1338, 1055, 920, 793, 759.

HRMS (EI, positive): Exact mass calcd. for $C_{25}H_{20}O_5$ $[M]^+$ requires *m*/*z*: 400.1311, found *m*/*z*: 400.1312.

Mp: 50.3-50.9 °C

Analytical HPLC [column: CHIRALPAK AD-3 (0.46 cm × 5.0 cm), eluent: *n*-C_6H_{14}/*i*-PrOH = 80:20, flow rate: 1.0 mL/min, detection: UV 240 nm, temperature: 15 °C]: t_1 = 2.9 min for (*P*)-isomer, t_2 = 6.4 min for (*M*)-isomer.

lactone **2cb**



s10 **s11** **2cb**

To a solution of **s10** (50.0 mg, 0.124 mmol) in AcOEt (6 mL) was added 10% palladium on active charcoal (132 mg, 0.124 mmol) at ambient temperature. The mixture was stirred for 5 h under atmospheric pressure of hydrogen at that temperature. The mixture was filtered through a pad of Celite using AcOEt as eluent, and the filtrate was concentrated under reduced pressure to afford **s11**. To a solution of crude **s11** in CH_2Cl_2 (5 mL) was added Hünig base (128 μL, 0.735 mmol) and SEMCl (66.0 μL, 0.373 mmol) at ambient temperature. After stirred at that temperature for 17 h, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 9:1) to afford 50.5 mg (92% in 2 steps) of **2cb** as a yellow amorphous.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 9.6 Hz, 1H), 7.68 (ddd, *J* = 7.2, 7.2, 1.1 Hz, 1H), 7.49-7.30 (m, 2H), 7.27-7.20 (m, 1H), 5.57 (d, *J* = 7.2 Hz, 1H), 5.53 (d, *J* = 7.2 Hz, 1H), 3.96-3.87 (m, 2H), 1.07-1.01 (m, 2H), 0.02 (s, 9H).

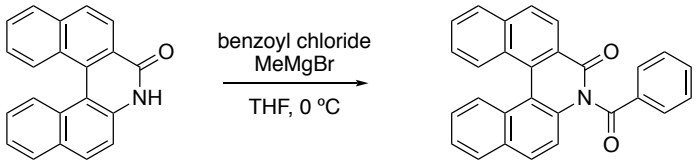
^{13}C NMR (75 MHz, $CDCl_3$): δ 161.3, 144.9, 142.8, 136.6, 134.8, 131.0, 129.5, 129.2, 129.1, 128.5, 128.3, 127.5, 126.9, 125.7, 125.4, 125.2, 124.0, 123.7, 121.5, 114.1, 113.7, 94.4, 66.9, 18.2, –1.4.

IR (reflection, cm^{-1}): 2953, 1735, 1592, 1248, 1056, 1001, 834.

HRMS (EI, positive): Exact mass calcd. for $C_{27}H_{26}O_4Si$ $[M]^+$ requires *m*/*z*: 442.1600, found *m*/*z*: 442.1600.

Analytical HPLC [column: CHIRALCEL OD-3 (0.46 cm × 5.0 cm), eluent: *n*-C_6H_{14}/EtOH = 90:10, flow rate: 0.5 mL/min, detection: UV 254 nm, temperature: 10 °C]: t_1 = 4.5 min for (*M*)-isomer, t_2 = 30.2 min for (*P*)-isomer.

lactam **3d**



3a **3d**

The compound **3a** was prepared according to the literature procedure.[7]

To a solution of **3a** (148 mg, 0.500 mmol) in THF (5 mL) was added MeMgBr (1.07 M in THF, 514 μL, 0.550 mmol) at 0 °C. The mixture was stirred at that temperature for 30 min, and benzoyl chloride (63.9 μL, 0.550 mmol) was added to the mixture. After stirred at that temperature for 48 h, the reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/$CHCl_3$/Et_2O = 8:20:1) to afford 206 mg (79%) of **3d** as a yellow crystal.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.65 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 8.4, 8.4 Hz, 2H), 7.38 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 7.33 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.0, 161.6, 136.0, 135.2, 134.7, 133.9, 132.58, 131.0, 130.8, 130.6, 130.4, 129.41, 129.38, 129.3, 129.1, 128.6, 128.4, 128.2, 127.8, 125.9, 125.5, 125.4, 125.3, 123.1, 114.9, 113.2.

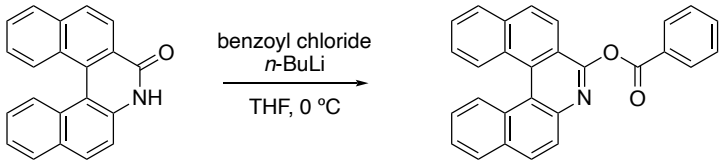
IR (reflection, cm^{-1}): 3062, 1734, 1647, 1251, 1176, 986, 808, 759.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{17}NO_2$ $[M]^+$ requires *m*/*z*: 399.1259, found *m*/*z*: 399.1260.

Mp: Due to the thermal tautomerization of **3** and **4**, it was difficult to measure the correct melting point of them. Actually, we attempted to measure the melting points of lactim **4d**, however, the resulting melted sample contained lactam **3d** and **4d**.

Analytical HPLC [column: CHIRALPAK IE (0.46 cm × 25 cm), eluent: *n*-C_6H_{14}/CH_2Cl_2 = 10:90, flow rate: 1.0 mL/min, detection: UV 254 nm, temperature: 10 °C]: t_1 = 12.8 min, t_2 = 14.5 min.

lactim **4d**



3a **4d**

To a solution of **3a** (395 mg, 1.00 mmol) in THF (5 mL) was added *n*-BuLi (1.31 M in *n*-C_6H_{14}, 840 μL, 1.10 mmol) at 0 °C. The mixture was stirred at ambient temperature for 30 min, and benzoyl chloride (174 μL, 1.50 mmol) was added to the mixture. After stirred at that temperature for 6 h, the reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The mixture was suspended to Et_2O and the filtration afforded 301 mg (75%) of **4d** as colorless crystals.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.41 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.03-7.99 (m, 4H), 7.79 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.66 (ddd, *J* = 6.6, 6.6, 1.2 Hz, 1H), 7.62-7.57 (m, 3H), 7.39 (ddd, *J* = 6.6, 6.6, 1.2 Hz, 1H), 7.35 (ddd, *J* = 6.6, 6.6, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 165.1, 154.9, 144.0, 135.1, 134.5, 134.2, 132.6, 130.7, 130.6, 130.0, 129.28, 129.25, 129.0, 128.84, 128.81, 128.6, 128.2, 128.1, 127.1, 126.9, 125.4, 124.9, 121.0, 120.1, 120.0. (one aromatic carbon is overlapping)

IR (reflection, cm^{-1}): 3074, 1742, 1600, 1577, 1404, 1234, 1061, 817.

HRMS (EI, positive): Exact mass calcd. for $C_{28}H_{17}NO_2$ $[M]^+$ requires *m*/*z*: 399.1259, found *m*/*z*: 399.1258.

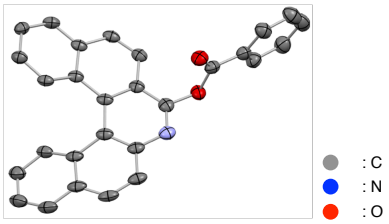
Analytical HPLC [column: CHIRALPAK IE (0.46 cm × 25 cm), eluent: *n*-C_6H_{14}/CH_2Cl_2 = 10:90, flow rate: 2.0 mL/min, detection: UV 300 nm, temperature: 10 °C]: t_1 = 6.4 min for (*M*)-isomer, t_2 = 12.3 min for (*P*)-isomer.

Specific rotation value:

$[\alpha]_D^{-10}$ = –1,073 (*c* 6.0 × 10^{-3}, *n*-C_6H_{14}/CH_2Cl_2 = 10:90) for (*M*)-isomer (96-86% ee).

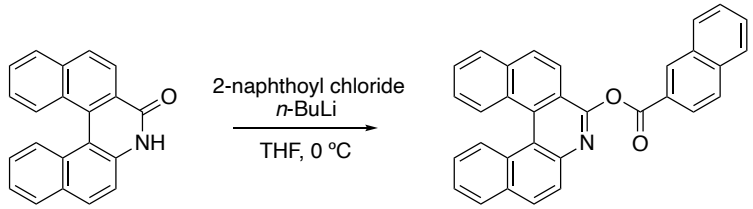
$[\alpha]_D^{-10}$ = +937 (*c* 3.0 × 10^{-2}, *n*-C_6H_{14}/CH_2Cl_2 = 10:90) for (*P*)-isomer (92-76% ee).

X-ray crystal structure analysis:



ORTEP Drawing of **4d** (50% probability ellipsoids)
selected crystal data:
crystal system; monoclinic
space group: $P2_1/c$, a = 14.4902(13) Å, b = 5.7693(5) Å, c = 25.421(2) Å, β = 102.486(9)°, V = 2074.9(3) Å^3, Z = 4, R_1 = 0.0627, wR_2 = 0.1539.
CCDC Number: 2025507.

lactim **4e**



3a **4e**

To a solution of **3a** (200 mg, 0.677 mmol) in THF (10 mL) was added *n*-BuLi (1.29 M in *n*-C_6H_{14}, 579 μL, 0.747 mmol) at 0 °C. The mixture was stirred at ambient temperature for 10 min and 2-naphthoyl chloride (194 mg, 1.02 mmol) was added to the mixture. After stirred at that temperature for 1 h, the reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The mixture was suspended to Et_2O and the filtration afforded 223 mg (73%) of **4e** as colorless crystals.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.36 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 8.07-8.05 (m, 2H), 8.04-8.00 (m, 4H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.69 (dd, *J* = 6.6, 6.6 Hz, 1H), 7.67 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.62 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.60 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.42 (ddd, *J* = 8.4, 8.4, 1.2 Hz, 1H), 7.37 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H).

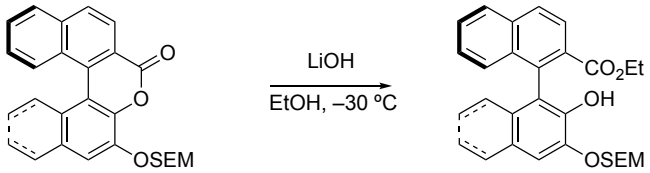
^{13}C NMR (151 MHz, $CDCl_3$): δ 165.3, 155.1, 144.0, 136.2, 135.1, 134.6, 132.8, 132.7, 132.6, 130.7, 130.1, 129.8, 129.33, 129.31, 129.1, 128.8, 128.72, 128.68, 128.24, 128.16, 128.2, 127.2, 127.1, 127.0, 126.2, 125.8, 125.38, 125.0, 121.1, 120.2, 120.1. (one aromatic carbon is overlapping)

IR (reflection, cm^{-1}): 3055, 1738, 1578, 1275, 1189, 1078, 813, 760.

HRMS (EI, positive): Exact mass calcd. for $C_{32}H_{19}NO_2$ $[M]^+$ requires *m*/*z*: 449.1416, found *m*/*z*: 449.1415.

Analytical HPLC [column: CHIRALPAK IE (0.46 cm × 25 cm), eluent: *n*-C_6H_{14}/CH_2Cl_2 = 10:90, flow rate: 2.0 mL/min, detection: UV 300 nm, temperature: 10 °C]: t_1 = 7.5 min for (*M*)-isomer, t_2 = 15.4 min for (*P*)-isomer.

binaphthyl (*S*)-**5cb**



(*P*)-**2cb** (*S*)-**5cb**

To a solution of (*P*)-**2cb** (20.0 mg, 0.0452 mmol, 96% ep) in EtOH (84 mL) was added LiOH (21.6 mg, 0.902 mmol) at –78 °C. After stirred at –30 °C for 15 min, the solvent was concentrated under reduced pressure. The mixture was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 3:1) to afford 19.1 mg (86%, 96% ep) of (*S*)-**5cb** as a yellow syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.54 (ddd, *J* = 6.9, 6.9, 1.5 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.35-7.26 (m, 2H), 7.12 (ddd, *J* = 7.2, 7.2, 1.2 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 1H), 5.49 (s, 2H), 3.94-3.85 (m, 4H), 1.08-1.02 (m, 2H), 0.72 (dd, *J* = 6.9, 6.9 Hz, 3H), 0.04 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 145.0, 143.0, 135.3, 135.2, 132.7, 130.1, 129.7, 128.7, 128.4, 128.2, 127.8, 127.5, 127.1, 126.9, 126.3, 124.8, 124.7, 123.9, 119.2, 109.9, 94.4, 67.2, 60.6, 18.3, 13.4, –1.3.

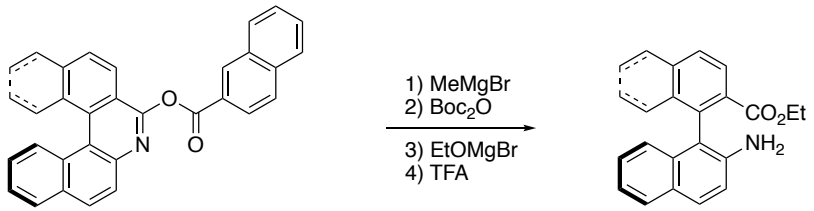
IR (neat, cm^{-1}): 2954, 1705, 1471, 1328, 1270, 1057, 983.

HRMS (EI, positive): Exact mass calcd. for $C_{29}H_{32}O_5Si$ $[M]^+$ requires *m*/*z*: 488.2019, found *m*/*z*: 488.2020.

Analytical HPLC [column: CHIRALPAK AS-H (0.46 cm × 25 cm), eluent: *n*-C_6H_{14}/*i*-PrOH = 95:5, flow rate: 0.5 mL/min, detection: UV 254 nm, temperature: 25 °C]: t_1 = 14.9 min for (*S*)-isomer, t_2 = 21.4 min for (*R*)-isomer.

Specific rotation value: $[\alpha]_D^{26}$ = –15.8 (*c* 1.00, $CHCl_3$) for (*S*)-isomer (>99% ep).

binaphthyl (*R*)-**6b**



(*M*)-**4e** (*R*)-**6b**

To a solution of (*M*)-**4e** (20.0 mg, 0.0445 mmol, 94% ep) in THF (1 mL) was added MeMgBr (1.06 M in THF, 1.68 mL, 1.78 mmol) at –20 °C. The mixture was stirred at –20 °C for 25 min and Boc_2O (292 μL, 1.34 mmol) was added to the mixture. After stirred at that temperature for 15 min, EtOH (2 mL) was added to the mixture and stirred at that temperature for 5 min then sat. aq. NH_4Cl was added to the mixture and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. Trifluoroacetic acid (3 mL) was added to the mixture at ambient temperature and stirred for 30 min then sat. aq. $NaHCO_3$ was added to the mixture and extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (*n*-C_6H_{14}/AcOEt = 90:10) to afford 12.5 mg (85%, 94% ep) of (*R*)-**6b** as a pale yellow amorphous.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.78 (dd, *J* = 9.0, 9.0 Hz, 1H), 7.57 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.20 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.15 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.87-3.94 (m, 2H), 0.66 (dd, *J* = 6.9, 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 141.6, 136.0, 135.5, 134.3, 132.5, 130.7, 129.1, 128.5, 128.3, 128.03, 127.96, 127.86, 127.3, 127.2, 126.5, 126.4, 124.1, 122.2, 118.0, 116.4, 60.8, 13.4.

IR (reflection, cm^{-1}): 3376, 3056, 1705, 1621, 1239, 1137, 815, 769.

HRMS (EI, positive): Exact mass calcd. for $C_{23}H_{19}NO_2$ $[M]^+$ requires *m*/*z*: 341.1416, found *m*/*z*: 341.1416.

Analytical HPLC [column: CHIRALPAK IB (0.46 cm × 25.0 cm), eluent: *n*-C_6H_{14}/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, detection: UV 300 nm, temperature: 25 °C]: t_1 = 8.1 min for (*S*)-isomer, t_2 = 10.2 min for (*R*)-isomer.

Specific rotation value: $[\alpha]_D^{25}$ = +28.9 (*c* 1.15, $CHCl_3$) for (*R*)-isomer (>99% ep).

3. Determination of the Absolute Stereochemistry:

The stereochemical stability of **2** and **4** is low at ambient temperature; thus, its absolute stereochemistry was determined after transformation to stereochemically more stable **5** and **6**.

Determination of the Absolute Stereochemistry of Lactone **2** and Binaphthyl **5**

Bringmann and colleagues determined the absolute stereochemistry of (*M*)-**2a** and (*R*)-**5a** [Nu = (–)-menthoxy, Z, Z' = H] by X-ray crystallography and reported correlation with CD spectra.[6] By comparison with these data, the absolute stereochemistry of **2a**, **2ba**, **2bb**, **2ca**, **2cb**, and **5cb** resulting from DYASIN using **OCS5** was determined as (*P*), (*P*), (*P*), (*P*), (*P*), and (*S*)-configuration, respectively.

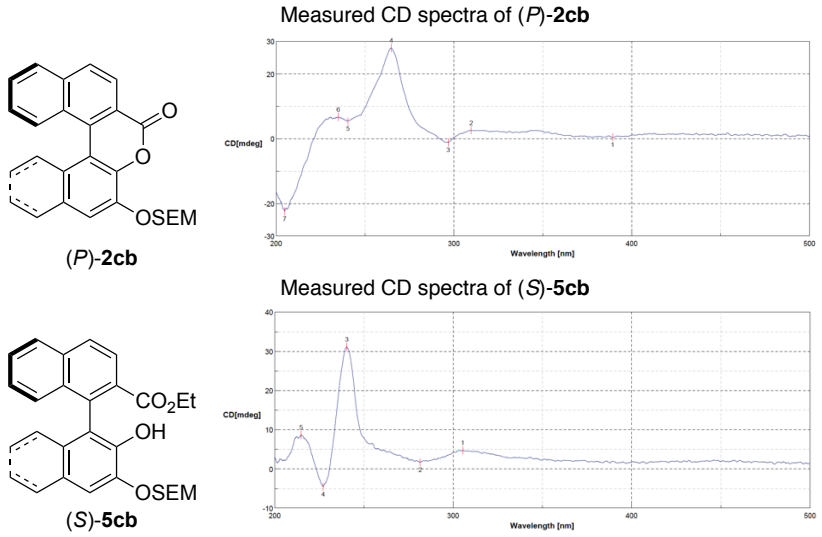


Figure S1. CD spectra of (*P*)-**2cb** and (*S*)-**5cb**.

Determination of the Absolute Stereochemistry of Lactim **4** and Binaphthyl **6**

Furuta, Kan, Kawabata, and colleagues reported the absolute stereochemistry and specific rotation values of (*S*)-**6a**.[7] We synthesized **6a** via **6b** from enantioenriched **4d** and **4e** prepared by DYASIN with **OCS1** and compared its specific rotation with the literature values of **6a**.

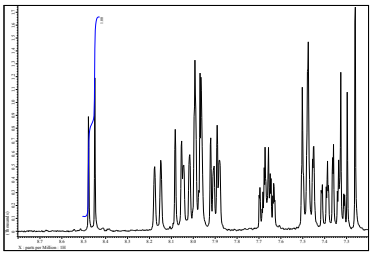
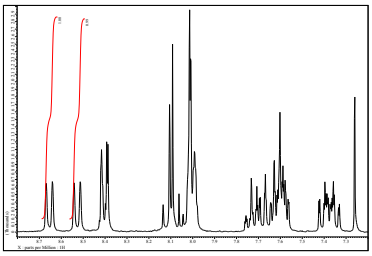
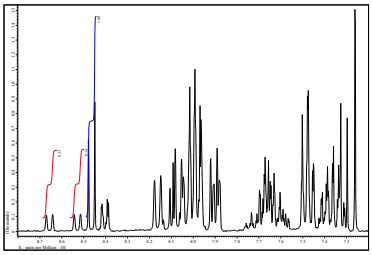
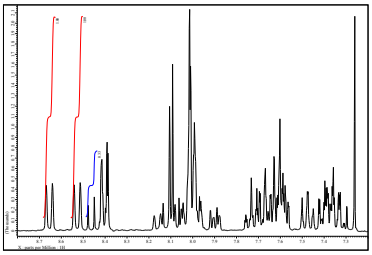
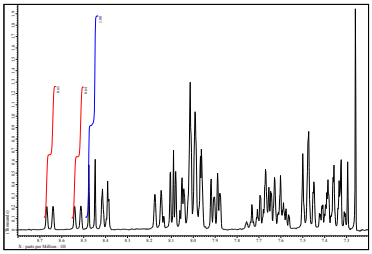
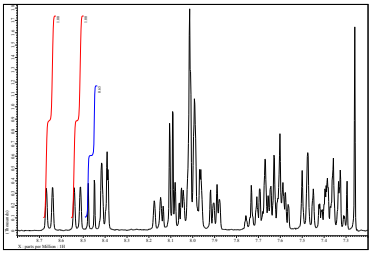
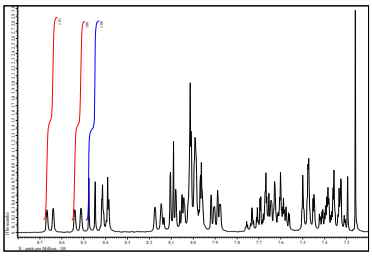
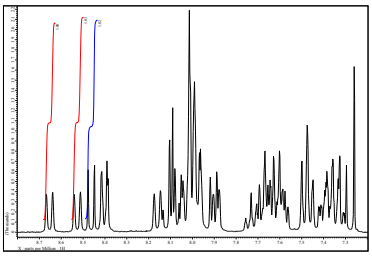
Reported specific rotation value of (*S*)-**6a**: $[\alpha]_D^{20} = -133$ (*c* 0.55, $CHCl_3$, >99% ep).

Observed specific rotation value of **6a**: $[\alpha]_D^{25} = +144$ (*c* 0.055, $CHCl_3$, >99% ep).

By comparison with these data, the absolute stereochemistry of **4d**, **4e**, and **6b** resulting from DYASIN using **OCS1** was determined as (*M*), (*M*), and (*R*)-configuration, respectively.

4. ^{1}H NMR Analysis for Tautomerization of Lactam 3d and Lactim 4d in $CDCl_3$ at 25 °C:

A solution of lactam **3d** or lactim **4d** in $CDCl_3$ was left at 25 °C and its tautomerization was measured using ^{1}H NMR (300 MHz) analysis.

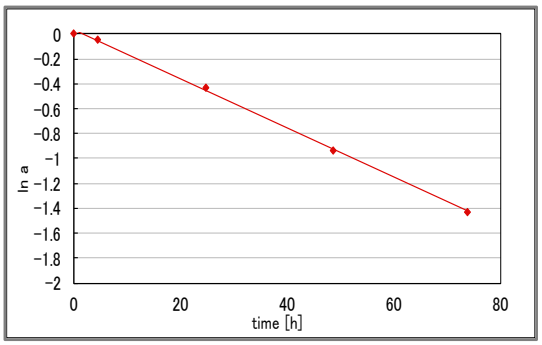
	tautomerization from lactam **3d** to lactim **4d**	tautomerization from lactim **4d** to lactam **3d**
0 h	 **3d** : **4d** = 1.00 : 0	 **3d** : **4d** = 0 : 1.00
48 h	 **3d** : **4d** = 1.00 : 0.33	 **3d** : **4d** = 0.33 : 1.00
120 h	 **3d** : **4d** = 1.00 : 0.65	 **3d** : **4d** = 0.65 : 1.00
290 h	 **3d** : **4d** = 1.00 : 1.00	 **3d** : **4d** = 1.00 : 1.00

5. Kinetic Measurements of the Racemization of Lactam 3 and Lactim 4:

HPLC analysis using a chiral stationary column equipped with a CD and a UV detector was carried out at 10 °C after proper time intervals in *n*-C_6H_{14}/CH_2Cl_2 = 10:90. Plotting ln *a* (*a* = *ee* / ee_0) against time, furnished a straight line, afforded the rate constants *k* and the half-lives of optical activity ($t_{1/2}$) of **3** and **4**.

"*ee*" is the observed enantiomeric excess value and "ee_0" is initial value.

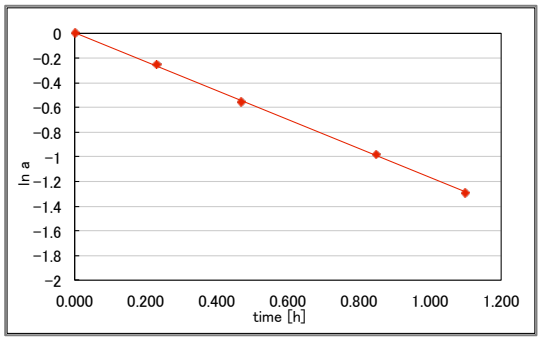
3d



time [h]	*ee* [%]	a	ln a
0.00	92.0	1.00	0.00
4.62	88.0	0.957	−0.0445
24.8	60.0	0.652	−0.427
48.7	36.0	0.391	−0.938
73.8	22.0	0.239	−1.43

$y = -1.98 \times 10^{-2}\ x + 0.031600$ ($R^2 = 0.9985$), $k = 1.98 \times 10^{-2}$, $t_{1/2}$ = 35.1 h at 10 °C

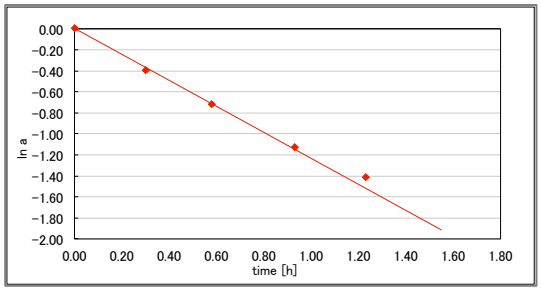
4d



time [h]	*ee* [%]	a	ln a
0.00	80.0	1.00	0.00
0.230	62.0	0.775	−0.255
0.470	46.0	0.575	−0.553
0.850	30.0	0.375	−0.981
1.10	22.0	0.275	−1.29

$y = -1.17\ x + 0.005370$ ($R^2 = 0.9997$), $k = 1.17$, $t_{1/2}$ = 0.592 h at 10 °C

4e



time [h]	*ee* [%]	a	ln a
0.00	74.0	1.00	0.00
0.300	50.0	0.676	−0.392
0.580	36.0	0.486	−0.721
0.930	24.0	0.324	−1.13
1.23	18.0	0.243	−1.41
1.55	10.0	0.135	−2.00

$y = -1.24\ x + 0.004719$ ($R^2 = 0.9925$), $k = 1.24$, $t_{1/2}$ = 0.559 h at 10 °C

6. General Procedure of DYASIN:

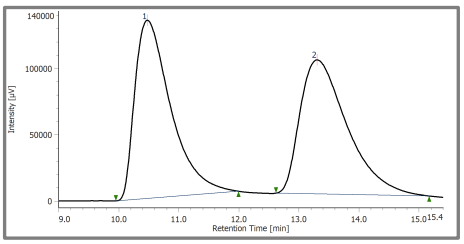
Typical procedure: To a solution of the *rac*-**2cb** [20.0 mg in a mixed solution of *n*-hexane / *i*-Pr_2O = 10 : 1 (3.5 mL)] in a sample bottle was added **OCS5** (4.0 g). After the mixture was shaken well by hand for a few seconds, the sample bottle was left at 25 °C for 24 h. The mixture was poured into the glass funnel attached PTFE filter (pore size: 0.48 μm) and washed with ice-cooled Et_2O (80 mL). The filtrate was concentrated under reduced pressure at –10 to 0°C to afford 96% ep of (*P*)-**2cb** quantitatively.

More large scale of DYASIN can be performed with a similar procedure.

7. HPLC Chromatograms for Determination of Enantiomeric Ratio:

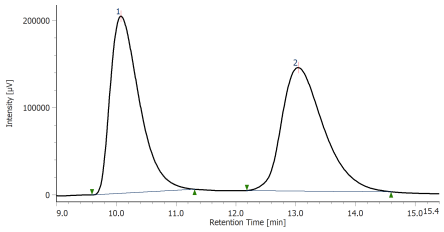
Measurement for DYASIN of Heterohelicenes: Lactone **2**

rac-**2a**



Analysis condition
Column: CHIRALPAK AS-H (0.46 cm × 25 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 90:10
Flow rate: 1.0 mL/min
Detection: UV 254 nm
Temp.: 10 °C
t_1 = 10.5 min for (*M*)-isomer, t_2 = 13.3 min for (*P*)-isomer.

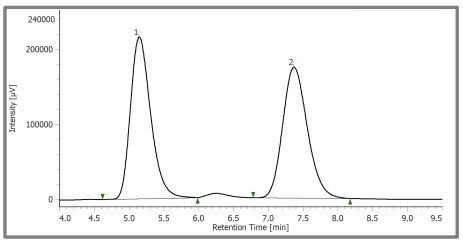
Entry 1: 50% ep (*rac*) of **2a**



OCS: **OCS1**
Solv.: *n*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 50 (*rac*)

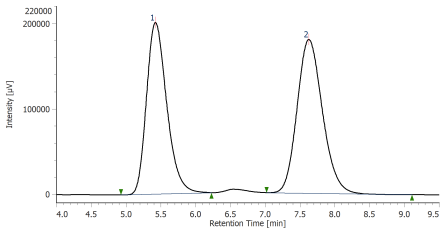
Peak	tR [min]	Area [μV·sec]	Area %
1	10.1	6887719	50.0
2	13.0	6887774	50.0

rac-**2a**



Analysis condition
Column: CHIRALPAK AS-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/EtOH = 90:10
Flow rate: 0.5 mL/min
Detection: UV 254 nm
Temp.: 10 °C
t_1 = 5.1 min for (*M*)-isomer, t_2 = 7.4 min for (*P*)-isomer.

Entry 2: 53% ep of (*P*)-**2a**

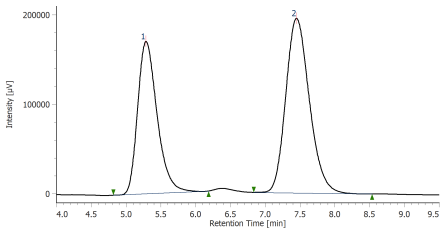


OCS: **OCS2**
Solv.: *n*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 53 (*P*)

Peak	tR [min]	Area [μV·sec]	Area %
1	5.4	4076168	47.1
2	7.6	4571967	52.9

same as above

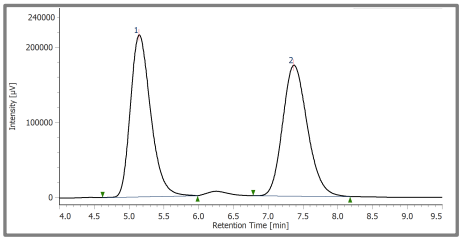
Entry 3: 58% ep of (*P*)-**2a**



OCS: **OCS3**
Solv.: *n*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 58 (*P*)

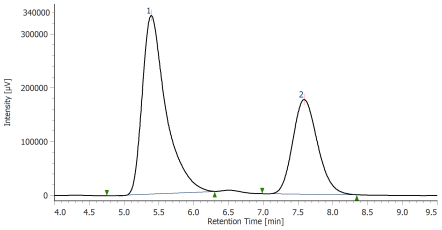
Peak	tR [min]	Area [μV·sec]	Area %
1	5.3	3306407	41.8
2	7.5	4607209	58.2

rac-**2a**



Analysis condition
Column: CHIRALPAK AS-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/EtOH = 90:10
Flow rate: 0.5 mL/min
Detection: UV 254 nm
Temp.: 10 °C
t_1 = 5.1 min for (*M*)-isomer, t_2 = 7.4 min for (*P*)-isomer.

Entry 4: 64% ep of (*M*)-**2a**

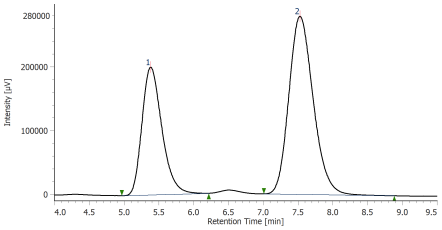


OCS: **OCS4**
Solv.: *n*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 64 (*M*)

Peak	tR [min]	Area [μV·sec]	Area %
1	5.4	7814308	64.2
2	7.6	4364606	35.8

Entry 5: 63% ep of (*P*)-**2a**

same as above

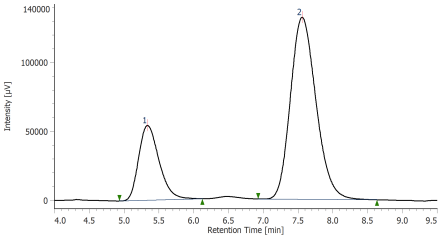


OCS: **OCS5**
Solv.: *n*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 63 (*P*)

Peak	tR [min]	Area [μV·sec]	Area %
1	5.4	3990405	37.0
2	7.5	6800802	63.0

Entry 6: 75% ep of (*P*)- **2a**

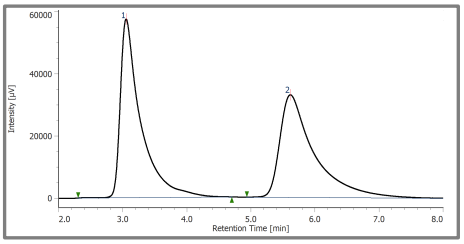
same as above



OCS: **OCS5**
Solv.: *c*-C_5H_{10}
Temp.: 25 °C
Time: 24 h
% ep: 75 (*P*)

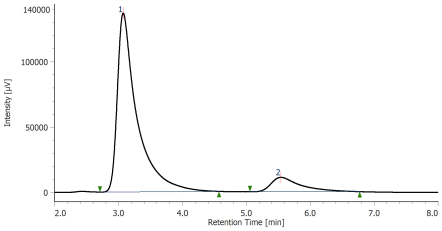
Peak	tR [min]	Area [μV·sec]	Area %
1	5.3	1113094	24.8
2	7.6	3381735	75.2

rac-**2ba**



Analysis condition
Column: CHIRALPAK AD-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 80:20
Flow rate: 1.0 mL/min
Detection: UV 240 nm
Temp.: 10 °C
t_1 = 3.0 min for (*P*)-isomer, t_2 = 5.8 min for (*M*)-isomer.

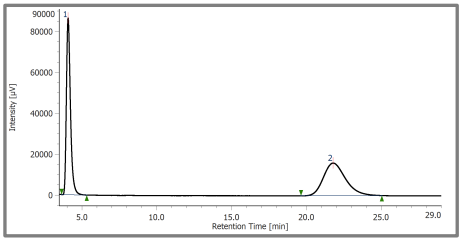
Entry 7: 89% ep of (*P*)-**2ba**



OCS: **OCS5**
Solv.: *c*-C_5H_{10}
Temp.: 25 °C
Time: 24 h
% ep: 89 (*P*)

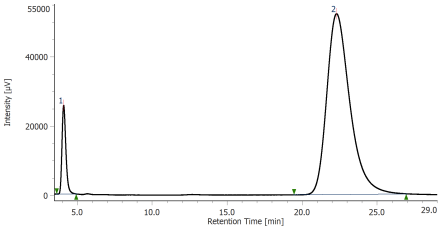
Peak	tR [min]	Area [μV·sec]	Area %
1	3.1	2910814	89.2
2	5.5	353288	10.8

rac-**2bb**



Analysis condition
Column: CHIRALCEL OD-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 50:50
Flow rate: 0.5 mL/min
Detection: UV 240 nm
Temp.: 15 °C
t_1 = 4.1 min for (*M*)-isomer, t_2 = 21.8 min for (*P*)-isomer.

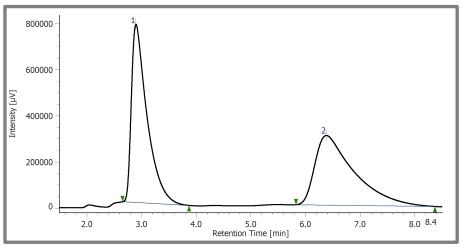
Entry 8: 93% ep of (*P*)-**2bb**



OCS: **OCS5**
Solv.: *c*-C_5H_{10}
Temp.: 25 °C
Time: 24 h
% ep: 93 (*P*)

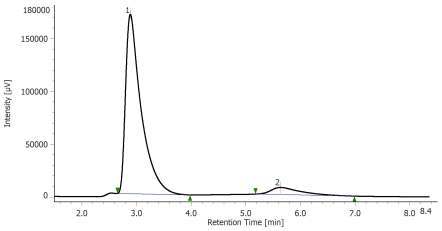
Peak	tR [min]	Area [μV·sec]	Area %
1	4.1	448807	7.4
2	22.3	5640678	92.6

rac-**2ca**



Analysis condition
Column: CHIRALPAK AD-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 80:20
Flow rate: 1.0 mL/min
Detection: UV 240 nm
Temp.: 15 °C
t_1 = 2.9 min for (*P*)-isomer, t_2 = 6.4 min for (*M*)-isomer.

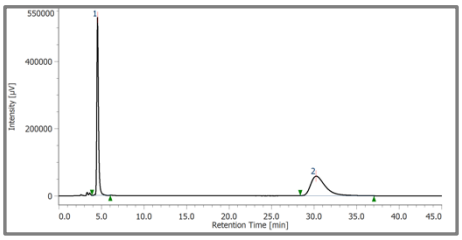
Entry 9: 93% ep of (*P*)-**2ca**



OCS: **OCS5**
Solv.: *i*-C_6H_{14}
Temp.: 25 °C
Time: 24 h
% ep: 93 (*P*)

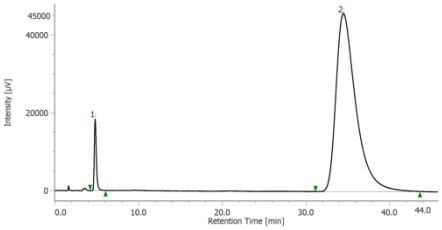
Peak	tR [min]	Area [μV·sec]	Area %
1	2.9	3365872	92.9
2	5.6	256547	7.1

rac-**2cb**



Analysis condition
Column: CHIRALCEL OD-3 (0.46 cm × 5.0 cm)
Eluent: *n*-C_6H_{14}/EtOH = 90:10
Flow rate: 0.5 mL/min
Detection: UV 254 nm
Temp.: 10 °C
t_1 = 4.5 min for (*M*)-isomer, t_2 = 30.2 min for (*P*)-isomer.

Entry10: 96% ep of (*P*)-**2cb**

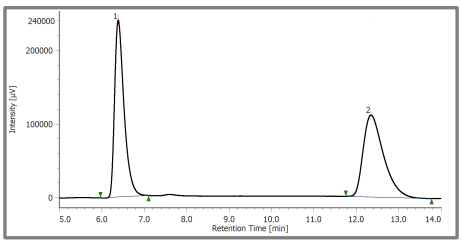


OCS: **OCS5**
Solv.: *n*-C_6H_{14}/*i*-Pr_2O
Temp.: 25 °C
Time: 24 h
% ep: 96 (*P*)

Peak	tR [min]	Area [μV·sec]	Area %
1	4.8	312357	4.0
2	34.5	7520328	96.0

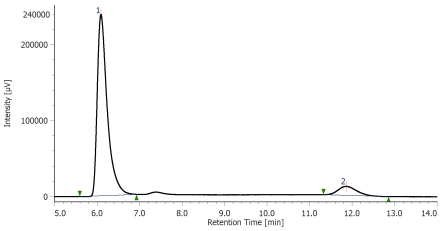
Measurement for DYASIN of Heterohelicenes: Lactim **4**

rac-**4d**



Analysis condition
Column: CHIRALPAK IE (0.46 cm × 25 cm)
Eluent: *n*-C_6H_{14}/CH_2Cl_2 = 10:90
Flow rate: 2.0 mL/min
Detection: UV 300 nm
Temp.: 10 °C
t_1 = 6.4 min for (*M*)-isomer, t_2 = 12.3 min for (*P*)-isomer.

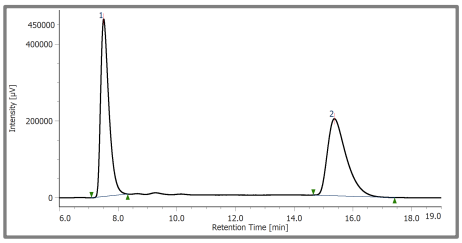
92% ep of (*M*)-**4d**



OCS: **OCS1**
Solv.: *n*-C_6H_{14}/*i*-PrOH
Temp.: 25 °C
Time: 1 h
% ep: 92 (*M*)

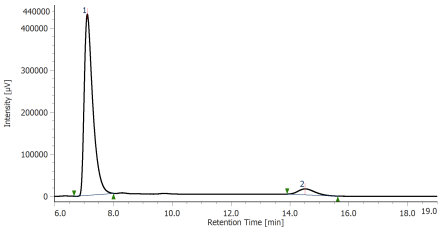
Peak	tR [min]	Area [μV·sec]	Area %
1	6.1	3902826	91.6
2	11.9	357226	8.4

rac-**4e**



Analysis condition
Column: CHIRALPAK IE (0.46 cm × 25 cm)
Eluent: *n*-C_6H_{14}/CH_2Cl_2 = 10:90
Flow rate: 2.0 mL/min
Detection: UV 300 nm
Temp.: 10 °C
t_1 = 7.5 min for (*M*)-isomer, t_2 = 15.4 min for (*P*)-isomer.

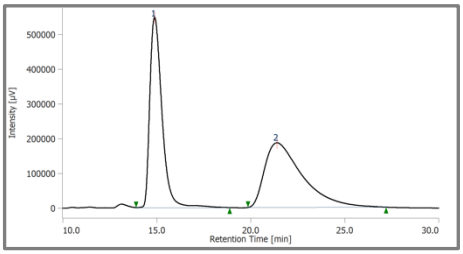
94% ep of (*M*)-**4e**



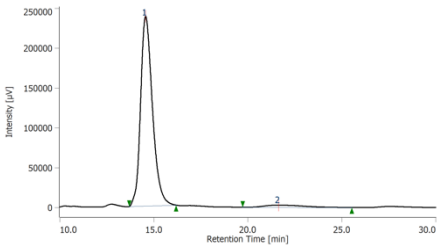
OCS: **OCS1**
Solv.: *n*-C_6H_{14}/*i*-PrOH
Temp.: 25 °C
Time: 1 h
% ep: 94 (*M*)

Peak	tR [min]	Area [μV·sec]	Area %
1	7.1	8757420	94.0
2	14.5	557326	6.0

rac-**5cb**



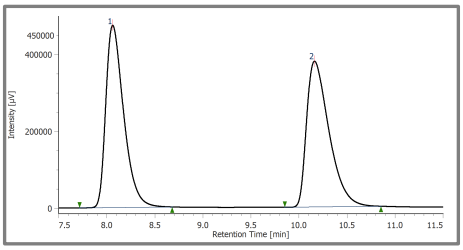
96% ep of (*S*)-**5cb**



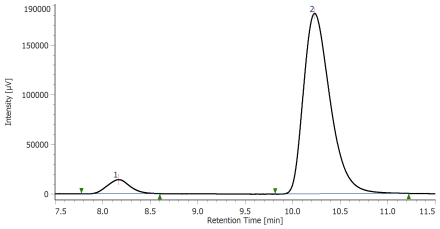
Peak	tR [min]	Area [μV·sec]	Area %
1	14.6	10441900	96.3
2	21.6	401421	3.7

Analysis condition
Column: CHIRALPAK AS-H (0.46 cm × 25 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 95:5
Flow rate: 0.5 mL/min
Detection: UV 254 nm
Temp.: 25 °C
t_1 = 14.9 min for (*S*)-isomer, t_2 = 21.4 min for (*R*)-isomer.

rac-**6b**



94% ep of (*R*)-**6b**



Peak	tR [min]	Area [μV·sec]	Area %
1	8.2	235385	6.2
2	10.2	3541851	93.8

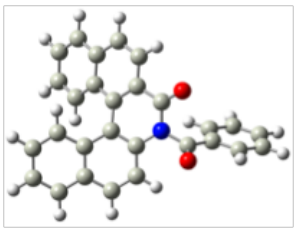
Analysis condition
Column: CHIRALPAK IB (0.46 cm × 25 cm)
Eluent: *n*-C_6H_{14}/*i*-PrOH = 90:10
Flow rate: 1.0 mL/min
Detection: UV 300 nm
Temp.: 25 °C
t_1 = 8.1 min for (*S*)-isomer, t_2 = 10.2 min for (*R*)-isomer.

8. Computational Results:

All the DFT and TD-DFT (NStates = 30) calculations were performed at B3LYP/6-311G(d,p) level of theory by use of Gaussian 16 program at the computer facilities at Research Institute for Information Technology, Kyushu University.[8] The initial structures were prepared by PM3 calculations using spartan 08 program.[9]

Standard state Gibbs free energies ($G°$) were obtained with thermal correction by frequency calculations of optimized geometries at the same level of theories.

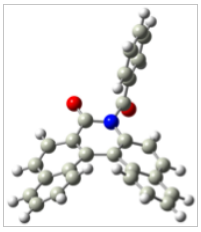
Minimum Structure of Lactam **3d**



G°: –1282.387843 a.u.

H	–0.99577	2.96028	–3.98538
C	–0.90923	2.33555	–3.08911
C	–0.82717	0.85814	–0.6836
C	0.15575	2.46246	–2.24613
C	–1.89614	1.34101	–2.84142
C	–1.8405	0.56913	–1.66054
C	0.22499	1.68186	–1.06282
H	0.96798	3.16751	–2.46341
C	–0.79388	0.2824	0.65826
C	–0.57027	–1.21247	3.04049
C	0.44852	0.0566	1.25227
C	–1.96892	0.00128	1.43575
C	–1.85409	–0.77714	2.60639
C	0.55357	–0.76852	2.41159
H	1.54068	–1.05126	2.80013
H	–0.50015	–1.87141	3.91396
C	–2.90632	1.08527	–3.80614
H	–2.96147	1.72391	–4.69524
C	–3.78178	0.04688	–3.63449
H	–4.55938	–0.15712	–4.37788
C	–3.67445	–0.78548	–2.49945
H	–4.35146	–1.6401	–2.39726
C	–2.73242	–0.53065	–1.53825
H	–2.64699	–1.18728	–0.6626
C	–3.2388	0.56036	1.12968
H	–3.32903	1.23046	0.26493
C	–4.33503	0.28829	1.90597
H	–5.30639	0.73239	1.66383
C	–4.22635	–0.56032	3.02784
H	–5.1189	–0.78445	3.62084
C	–3.0071	–1.07835	3.37588
H	–2.90142	–1.71747	4.26
C	1.47316	1.6958	–0.27949
N	1.62331	0.63992	0.68585
C	2.929	0.53054	1.40662
O	2.42098	2.45135	–0.43736
O	3.07592	1.12671	2.44498
C	3.95216	–0.32422	0.74371
C	5.88503	–1.91077	–0.46464
C	3.86675	–1.71299	0.83836
C	5.00139	0.27435	0.04704
C	5.96572	–0.52527	–0.55809
C	4.83669	–2.50356	0.23277
H	3.04144	–2.18039	1.38841
H	5.06014	1.36735	–0.02692
H	6.78974	–0.0596	–1.10898
H	4.77318	–3.59444	0.30429
H	6.64732	–2.53655	–0.94066

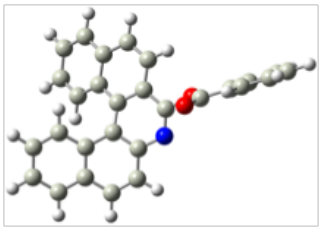
Transition Sate of Lactam **3d**



G°: –1282.350000 a.u.
Imaginary Frequency: –104.1115

H	–1.26324	2.83732	–4.35962
C	–0.83314	2.24989	–3.54095
C	0.1055	0.93258	–1.19514
C	–1.3308	1.02964	–3.2027
C	0.33402	2.72376	–2.87552
C	0.90263	1.9734	–1.81817
C	–0.86425	0.37314	–2.03007
H	–2.131	0.56073	–3.78887
C	0.03241	0.58403	0.22836
C	–1.15589	0.73313	2.81586
C	–1.00271	–0.27754	0.62692
C	0.72893	1.23404	1.32345
C	0.04453	1.45041	2.54233
C	–1.58762	–0.20129	1.92998
H	–2.43969	–0.84201	2.19244
H	–1.67678	0.89952	3.766
C	0.9859	3.88375	–3.36474
H	0.47282	4.50459	–4.10849
C	2.24881	4.20132	–2.9365
H	2.75564	5.10309	–3.29513
C	2.92072	3.31631	–2.07304
H	3.97602	3.49163	–1.83883
C	2.26882	2.22588	–1.55143
H	2.85489	1.48449	–0.99961
C	2.10108	1.57725	1.32611
H	2.76335	1.15231	0.56635
C	2.65905	2.33462	2.32752
H	3.7217	2.59805	2.29148
C	1.88016	2.7575	3.41953
H	2.31392	3.41792	4.17691
C	0.60068	2.27913	3.54674
H	0.00009	2.5135	4.43319
C	–1.52705	–0.89222	–1.68576
N	–1.55253	–1.21216	–0.29458
O	–2.02015	–1.69763	–2.46233
C	–2.44008	–2.31721	0.17851
O	–3.62931	–2.1187	0.2309
C	–1.75308	–3.59404	0.51217
C	–0.49014	–5.99332	1.11698
C	–1.93139	–4.69889	–0.32068
C	–0.94767	–3.68627	1.64722
C	–0.31872	–4.88961	1.94733
C	–1.29475	–5.89765	–0.01394
H	–2.5642	–4.61968	–1.21319
H	–0.81255	–2.81288	2.2978
H	0.31413	–4.96657	2.83801
H	–1.42872	–6.76651	–0.66725
H	0.00964	–6.93874	1.35445

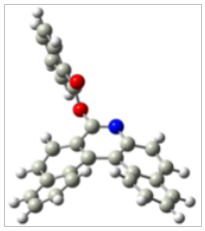
Minimum Structure of Lactim **4d**



G°: –1282.390740 a.u.

H	–0.62348	2.55788	–3.97801
C	–0.60115	2.01142	–3.02813
C	–0.70071	0.78689	–0.47346
C	0.48468	2.06212	–2.21552
C	–1.71619	1.18368	–2.68336
C	–1.74841	0.52801	–1.43616
C	0.46913	1.39948	–0.94958
H	1.37782	2.62746	–2.50741
C	–0.73752	0.39069	0.91267
C	–0.57322	–0.80215	3.48361
C	0.4916	0.20653	1.56766
C	–1.93232	0.23877	1.71132
C	–1.84645	–0.40145	2.96457
C	0.56812	–0.45485	2.83786
H	1.5541	–0.67586	3.2639
H	–0.5417	–1.34631	4.43468
C	–2.74881	0.96435	–3.62544
H	–2.73403	1.521	–4.56958
C	–3.74096	0.05101	–3.3673
H	–4.54053	–0.12359	–4.09467
C	–3.71932	–0.68666	–2.16954
H	–4.48325	–1.4517	–1.99535
C	–2.74706	–0.45423	–1.22697
H	–2.72878	–1.04584	–0.30213
C	–3.17127	0.8172	1.3434
H	–3.23231	1.40539	0.41849
C	–4.28425	0.67001	2.13575
H	–5.23462	1.12675	1.84011
C	–4.21292	–0.06158	3.33485
H	–5.11487	–0.19509	3.9408
C	–3.01022	–0.57987	3.7483
H	–2.93362	–1.12107	4.69842
N	1.68739	0.66904	1.02585
C	1.65062	1.31034	–0.13388
O	2.79481	1.96538	–0.53145
C	4.03158	1.35702	–0.46941
O	4.86625	2.22471	–0.5816
C	4.24009	–0.1094	–0.37932
C	4.71232	–2.84331	–0.24402
C	3.84093	–0.93481	–1.43102
C	4.88051	–0.64659	0.73675
C	5.11093	–2.01702	0.80125
C	4.08017	–2.30227	–1.35937
H	3.34506	–0.50904	–2.31057
H	5.19608	0.00646	1.55837
H	5.60908	–2.44409	1.6782
H	3.76984	–2.95337	–2.18332
H	4.89684	–3.92146	–0.19026

Transition Sate of Lactim **4d**



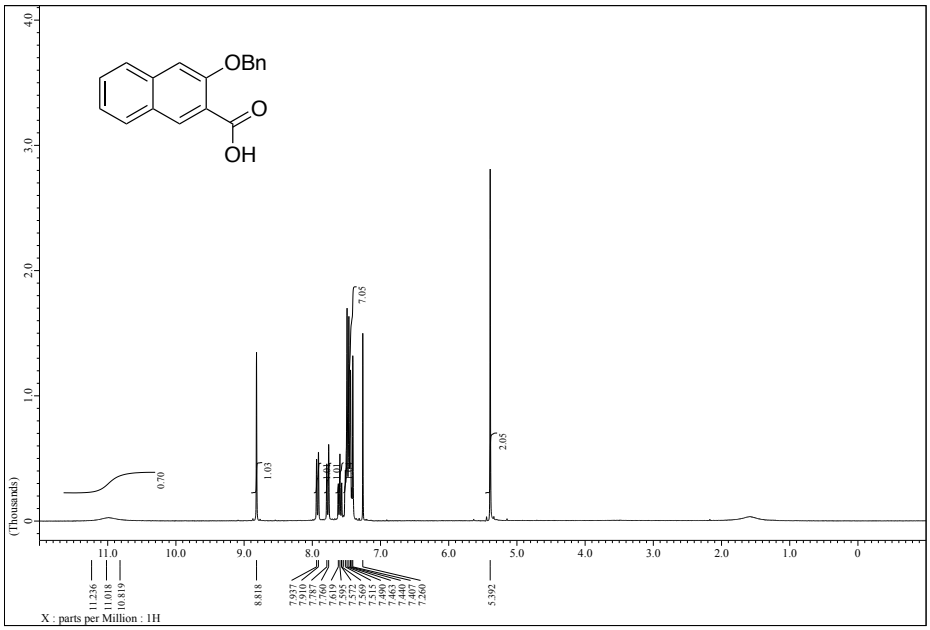
G°: –1282.357924 a.u.

Imaginary Frequency: –106.5808

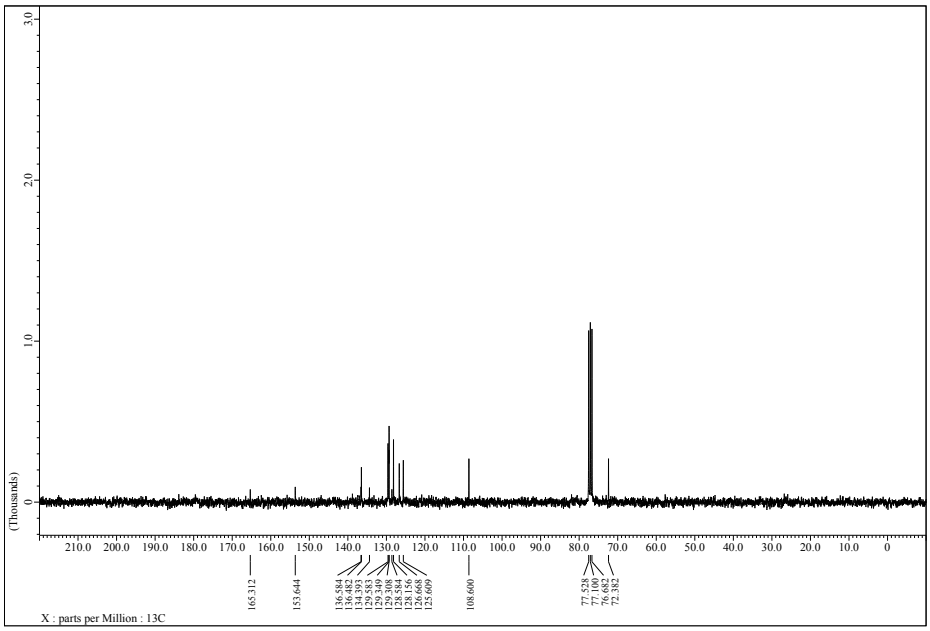
H	–1.34534	1.83783	–3.73981
C	–0.65774	1.38857	–3.0146
C	0.9615	0.37236	–0.88538
C	–0.72155	0.07453	–2.69444
C	0.39831	2.18623	–2.46893
C	1.32026	1.6148	–1.56116
C	0.06577	–0.43707	–1.61453
H	–1.42568	–0.59706	–3.20048
C	1.24808	–0.02638	0.47787
C	0.6583	–0.47247	3.24881
C	0.59323	–1.18611	0.94915
C	1.95954	0.71151	1.51544
C	1.51032	0.60988	2.85346
C	0.32575	–1.4199	2.34173
H	–0.21125	–2.3305	2.63604
H	0.35219	–0.55134	4.29833
C	0.59155	3.49607	–2.962
H	–0.18942	3.95214	–3.58146
C	1.75877	4.17197	–2.69604
H	1.91099	5.19443	–3.05582
C	2.7883	3.50651	–2.01326
H	3.77014	3.9828	–1.91939
C	2.57583	2.2526	–1.48527
H	3.43684	1.70735	–1.0895
C	3.14762	1.44652	1.32781
H	3.73625	1.30411	0.418
C	3.66797	2.25622	2.31296
H	4.58139	2.82966	2.12568
C	3.04859	2.33325	3.56865
H	3.42757	3.02587	4.32655
C	2.00799	1.48	3.84852
H	1.57048	1.44563	4.85287
N	0.047	–2.13665	0.09518
C	–0.19227	–1.77112	–1.15294
O	–0.63384	–2.73282	–2.03402
C	–1.70854	–3.54076	–1.72283
O	–1.68866	–4.48505	–2.4774
C	–2.73115	–3.20248	–0.70169
C	–4.70775	–2.61759	1.16057
C	–2.95854	–4.07418	0.36282
C	–3.49247	–2.04081	–0.83949
C	–4.48177	–1.75295	0.09338
C	–3.94696	–3.77424	1.29511
H	–2.36123	–4.98774	0.46402
H	–3.30985	–1.35916	–1.67944
H	–5.08298	–0.84374	–0.01267
H	–4.12663	–4.45409	2.13481
H	–5.4869	–2.38664	1.89479

9. ^{1}H, ^{13}C NMR Spectra:

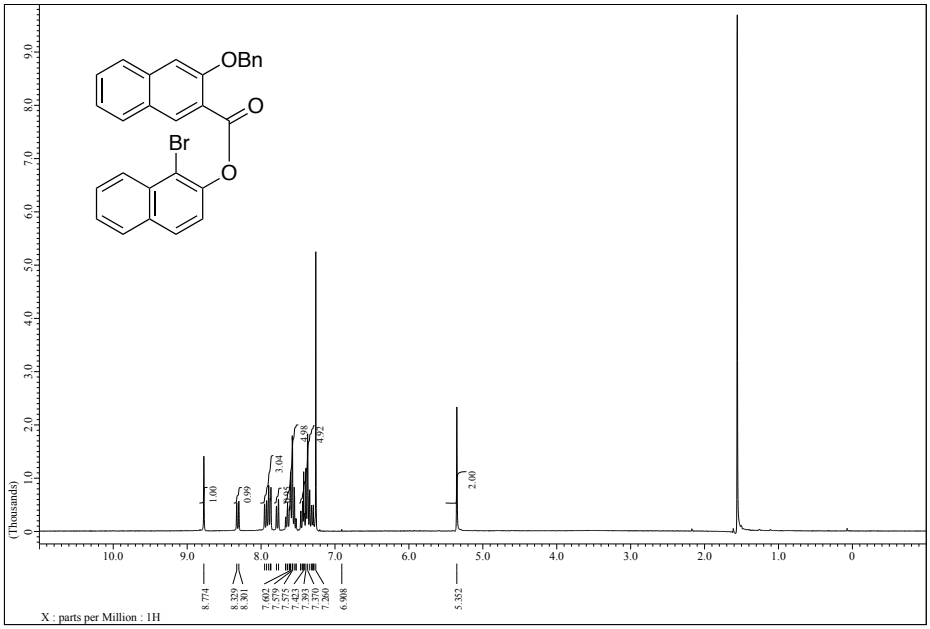
^{1}H NMR (300 MHz) Chart of **s4** in $CDCl_3$



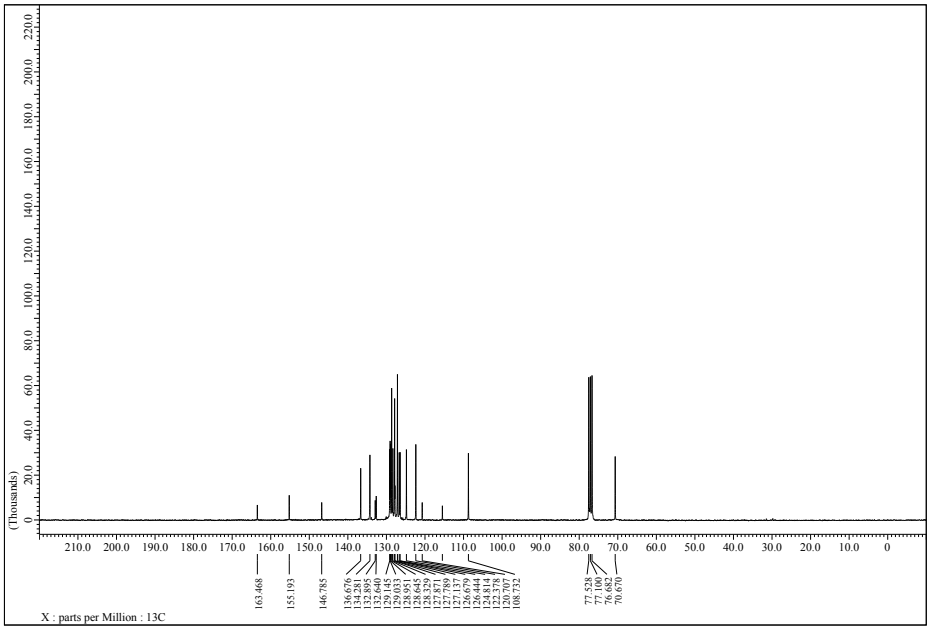
^{13}C NMR (75 MHz) Chart of **s4** in $CDCl_3$



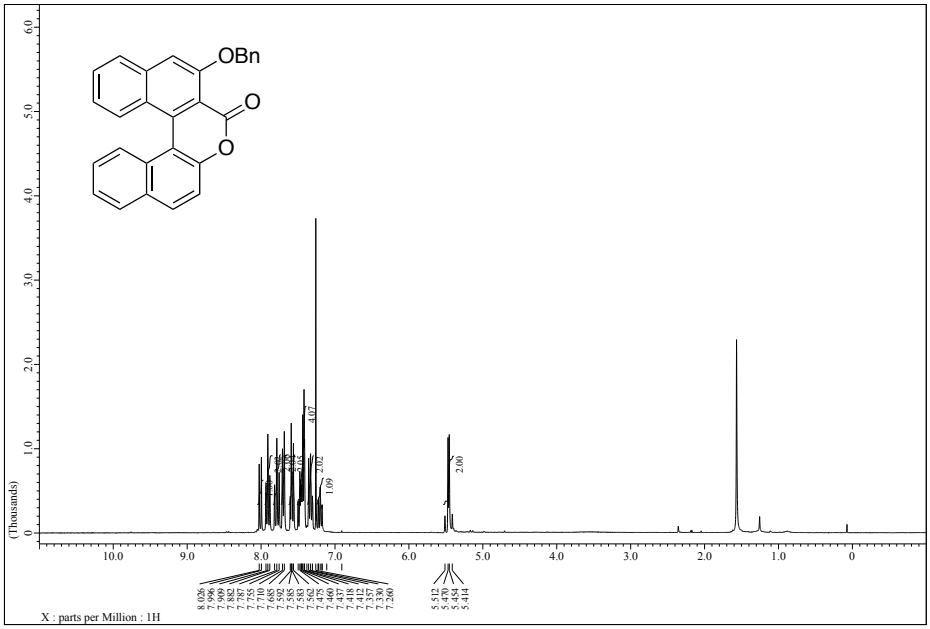
^{1}H NMR (300 MHz) Chart of **s5** in $CDCl_3$



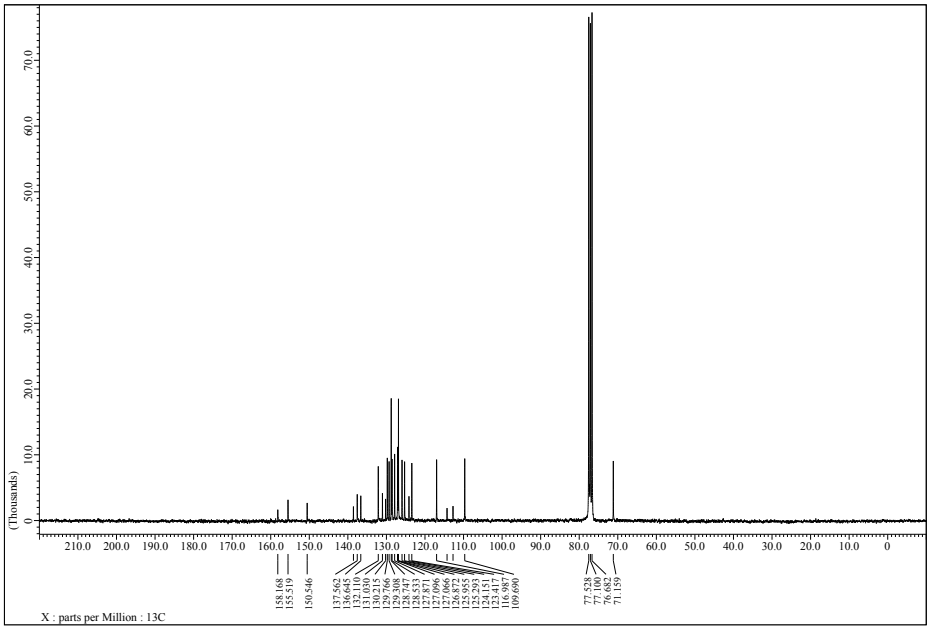
^{13}C NMR (75 MHz) Chart of **s5** in $CDCl_3$



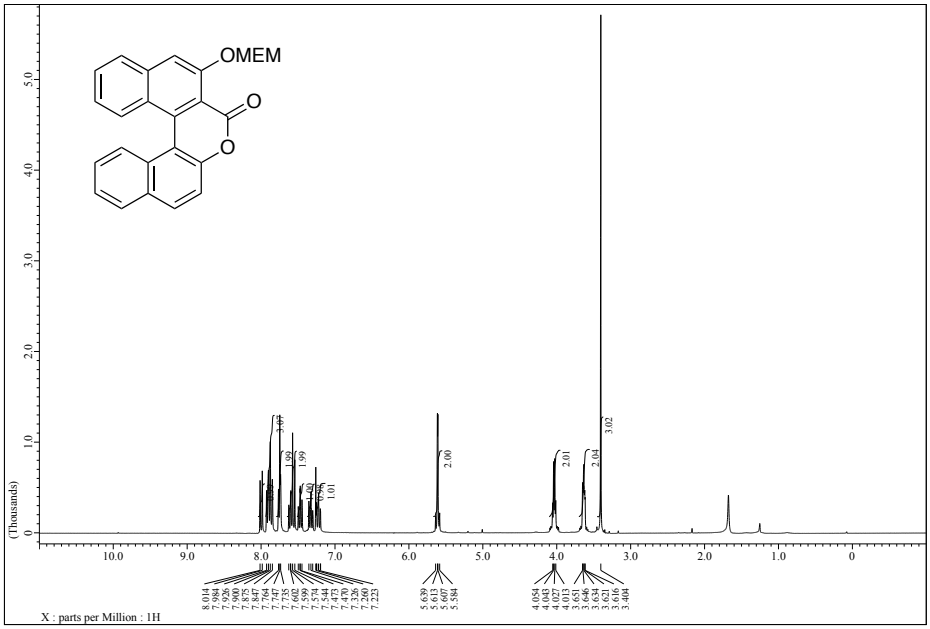
^{1}H NMR (300 MHz) Chart of **s6** in $CDCl_3$



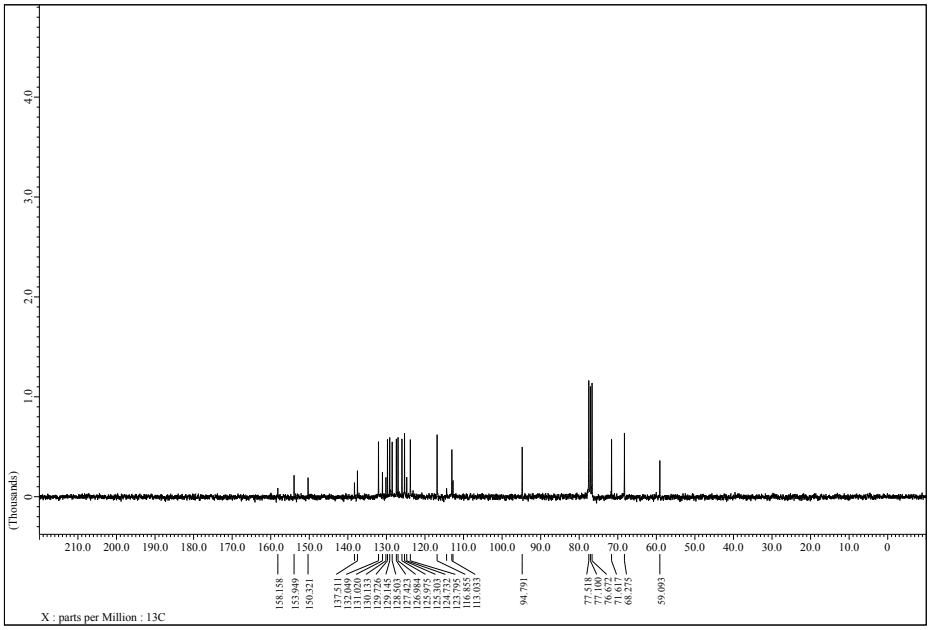
^{13}C NMR (75 MHz) Chart of **s6** in $CDCl_3$



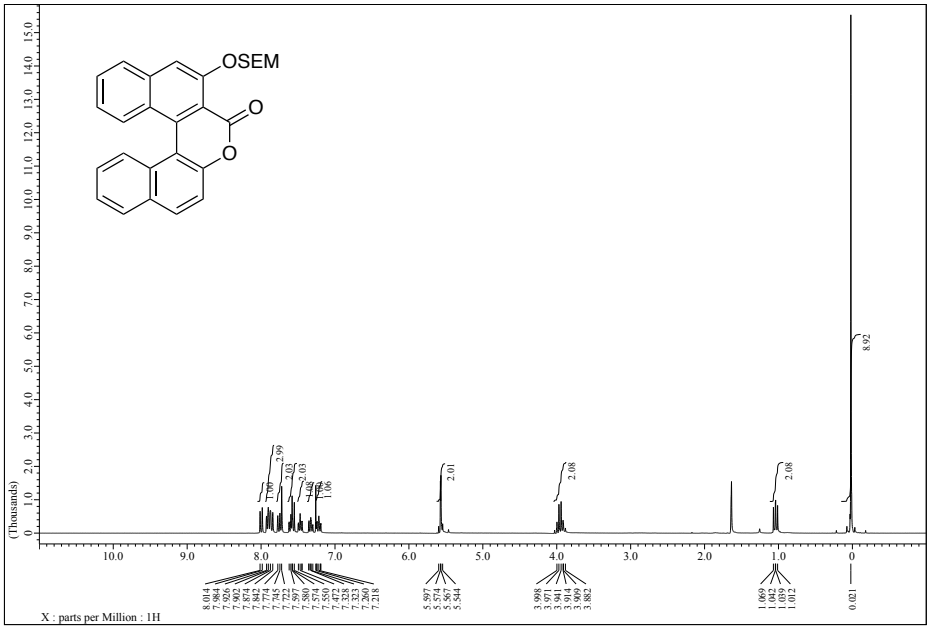
^{1}H NMR (300 MHz) Chart of **2ba** in $CDCl_3$



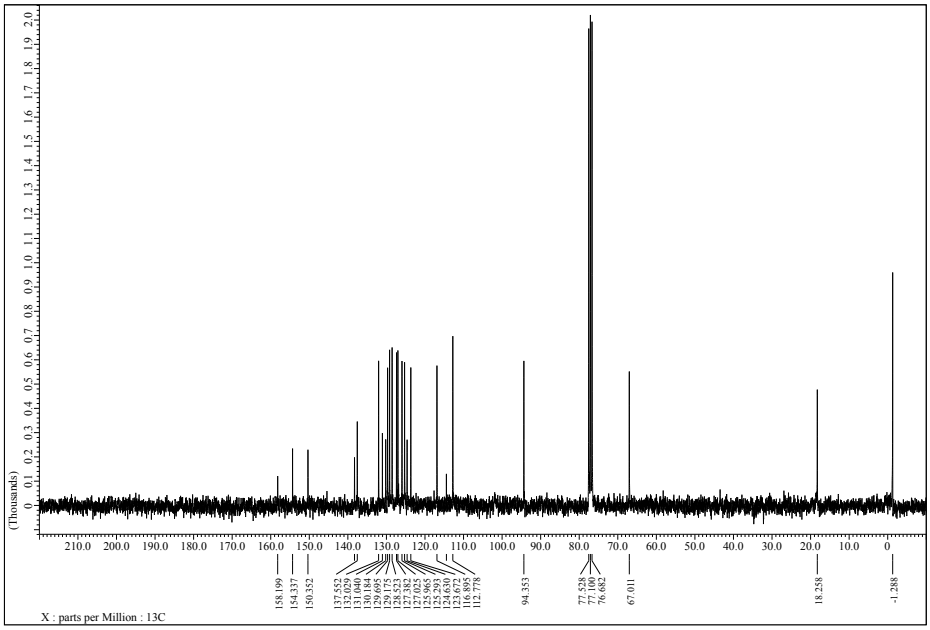
^{13}C NMR (75 MHz) Chart of **2ba** in $CDCl_3$



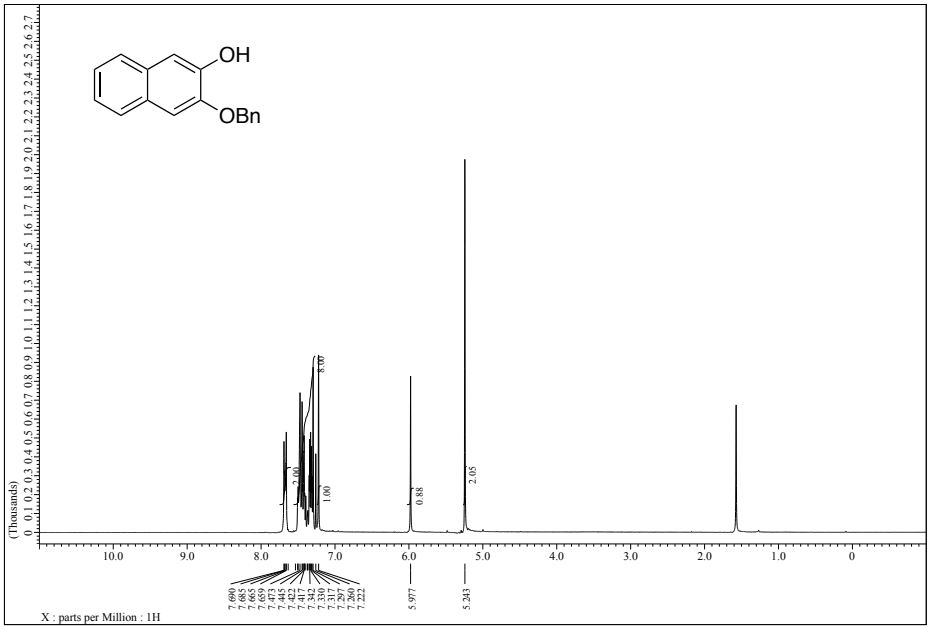
^{1}H NMR (300 MHz) Chart of **2bb** in $CDCl_3$



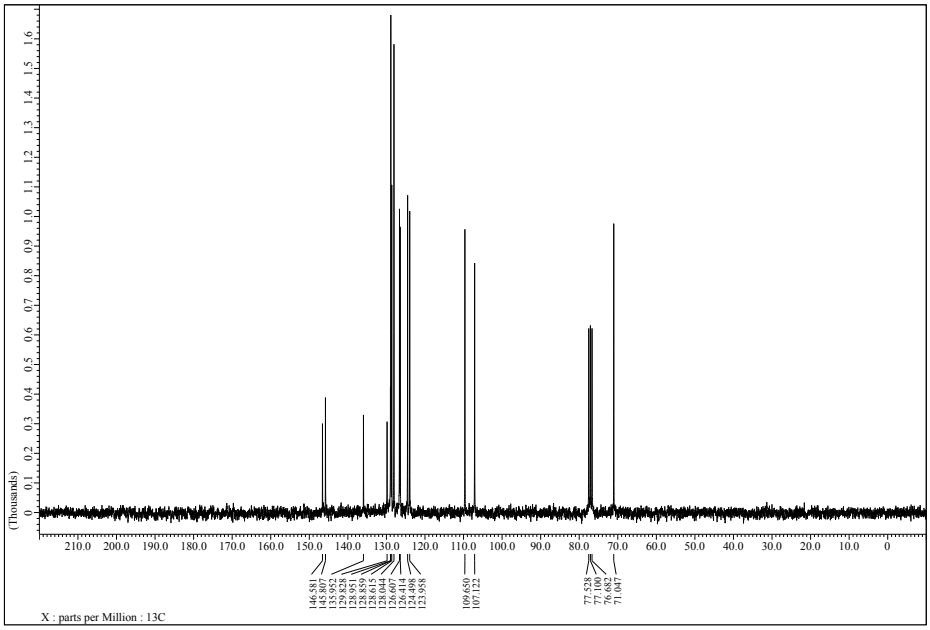
^{13}C NMR (75 MHz) Chart of **2bb** in $CDCl_3$



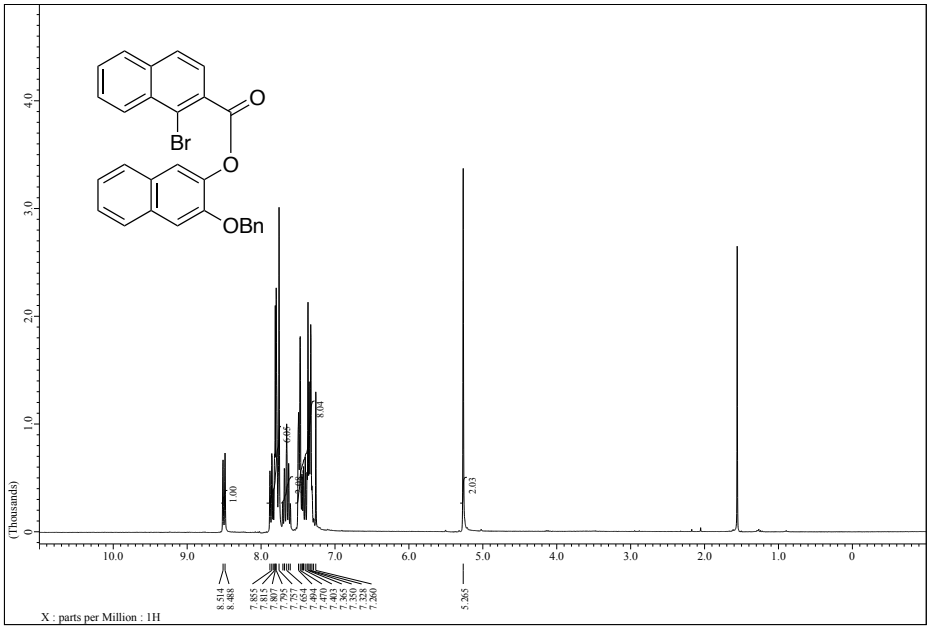
^{1}H NMR (300 MHz) Chart of **s8** in $CDCl_3$



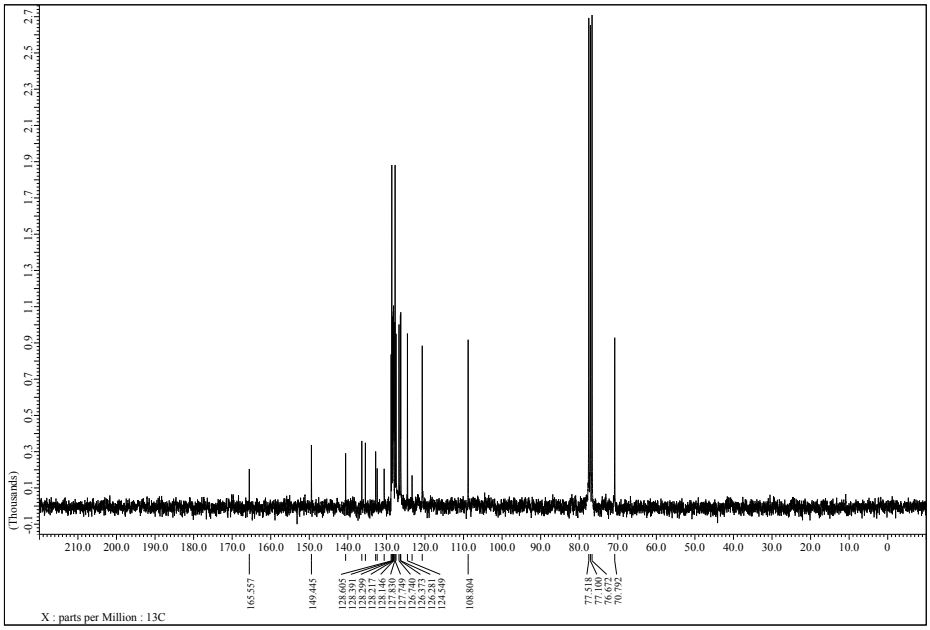
^{13}C NMR (75 MHz) Chart of **s8** in $CDCl_3$



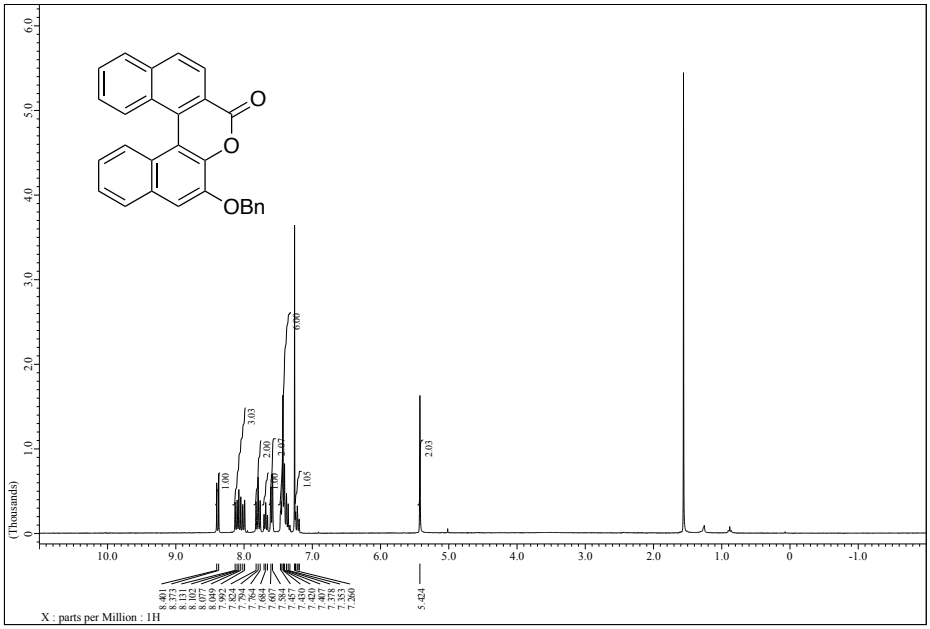
^{1}H NMR (300 MHz) Chart of **s9** in $CDCl_3$



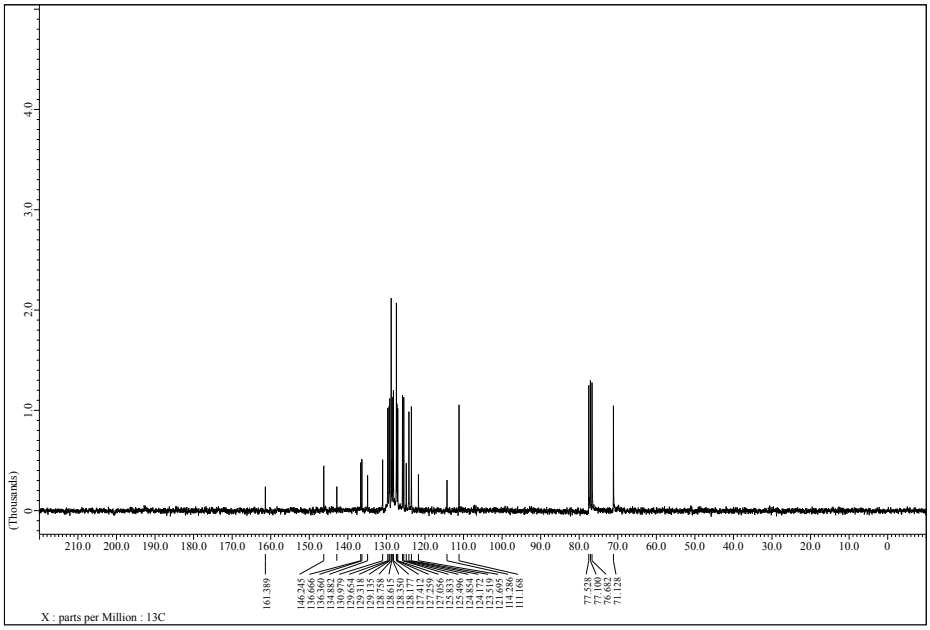
^{13}C NMR (75 MHz) Chart of **s9** in $CDCl_3$



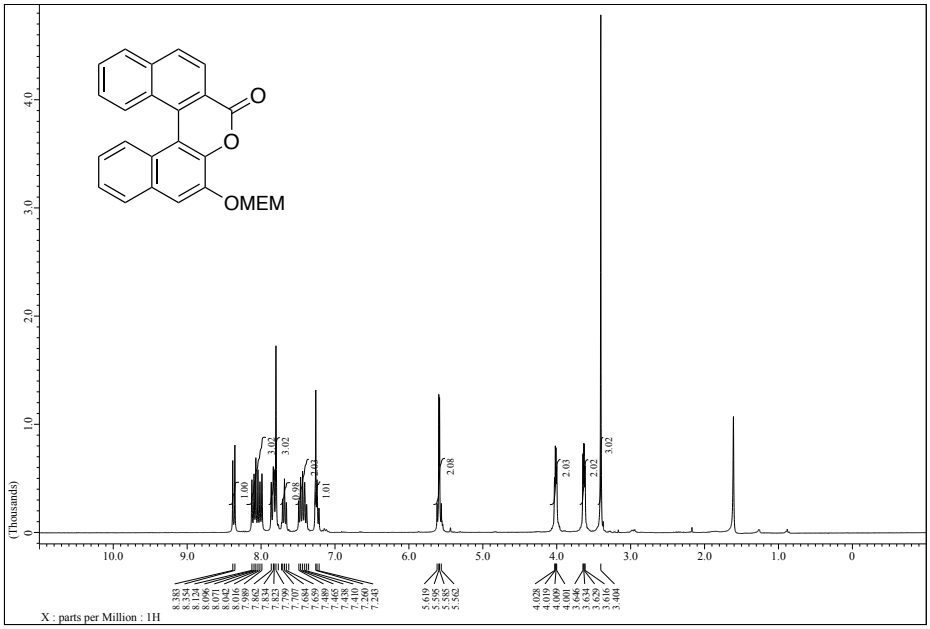
^{1}H NMR (300 MHz) Chart of **s10** in $CDCl_3$



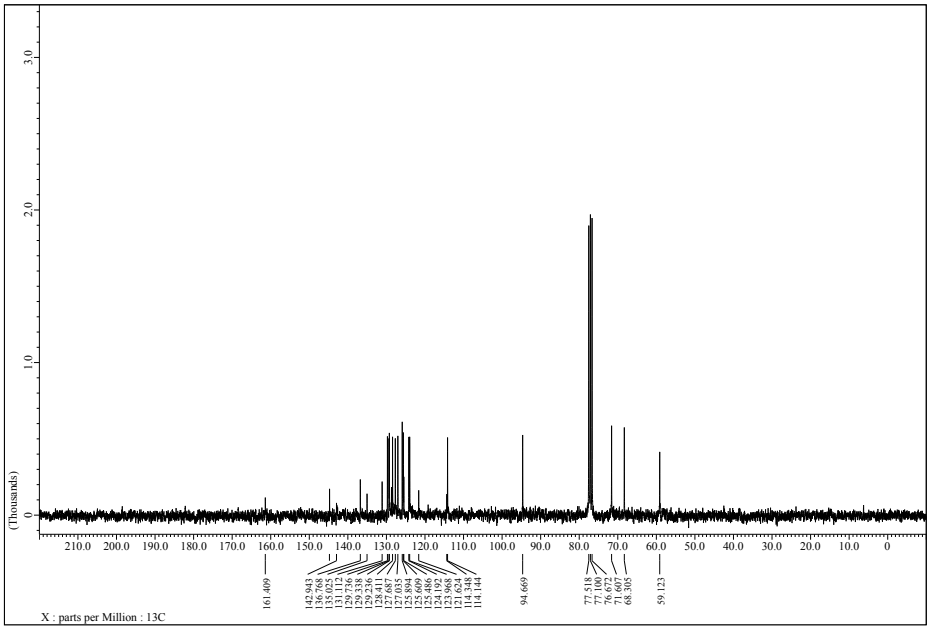
^{13}C NMR (75 MHz) Chart of **s10** in $CDCl_3$



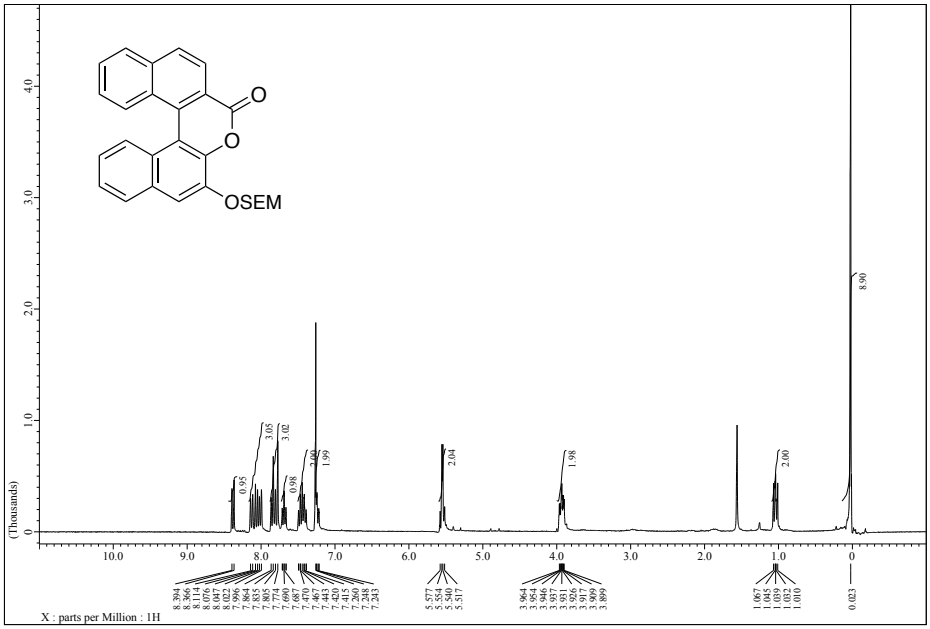
^{1}H NMR (300 MHz) Chart of **2ca** in $CDCl_3$



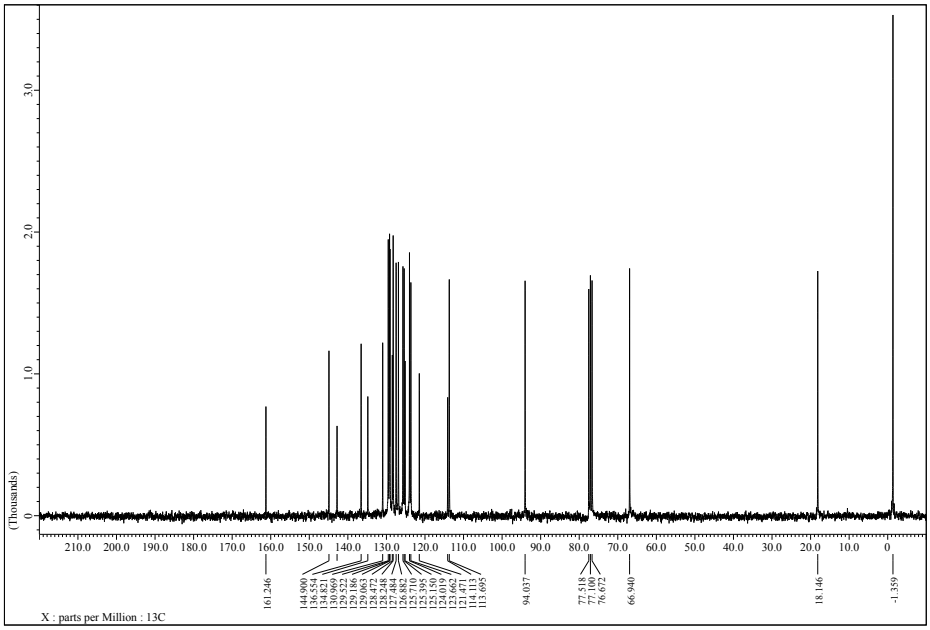
^{13}C NMR (75 MHz) Chart of **2ca** in $CDCl_3$



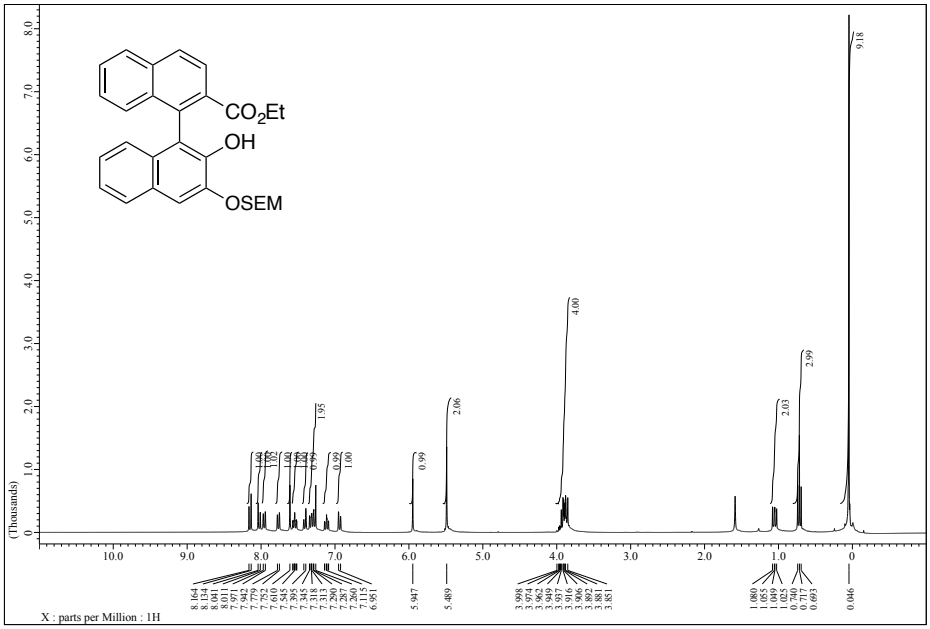
^{1}H NMR (300 MHz) Chart of **2cb** in $CDCl_3$



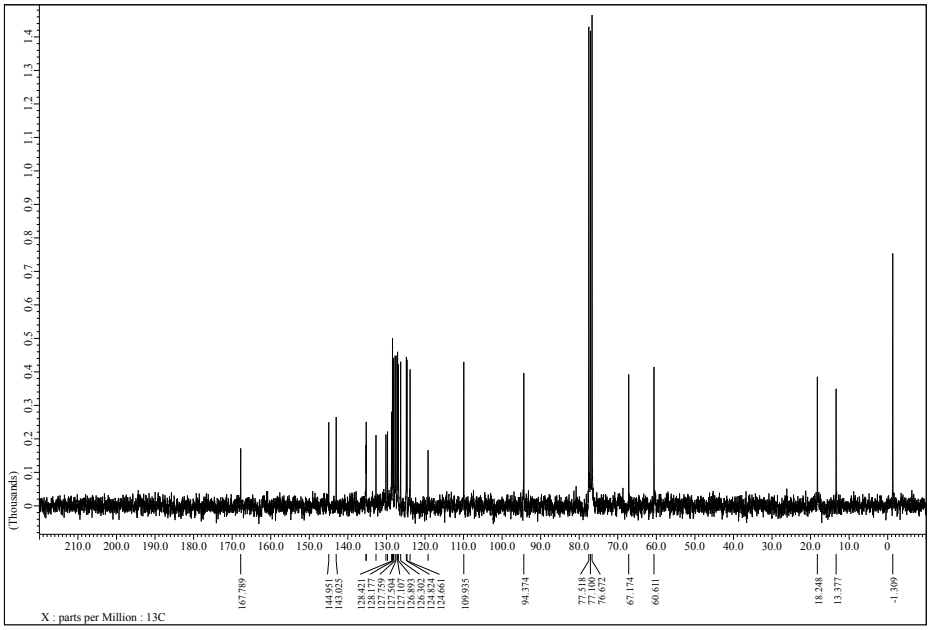
^{13}C NMR (75 MHz) Chart of **2cb** in $CDCl_3$



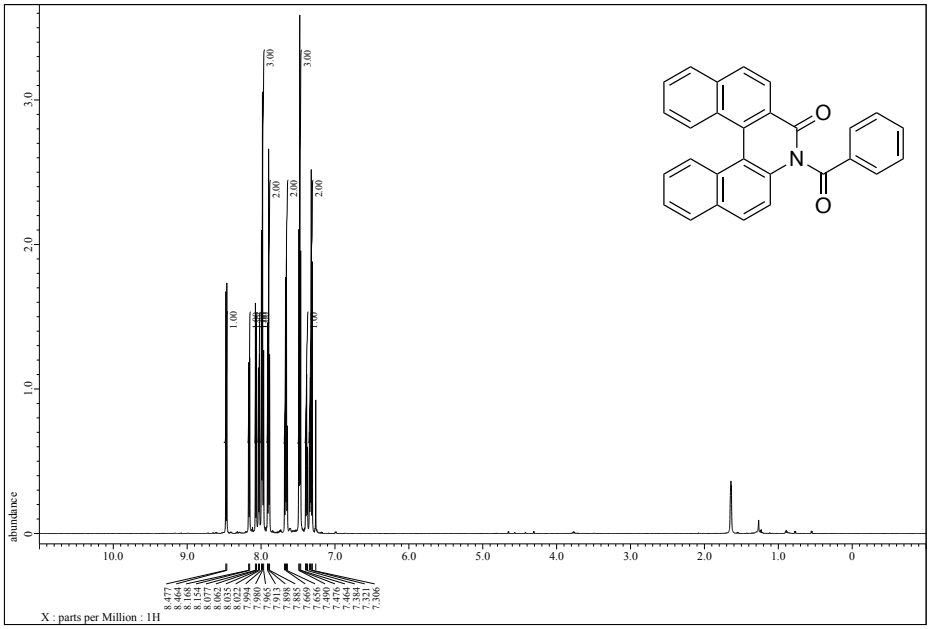
^{1}H NMR (300 MHz) Chart of **5cb** in $CDCl_3$



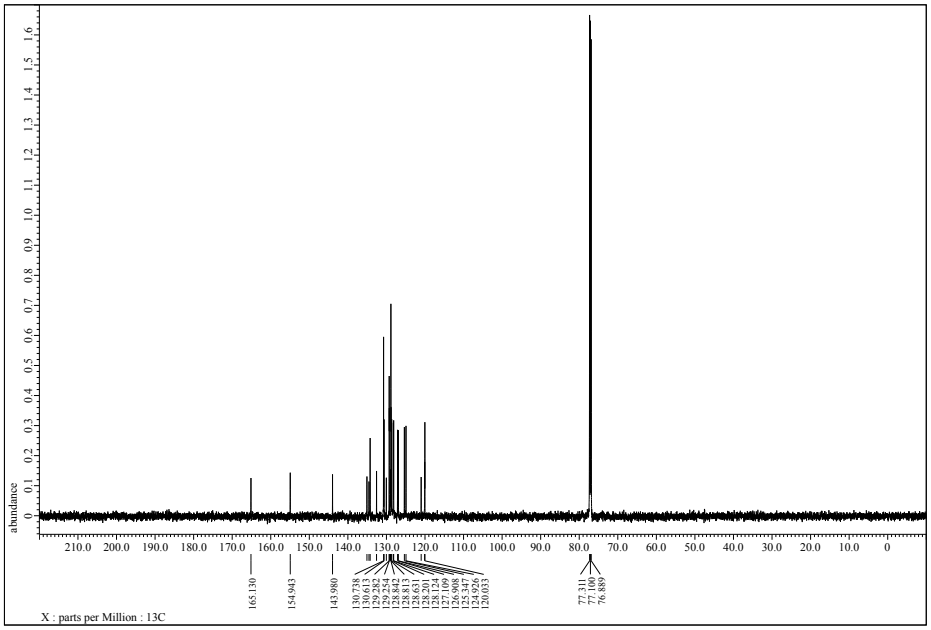
^{13}C NMR (75 MHz) Chart of **5cb** in $CDCl_3$



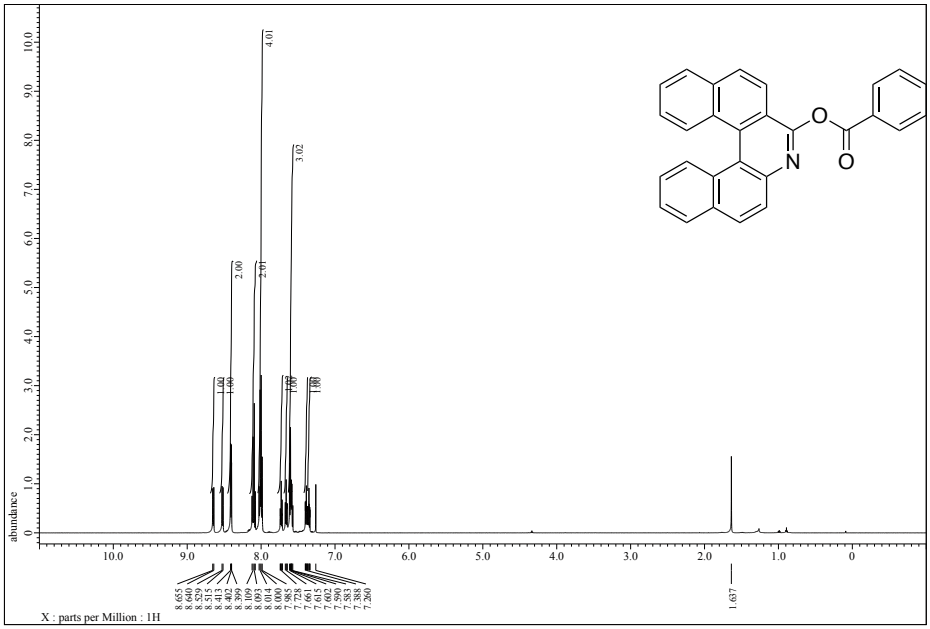
^{1}H NMR (600 MHz) Chart of **3d** in $CDCl_3$



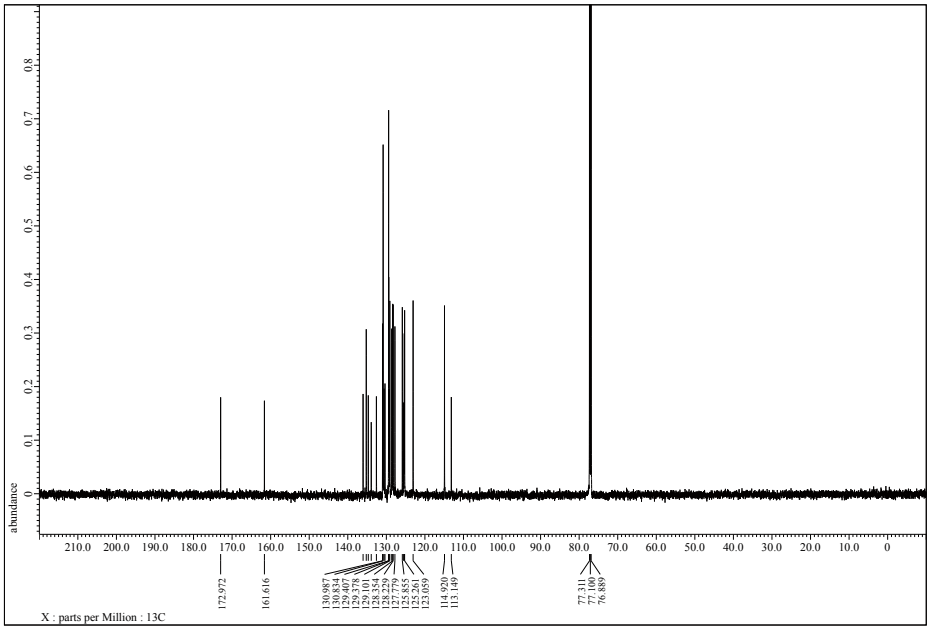
^{13}C NMR (151 MHz) Chart of **3d** in $CDCl_3$



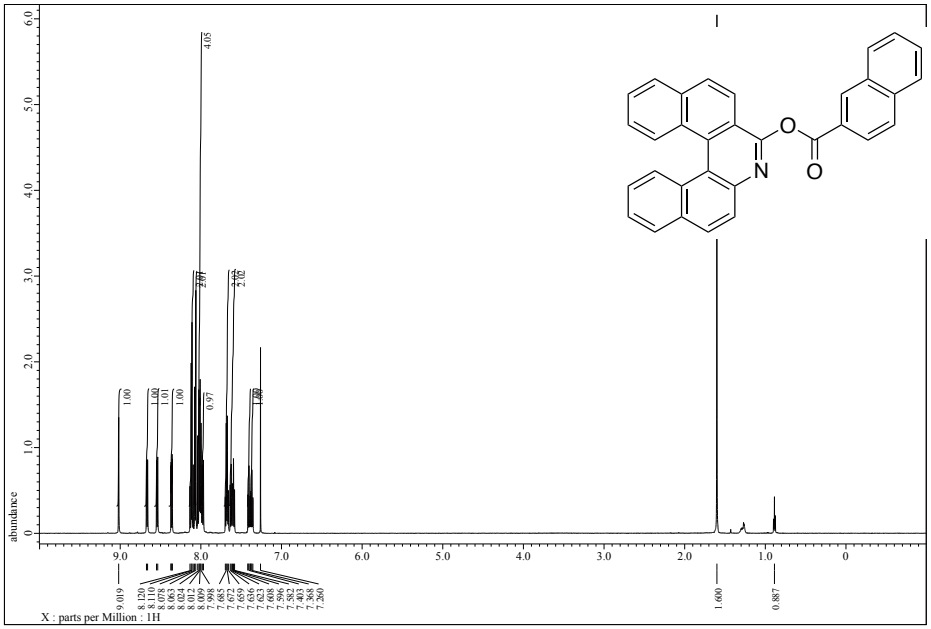
^{1}H NMR (600 MHz) Chart of **4d** in $CDCl_3$



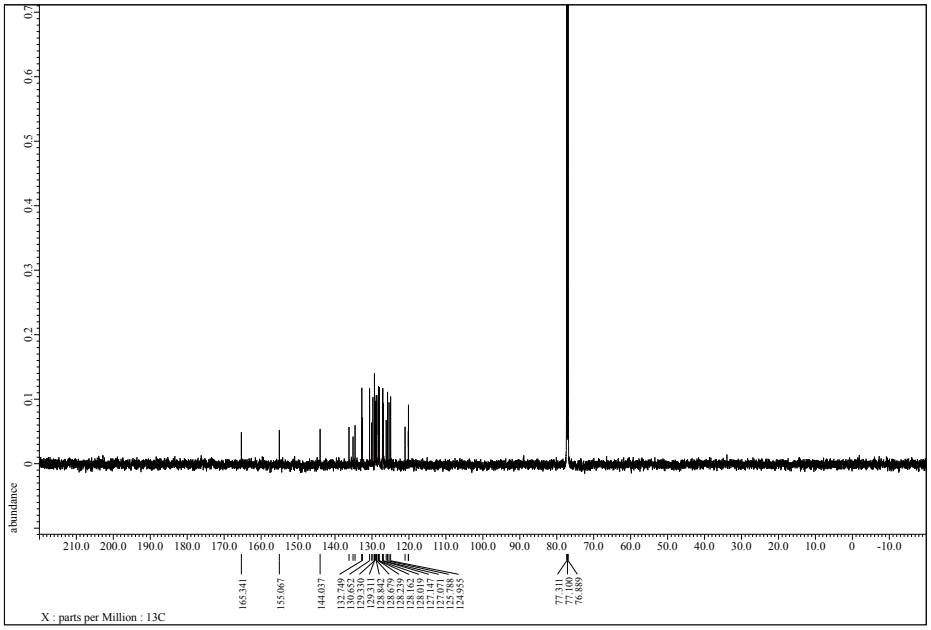
^{13}C NMR (151 MHz) Chart of **4d** in $CDCl_3$



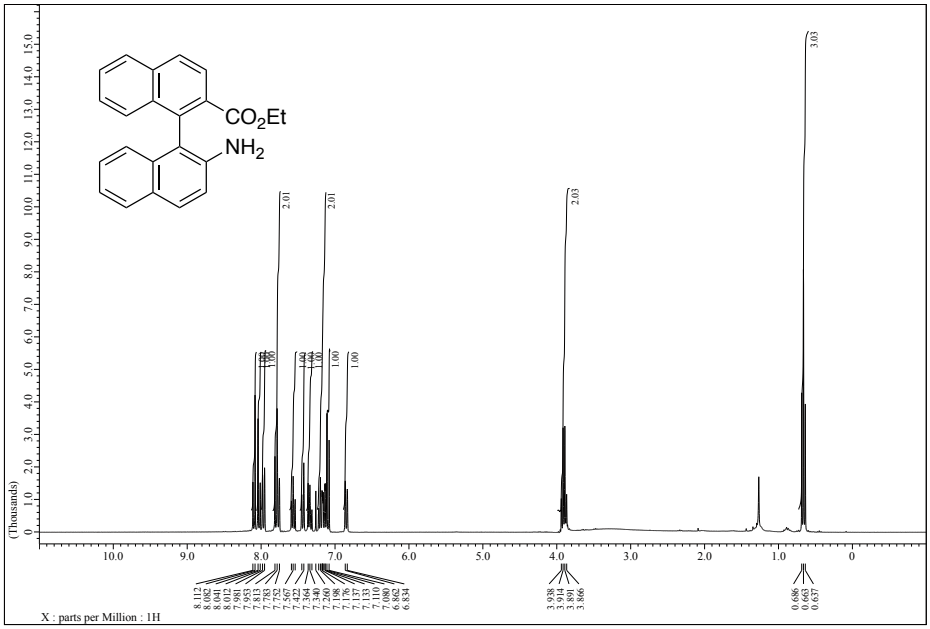
^{1}H NMR (600 MHz) Chart of **4e** in $CDCl_3$



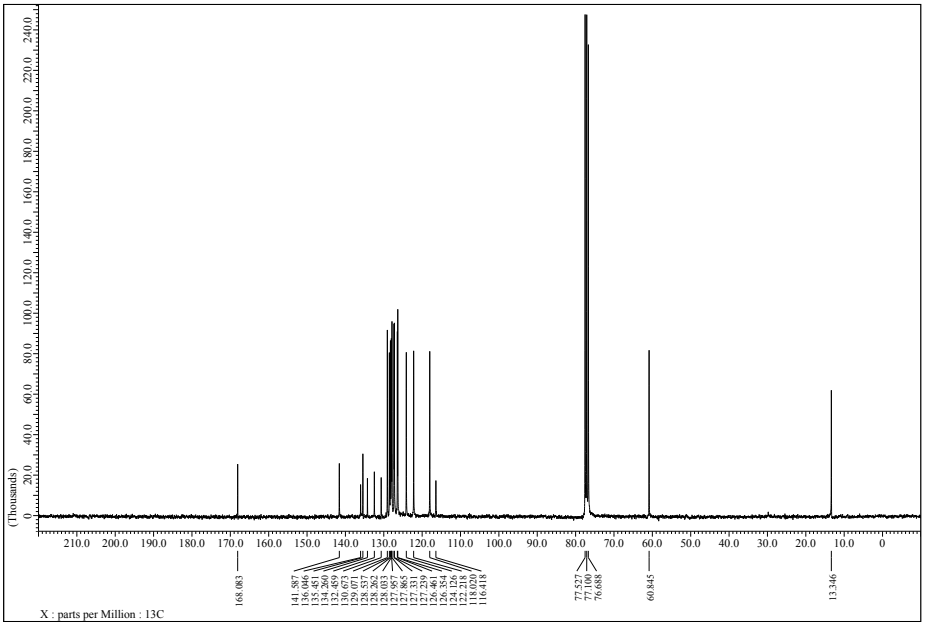
^{13}C NMR (151 MHz) Chart of **4e** in $CDCl_3$



^{1}H NMR (300 MHz) Chart of **6b** in $CDCl_3$



^{13}C NMR (75 MHz) Chart of **6b** in $CDCl_3$



10. References and Notes:

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