Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Enantioselective oxidative coupling reaction of 2-naphthol derivatives catalyzed by chiral diphosphine oxide–iron(II) complexes

Takahiro Horibe, Keita Nakagawa, Takashi Hazeyama, Kazuki Takeda and Kazuaki Ishihara*

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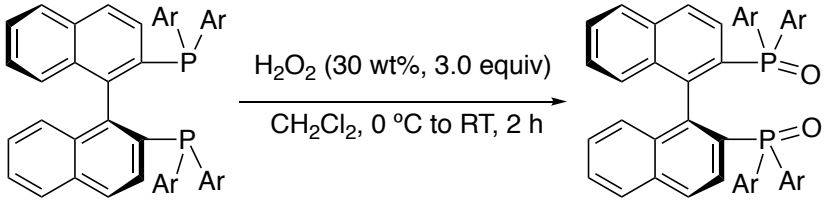
Appendix: ^{1}H and ^{13}C NMR spectra.

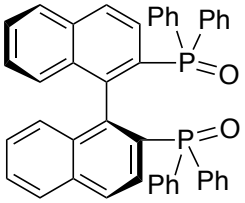
1. General methods.

^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature unless otherwise noted. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterated chloroform at 77.16 ppm, deuterated acetone at 29.84 ppm). The products were purified by column chromatography on silica gel (E. Merck Art. 9385). High resolution mass spectral analyses (HRMS) was performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700, JEOL JMS-T100GCV, Bruker Daltonics compact). Analytical HPLC was performed on a Shimadzu Model LC-10AD instrument coupled diode array-detector SPD-MA-10A-VP and a chiral column of Daicel CHIRALPACK. X-ray analysis was performed by Rigaku PILATUS-200K. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm) and phosphomolybdic acid. Anhydrous nitromethane and acetonitrile was purchased from Wako and stored under nitrogen.

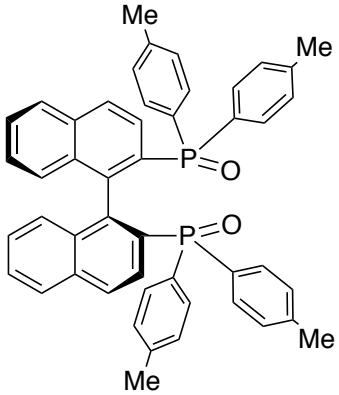
2. General procedure for the synthesis of chiral diphosphine oxide.



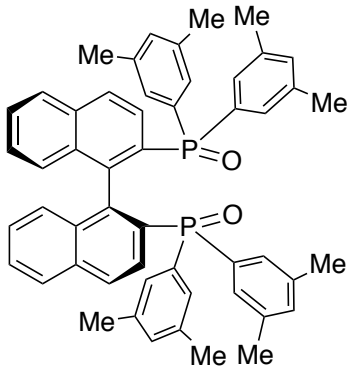
To a solution of BINAP derivatives (0.8 mmol, 1.0 equiv) in CH_2Cl_2 was added H_2O_2 (30 wt% in H_2O, 2.4 mmol, 3.0 equiv) at 0 ºC. The reaction mixture was warmed to room temperature. After being stirred at room temperature for 2 h, sat. $Na_2S_2O_3$ was added to the reaction mixture. Aqueous layer was extracted with $CHCl_3$ (5 mL × 3). The combined organic layer was washed with water and concentrated under reduced pressure to give chiral diphosphine oxide. The resulting chiral diphosphine oxide was heated under azeotropic reflux in toluene (20 mL) with removal of water. After 12 h, the solution was concentrated in vacuo, to afford the desired chiral diphosphine oxide.



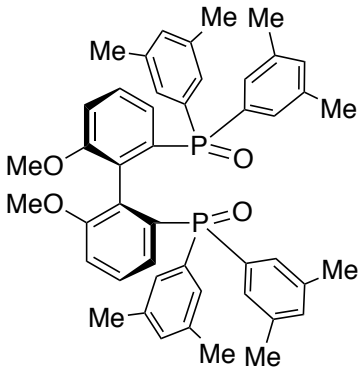
(*S*)-[1,1'-Binaphthalene]-2,2'-diylbis(diphenylphosphine oxide) (L1): Prepared according to the *General Procedure* using (*S*)-2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene (500mg, 0.803 mmol), H_2O_2 (30 wt% in H_2O, 246 μL, 2.410 mmol) and CH_2Cl_2 (1.5 mL). Isolated 490 mg (0.748 mmol, 93% yield). ^1H and ^{31}P NMR were in accordance with previously reported data.[1]



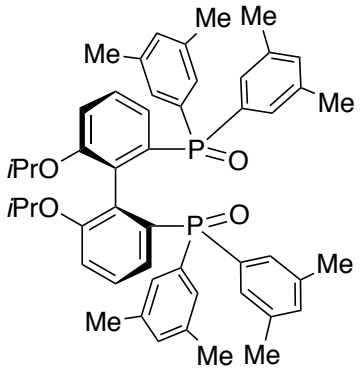
(*S*)-[1,1'-Binaphthalene]-2,2'-diylbis(di-*p*-tolylphosphine oxide) (L2): Prepared according to the *General Procedure* using (*S*)-2,2'-bis(di-*p*-tolylphosphanyl)-1,1'-binaphthalene (586mg, 0.863 mmol), H_2O_2 (30 wt% in H_2O, 265 μL, 2.59 mmol) and CH_2Cl_2 (2 mL). Isolated 586 mg (0.824 mmol, 96% yield). ^1H and ^{31}P NMR were in accordance with previously reported data.[2]



(*S*)-[1,1'-Binaphthalene]-2,2'-diylbis(bis(3,5-dimethylphenyl)phosphine oxide) (L3): Prepared according to the *General Procedure* using (*S*)-2,2'-bis(bis(3,5-dimethylphenyl)phosphanyl)-1,1'-binaphthalene (1.20 g, 1.63 mmol), H_2O_2 (30 wt% in H_2O, 500 μL, 4.90 mmol) and CH_2Cl_2 (4.0 mL). Isolated 1.18 g (1.54 mmol, 95% yield). ^1H and ^{31}P NMR were in accordance with previously reported data.[3]



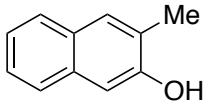
(*S*)-(6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(bis(3,5-dimethylphenyl)phosphine oxide) (L4): Prepared according to the *General Procedure* using (*S*)-(6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(bis(3,5-dimethylphanyl)phosphine (500 mg, 0.720 mmol), H_2O_2 (30 wt% in H_2O, 221 μL, 2.16 mmol) and CH_2Cl_2 (7.2 mL). Isolated 518 mg (0.713 mmol, 98% yield).
^1H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 12H), 2.30 (s, 12H), 3.26 (s, 6H), 6.76 (d, J_{H-H} = 8.4, 2H), 6.90 (s, 2H), 6.98 (dd, J_{H-H} = 7.2 Hz, J_{H-P} = 12.8 Hz, 2H), 7.07 (d, J_{H-P} = 12.8, 4H), 7.09 (s, 2H), 7.18 (dd, J_{H-H} = 7.2 Hz, J_{H-P} = 8.4 Hz, 2H), 7.35 (d, J_{H-P} = 12.8, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.3, 54.6, 112.3 (d, J = 1.9 Hz), 125.3 (d, J_{C-P} = 11.5 Hz), 127.8 (d, J_{C-P} = 15.3 Hz), 129.8-130.1 (m), 131.4 (d, J_{C-P} = 102.0 Hz), 132.6-132.7 (m), 135.0 (d, J_{C-P} = 102.0 Hz), 137.0-137.4 (m), 157.2 (d, J_{C-P} = 14.3 Hz). ^{31}P NMR ($CDCl_3$) δ 30.9. IR (KBr) 2920, 1567, 1460, 1420, 1256, 1204, 1189, 1154, 1128, 1054, 869, 852, 746, 694 cm^{-1}. HRMS (FAB+) calcd for $C_{46}H_{49}O_4P_2$ $[M+H]^+$ 727.3106, found 727.3103.



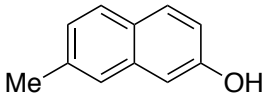
(*S*)-(6,6'-diisopropoxy-[1,1'-biphenyl]-2,2'-diyl)bis(bis(3,5-dimethylphenyl)phosphine oxide) (L5): A well-dried pyrex Schlenk tube equipped with a Teflon-coated magnetic stir bar was charged with **L4** (155 mg, 0.214 mmol) at 0 ºC under nitrogen atmosphere. A solution of BBr_3 (1.0 *M* in CH_2Cl_2, 2.14 mL) was added to the mixture at 0 ºC, and stirred for 30 min at that temperature. The mixture was heated at 40 °C for 72 h. Anhydrous MeOH (2.8 mL) was carefully added at 0 ºC, and the resulting mixture was stirred for 30 min at that temperature. All the volatile matters were removed under vacuum for 12 h. The resulting residue was dissolved in DMF (1.07 mL). To the solution was added Cs_2CO_3 (1.73 g, 5.35 mmol) and isopropyl bromide (0.402 mL, 4.28 mmol) at room temperature. After being stirred for 24 h, H_2O was added to the reaction mixture. The aqueous layer was extracted with EtOAc (5 mL × 2), and the combined organic layer was washed with H_2O twice, brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography to give the product **L5**. Isolated 141 mg (0.181 mmol, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.840 (d, $J_{H\text{-}H}$ = 6.0 Hz, 6H), 0.914 (d, $J_{H\text{-}H}$ = 6.0 Hz, 6H), 2.04 (s, 12H), 2.27 (s, 12H), 4.19 (sep, $J_{H\text{-}H}$ = 6.0 Hz, 2H). 6.74 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 6.85 (s, 2H), 6.95 (dd, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 13.4 Hz, 2H), 7.06 (s, 2H), 7.10–7.15 (m, 6H), 7.35 (d, $J_{H\text{-}P}$ = 12.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 21.8, 69.7, 114.8, 125.0 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.3 (d, $J_{C\text{-}P}$ = 15.3 Hz), 130.2-130.4 (m), 131.5 (d, $J_{C\text{-}P}$ = 102.0 Hz), 132.4-132.6 (m), 135.3 (d, $J_{C\text{-}P}$ = 102.0 Hz), 136.8-137.3 (m), 155.9 (d, $J_{C\text{-}P}$ = 14.3 Hz). ^{31}P NMR ($CDCl_3$) δ 30.4. IR (KBr) 2977, 2932, 1599, 1566, 1450, 1422, 1371, 1254, 1185, 1154, 1136, 1118, 849, 745, 723 cm^{-1}. HRMS (FAB+) calcd for $C_{50}H_{57}O_4P_2$ $[M+H]^+$ 783.3732, found 783.3730.

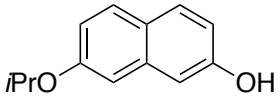
3. Preparation of 2-naphthol derivatives.



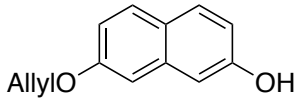
3-Methylnaphthalen-2-ol (1b): The title compound was synthesized according to the literature.[4] ^{1}H and ^{13}C NMR were in accordance with previously reported data.



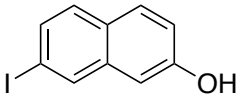
7-Methylnaphthalen-2-ol (1c): The title compound was synthesized according to the literature.[5] ^{1}H and ^{13}C NMR were in accordance with previously reported data.



7-Isopropoxynaphthalen-2-ol (1e): The title compound was synthesized according to the literature.[6] ^{1}H and ^{13}C NMR were in accordance with previously reported data.

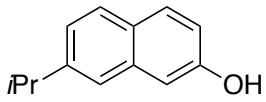


7-Allyloxynaphthalen-2-ol (1f): The title compound was synthesized according to the literature.[6] ^{1}H and ^{13}C NMR were in accordance with previously reported data.

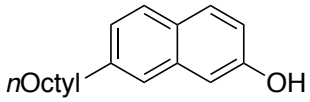


7-Iodonaphthalen-2-ol (1h): To a solution of 2-bromo-7-[[(1,1-dimethylethyl) dimethylsilyl]oxy]naphthalene[7] (2.0 g, 5.93 mmol) in THF (31 mL) was added *n*-butyllithium (1.6 *M* solution in hexane, 4.9 mL, 7.71 mmol) at –78 ºC under nitrogen atmosphere. After being stirred for 30 min, iodine (1.96 g, 7.71 mmol) was slowly added to the reaction mixture. The resulting mixture was gradually warmed to room temperature followed by being stirred for 12 h. Water was added to the reaction mixture. Aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the 2-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-7-iodonaphthalene in 88% yield (2.01 g, 5.22 mmol).

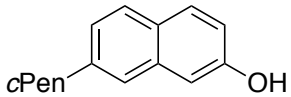
To a solution of 2-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-7-iodonaphthalene (1.08 g, 2.81 mmol) in THF (21 mL) at room temperature was added tetrabutylammonium fluoride (1.0 *M* solution in THF, 3.1 mL, 3.1 mmol). After being stirred for 2 h, the mixture was diluted with ethyl acetate (20 mL) and water (10 mL). The organic phase was washed with sat. NH_4Cl twice. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1h** in 65% yield (496 mg, 1.84 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.00 (s, 1H), 7.02 (d, J = 2.8 Hz, 1H), 7.10 (dd, J = 2.8, 8.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 8.08 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 92.7, 108.7, 119.9, 127.8, 130.2, 130.4, 132.0, 135.5, 137.5, 156.7. IR (KBr) 3280, 3052, 1624, 1436, 1235, 1202, 1053, 830 cm^{-1}. HRMS (EI) calcd for $C_{10}H_7IO$ $[M]^+$ 269.9542, found 269.9537.



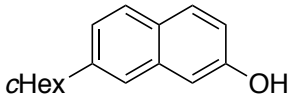
7-Isopropylnaphthalen-2-ol (1i): The title compound was synthesized according to the literature.[8] ^{1}H and ^{13}C NMR were in accordance with previously reported data.



7-Octylnaphthalen-2-ol (1j): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (335 mg, 1.50 mmol) and $PdCl_2(dppf)\bullet CH_2Cl_2$ (123 mg, 0.15 mmol) in THF (15 mL) was added *n*-octyl magnesium bromide (7.5 mL, 7.50 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 5 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1j** in 83% yield (318 mg, 1.24 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.89 (m, 3H), 1.27-1.33 (m, 10H), 1.64-1.71 (m, 2H), 2.70-2.74 (m, 2H), 4.98 (brs, 1H). 7.02 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 29.4, 29.5, 29.7, 31.5, 32.0, 36.3, 109.3, 116.9, 125.0, 125.4, 127.5, 127.7, 129.7, 134.9, 141.4, 153.4. IR (KBr) 3499, 2920, 2849, 1635, 1514, 1466, 1365, 1272, 1219, 1182, 835 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{24}O$ $[M]^+$ 256.1827, found 256.1824.

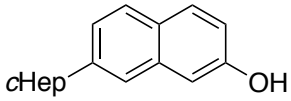


7-Cyclopentylnaphthalen-2-ol (1k): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (446 mg, 2.00 mmol) and $PdCl_2(dppf)\bullet CH_2Cl_2$ (163 mg, 0.20 mmol) in THF (20 mL) was added *c*-pentyl magnesium chloride (2.0 *M* in THF, 5 mL, 10 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 5 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1k** in 83% yield (353 mg, 1.66 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64-1.77 (m, 4H), 1.80-1.90 (m, 2H), 2.07-2.18 (m, 2H), 3.08-3.17 (m, 1H), 4.89 (s, 1H). 7.02 (dd, *J* = 2.6, 9.0 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.50 (s, 1H), 7.70 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 34.6, 46.2, 109.3, 116.9, 123.6, 124.2, 127.6, 127.8, 129.6, 134.8, 144.9, 153.5. IR (KBr) 3485, 2952, 2862, 1631, 1514, 1448, 1291, 1211, 1175, 842 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{16}O$ $[M]^+$ 212.1201, found 212.1210.

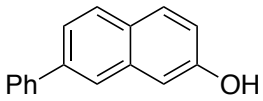


7-Cyclohexylnaphthalen-2-ol (1l): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (892 mg, 4.00 mmol) and $PdCl_2(dppf)\bullet CH_2Cl_2$ (327 mg, 0.40 mmol) in THF (40 mL) was added *c*-hexyl magnesium chloride (1.0 *M* in THF, 20 mL, 20 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 5 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1l** in 78% yield (708 mg, 3.13 mmol). ^{1}H NMR (400

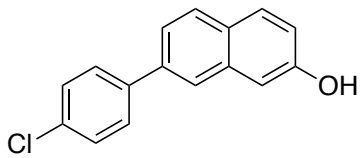
MHz, $CDCl_3$) δ 1.24-1.34 (m, 1H), 1.38-1.56 (m, 4H), 1.76-1.80 (m, 1H), 1.86-1.96 (m, 4H), 2.59-2.66 (m, 1H), 4.82 (s, 1H). 7.02 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 26.8, 27.6, 35.1, 45.5, 109.7, 118.3, 123.7, 123.9, 128.1, 128.4, 129.9, 136.2, 146.6, 156.1. IR (KBr) 3464, 2926, 2850, 1633, 1512, 1448, 1348, 1264, 1210, 1184, 835 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{18}O$ $[M]^+$ 226.1358, found 226.1362.



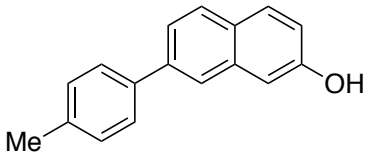
7-Cycloheptylnaphthalen-2-ol (1m): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (1.115 g, 5.00 mmol) and $PdCl_2$(dppf)•CH_2Cl_2 (408 mg, 0.50 mmol) in THF (37 mL) was added *c*-heptyl magnesium chloride (1.9 *M* in THF, 13 mL, 25 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 12 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1m** in 72% yield (861 mg, 3.58 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59-1.66 (m, 4H), 1.68-1.78 (m, 4H), 1.79-1.87 (m, 2H), 1.94-2.01 (m, 2H), 2.76-2.83 (m, 1H), 4.83 (s, 1H). 7.02 (dd, *J* = 2.6, 8.4 Hz, 1H), 7.08 (d, *J* = 2.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 28.1, 36.8, 47.3, 109.4, 116.8, 123.0, 124.1, 127.6, 127.8, 129.6, 134.9, 148.4, 153.4. IR (KBr) 3524, 2922, 2851, 1636, 1510, 1459, 1274, 1212, 1176, 837 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{20}O$ $[M]^+$ 240.1514, found 240.1507.



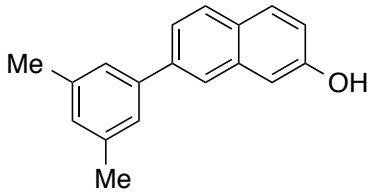
7-Phenylnaphthalen-2-ol (1n): The title compound was synthesized according to the literature.[9] ^{1}H and ^{13}C NMR were in accordance with previously reported data.



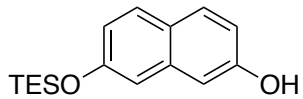
7-(4-Chlorophenyl)naphthalen-2-ol (1o): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (360 mg, 1.61 mmol) and $PdCl_2$(dppf)•CH_2Cl_2 (117 mg, 0.14 mmol) in THF (2 mL) was added 4-chlorophenyl magnesium bromide (1.0 *M* in THF, 8.05 mL, 8.05 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 3 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1o** in 85% yield (350 mg, 1.37 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (s, 1H). 7.11 (dd, *J* = 2.6, 8.4 Hz, 1H), 7.20 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 2.6, 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.82-7.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.9, 118.1, 123.2, 124.4, 128.3, 128.6, 128.7 1291, 129.8, 133.6, 134.9, 138.1, 139.7, 153.9. IR (KBr) 3376, 2960, 2921, 1630, 1496, 1178, 1101, 1010, 862 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}ClO$ $[M]^+$ 254.0498, found 254.0494.



7-(*p*-Tolyl)naphthalen-2-ol (1p): The title compound was prepared by modification of a published method.[8] To a solution of 7-bromo-2-naphthol (360 mg, 1.61 mmol) and $PdCl_2(dppf)•CH_2Cl_2$ (117 mg, 0.14 mmol) in THF (2 mL) was added *p*-tolyl magnesium bromide (1.0 *M* in THF, 8.05 mL, 8.05 mmol) with constant stirring at 0 °C. The reaction mixture was refluxed for 3 h. After complete consumption of starting material, the mixture was cooled to room temperature, quenched with sat. NH_4Cl and extracted with ethyl acetate and washed with brine. The separated organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1p** in 62% yield (233 mg, 0.99 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 4.88 (s, 1H), 7.08 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.19 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.56–7.62 (m, 3H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.81–7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 110.0, 117.8, 123.6, 124.1, 127.4, 128.3, 128.4, 129.7, 129.8, 135.2, 137.3, 138.5, 139.5, 153.9. IR (KBr) 3408, 2917, 2849, 1628, 1508, 1459, 1178, 819 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}O$ $[M]^+$ 234.1045, found 234.1042.



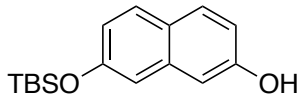
7-(3,5-Dimethylphenyl)naphthalen-2-ol (1q): The title compound was prepared by modification of a published method.[9] A round bottom flask equipped with a magnetic stir bar was charged with 7-bromo-2-naphthol (669 mg, 3.00 mmol), 3,5-dimethylphenylboronic acid (585 mg, 3.90 mmol) and barium hydroxide octahydrate (1.89 g, 6.00 mmol), tetrakis(triphenylphosphine)palladium (173 mg, 0.150 mmol), 1,4-dioxane (20 mL) and water (6 mL) under nitrogen atmosphere. The mixture was heated at reflux for 24 h, and cooled to room temperature. 1,4-Dioxane was removed under reduced pressure, and the resulting residue was dissolved in CH_2Cl_2 (60 mL), washed with 1*M* HCl (40 mL × 3), brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to give the product **1q** in 81% yield (600 mg, 2.42 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 6H), 5.01 (s, 1H), 7.03 (s, 1H), 7.09 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.32 (s, 2H), 7.58 (dd, *J* = 1.6, 8.6 Hz, 1H), 7.76 (d, *J* = 8.4 Hz 1H), 7.82 (d, *J* = 8.6 Hz 1H), 7.85 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 109.9, 117.8, 123.7, 124.4, 125.5, 128.2, 128.3, 129.2, 129.7, 135.0, 138.5, 139.6, 141.3, 153.7. IR (KBr) 3357, 2913, 2857, 1604, 1522, 1455, 1373, 1181, 838 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{16}O$ $[M]^+$ 248.1201, found 248.1204.



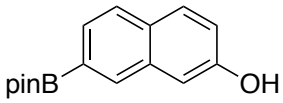
7-((Triethylsilyl)oxy)naphthalen-2-ol (1r): The title compound was prepared by modification of a published method.[10]

To a solution of naphthalene-2,7-diol (800 mg, 5.00 mmol), imidazole (343 mg, 5.04 mmol) and DMF (4.8 mL) was slowly added triethysilylchloride (678 mg, 4.5 mmol) at 0 °C under N_2 atmosphere. The resulting mixture was stirred for 2 h at that temperature. After an addition of H_2O, the mixture was extracted with Et_2O (10 mL × 3) and the organic layer was washed with H_2O, brine and dried over $MgSO_4$. After filtration and evaporation of solvent, the residue was purified by silica gel column chromatography to give the product **1r** in 41% yield (569 mg, 2.07 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (q, *J* = 7.8 Hz, 6H), 1.02 (t, *J* = 7.8 Hz, 9H), 4.86 (s, 1H), 6.92-6.95 (m, 2H), 7.00 (d, *J* = 2.2 Hz, 1H), 7.04 (d, *J* = 2.2 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.2, 6.8, 108.6, 113.6, 115.7, 119.7, 124.9, 129.4, 129.7, 136.1, 154.0, 154.2. IR (KBr)

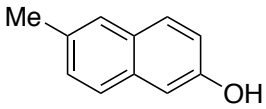
3388, 2956, 2911, 2877, 1634, 1511, 1469, 1413, 1369, 1239, 1211, 1153, 832 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{22}O_2Si$ $[M]^+$ 274.1389, found 274.1382.



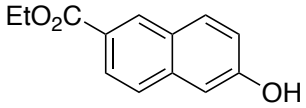
7-((*tert*-Butyldimethylsilyl)oxy)naphthalen-2-ol (1s): The title compound was synthesized according to the literature.[10] ^1H and ^{13}C NMR were in accordance with previously reported data.



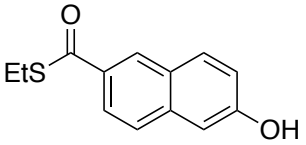
7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-ol (1t): The title compound was synthesized according to the literature.[11] ^1H and ^{13}C NMR were in accordance with previously reported data.



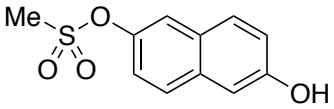
6-Methylnaphthalen-2-ol (1u): The title compound was synthesized according to the literature.[12] ^1H and ^{13}C NMR were in accordance with previously reported data.



Ethyl 6-hydroxy-2-naphthoate (1x): The title compound was synthesized according to the literature.[13] ^1H and ^{13}C NMR were in accordance with previously reported data.



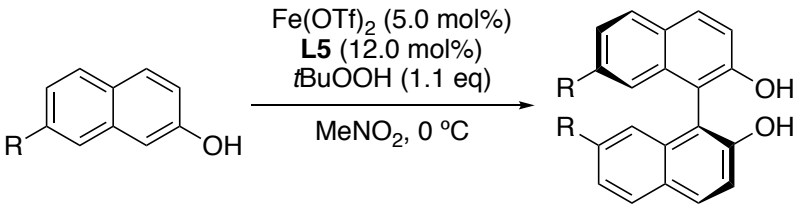
***S*-Ethyl 6-hydroxynaphthalene-2-carbothioate (1y):** To a solution of ethanethiol (488 μL, 6.75 mmol) in toluene (3.7 mL) was slowly added trimethylaluminum (1.8 *M* solution in toluene, 1.1 mL, 2.00 mmol) at room temperature. After being stirred for 30 min at room temperature and additional 30 min at 50 °C under nitrogen atmosphere, ethyl 6-hydroxy-2-naphthoate (541 mg, 2.5 mmol) was added at 55 °C. The resulting mixture was stirred at that temperature for 18 h, and then being cooled to 0 °C. After an addition of 5% aq. HCl (7.4 mL), aqueous layer was extracted with Et_2O (10 mL × 3). The collected organic extracts were dried over $MgSO_4$, filtered, and concenturated under reduced pressure. The crude product was purified by silica gel column chromatography to give the pure **1y** in 77% yield (447 mg, 1.92 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J = 7.4 Hz, 3H), 3.09 (q, J = 7.4 Hz, 2H), 7.25-7.29 (m, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.89 (dd, J = 2.0, 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 8.48 (s, 1H), 9.16 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 15.2, 23.7, 109.9, 120.3, 124.0, 127.3, 127.9, 129.1, 132.2, 132.5, 138.5, 158.4, 191.4. IR (KBr) 3478, 2962, 2925, 1647, 1628, 1505, 1433, 1416, 1284, 1272, 1249, 820 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{12}O_2S$ $[M]^+$ 232.0558, found 232.0566.



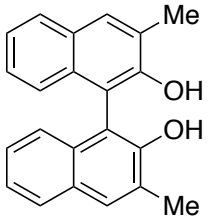
6-Hydroxynaphthalen-2-yl methanesulfonate (1z): A well-dried round bottom flask equipped with magnetic stir bar was charged with naphthalene-2,6-diol (961 mg, 6.00 mmol) and CH_2Cl_2 (18 mL).

After being cooled to 0 °C, to the mixture was slowly added Et_3N (1.25 mL, 9.00 mmol) and methanesulfonyl chloride (511 μL, 6.6 mmol). After being stirred for 16 h at room temperature, the mixuture was quenched with H_2O and extracted with $CHCl_3$ (20 mL × 3). The separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the pure **1z** in 29% yield (411 mg, 1.72 mmol). ^{1}H NMR (400 MHz, acetone-d_6) δ 3.31 (s, 3H), 7.20-7.29 (m, 2H), 7.39 (dd, J = 2.6, 9.0 Hz, 1H), 7.75-7.87 (m, 3H), 8.83 (s, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ 37.4, 109.9, 120.4, 120.5, 122.3, 129.0, 129.1, 130.4, 134.6, 146.1, 156.8. IR (KBr) 3434, 3035, 3019, 2941, 1601, 1523, 1392, 1360, 1327, 1212, 1179, 1166, 1134, 817 cm^{-1}. HRMS (EI) calcd for $C_{11}H_{10}O_4S$ $[M]^+$ 238.0300, found 238.0297.

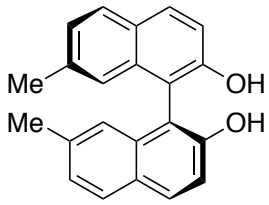
4. General procedure for enantioselective oxidative coupling of 7-substituted 2-naphthols.



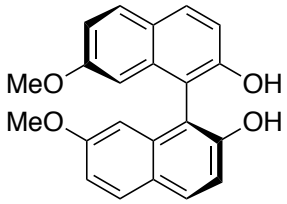
A well-dried 5 mL vial was charged with $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol) and $MeNO_2$ (300 μL) at room temperature. After being stirred for 1 h, the mixture was passed through grass fiber filter. To the filtrate was added $MeNO_2$ (900 μL) and 2-naphthol derivatives (0.288 mmol) at room temperature. After being cooled to 0 ºC, to the mixture was added *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol). After completion of the reaction (monitored by TLC), sat. $Na_2S_2O_3$ (0.2 mL) was added to the reaction mixture. It was directly subjected to column chromatography on silica gel (Hexane/AcOEt = 4/1) to give a pure product.



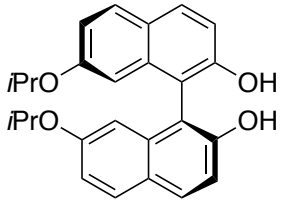
3,3'-Dimethyl-[1,1'-binaphthalene]-2,2'-diol (2b): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 3-methylnaphthalen-2-ol (45.6 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 2.51 (s, 6H), 5.11 (s, 2H), 7.06-7.08 (m, 2H), 7.21-7.26 (m, 2H), 7.32-7.36 (m, 2H), 7.81-7.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 110.6, 124.1, 124.2, 126.5, 127.1, 127.7, 129.6, 130.9, 132.3, 152.2. IR (KBr) 3508, 3060, 2925, 2852, 1625, 1505, 1431, 1386, 1342, 1213, 1097, 1022, 749 cm^{-1}. $[\alpha]_D^{25}$ –8.0º (c 0.3, $CHCl_3$, 10% ee). HRMS (EI) calcd for $C_{22}H_{18}O_2$ $[M]^+$ 314.1307, found 314.1303.
HPLC analysis; AS-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 6.3 min (minor), 7.6 min (major).



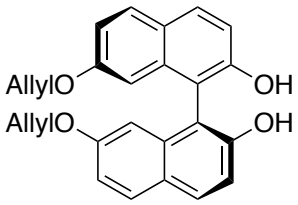
(*S*)-7,7'-Dimethyl-[1,1'-binaphthalene]-2,2'-diol (2c): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-methylnaphthalen-2-ol (45.6 mg, 0.288 mmol) and $MeNO_2$ (total 600 μL: 300 μL for the preparation of iron complex and 300 μL for the reaction) at 0 ºC for 15 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 2.29 (s, 6H), 4.98 (s, 2H), 6.93 (s, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 110.4, 116.9, 123.2, 126.4, 127.8, 128.4, 131.2, 133.7, 137.6, 153.0. IR (KBr) 3483, 2919, 1620, 1509, 1362, 1315, 1187, 1167, 834 cm^{-1}. $[\alpha]_D^{24}$ 39.3º (c 1.0, $CHCl_3$, for *S* enantiomer with 87% ee). HRMS (ESI) m/z calcd for $C_{22}H_{18}O_2$ $[M + Na]^+$ 337.1199, found 337.1209.
HPLC analysis; AS-3, hexane:*i*-PrOH = 9:1, 0.5 mL/min, t_R = 21.2 min (major), 30.4 min (minor).



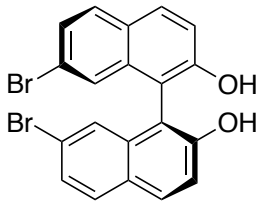
(*S*)-7,7'-Dimethoxy-[1,1'-binaphthalene]-2,2'-diol (2d):[14] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-methoxynaphthalen-2-ol (50.2 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h. ^{1}H NMR (400 MHz, CD_3Cl) δ 3.58 (s, 6H), 5.04 (s, 2H), 6.49 (d, *J* = 2.0 Hz, 2H), 7.04 (dd, *J* = 2.0, 8.4 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 103.2, 110.1, 115.2, 116.2, 124.9, 130.1, 131.2, 134.8, 153.4, 159.2. IR (KBr) 3418, 2936, 2832, 1620, 1513, 1464, 1427, 1371, 1271, 1221, 1163, 1031, 832 cm^{-1}. $[\alpha]_D^{23}$ 124.7º (c 0.34, $CHCl_3$, for *S* enantiomer with 84% ee). HRMS (EI) calcd for $C_{22}H_{18}O_4$ $[M]^+$ 346.1205, found 346.1204.
HPLC analysis; IC-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 14.4 min (minor, *R*), 22.3 min (major, *S*).



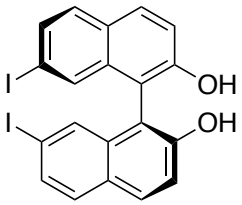
(*S*)-7,7'-Diisopropoxy-[1,1'-binaphthalene]-2,2'-diol (2e):[14] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-isopropoxynaphthalen-2-ol (58.3 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h. ^{1}H NMR (400 MHz, CD_3Cl) δ 1.11 (d, *J* = 6.0 Hz, 6H), 1.19 (d, *J* = 6.0 Hz, 6H), 4.30 (sep, *J* = 6.0 Hz, 2H), 5.05 (s, 2H), 6.48 (d, *J* = 2.4 Hz, 2H), 7.00 (dd, *J* = 2.4, 8.4 Hz, 2H), 7.20 (d, *J* = 9.2 Hz, 2H), 7.77 (d, *J* = 9.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 21.8, 69.6, 106.0, 109.9, 115.1, 116.9, 124.7, 130.1, 131.1, 134.9, 153.3, 157.2. IR (KBr) 3480, 2976, 2931, 2872, 1619, 1510, 1452, 1434, 1373, 1270, 1214, 1112, 832 cm^{-1}. $[\alpha]_D^{25}$ 224.9º (c 0.98, $CHCl_3$, for *S* enantiomer with 82% ee). HRMS (EI) calcd for $C_{26}H_{26}O_4$ $[M]^+$ 402.1831, found 402.1823.
HPLC analysis; OD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 10.6 min (major, *S*), 15.0 min (minor, *R*).



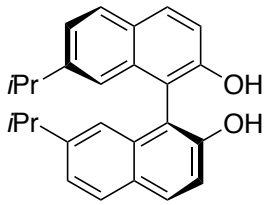
(*S*)-7,7'-Bis(allyloxy)-[1,1'-binaphthalene]-2,2'-diol (2f):[15] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-allyloxynaphthalen-2-ol (57.7 mg, 0.288 mmol) and $MeNO_2$ (total 600 μL: 300 μL for the preparation of iron complex and 300 μL for the reaction) at 0 ºC for 26 h. ^{1}H NMR (400 MHz, CD_3Cl) δ 4.25 (dd, *J* = 5.6, 12.8 Hz, 2H), 4.31 (dd, *J* = 5.6, 12.8 Hz, 2H), 5.03 (s, 2H), 5.11 (dd, *J* = 1.6, 7.2 Hz, 2H), 5.14 (dd, *J* = 1.6, 13.6 Hz, 2H), 5.81-5.91 (m, 2H), 6.49 (d, *J* = 2.0 Hz, 2H), 7.06 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 104.6, 110.2, 115.3, 116.5, 118.3, 124.9, 130.1, 131.2, 132.9, 134.8, 153.4, 158.1. IR (KBr) 3466, 2918, 2850, 1619, 1509, 1458, 1433, 1372, 1270, 1216, 1138, 836 cm^{-1}. $[\alpha]_D^{26}$ 190.0º (c 1.0, $CHCl_3$, for *S* enantiomer with 81% ee).
HPLC analysis; IC-3, hexane:*i*-PrOH =9:1, 1.0 mL/min, t_R = 10.8 min (minor), 13.3 min (major).



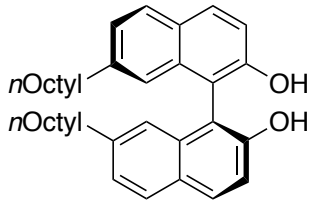
(*S*)-7,7'-Dibromo-[1,1'-binaphthalene]-2,2'-diol (2g):[16] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-bromonaphthalen-2-ol (64.2 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 7.23 (d, *J* = 2.0 Hz, 2H), 7.38 (d, *J* = 9.2 Hz, 2H), 7.47 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.6, 118.4, 122.6, 126.1, 127.9, 128.1, 130.3, 131.8, 134.8, 153.7. IR (KBr) 3469, 3053, 1612, 1587, 1497, 1446, 1419, 1378, 1351, 1314, 1252, 1162, 1068, 831 cm^{-1}. $[\alpha]_D^{26}$ 167.2º (c 0.55, $CHCl_3$, for *S* enantiomer with 83% ee). HRMS (EI) calcd for $C_{20}H_{12}Br_2O_2$ $[M]^+$ 441.9204, found 441.9204.
HPLC analysis; OD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 16.4 min (major, *S*), 35.2 min (minor, *R*).



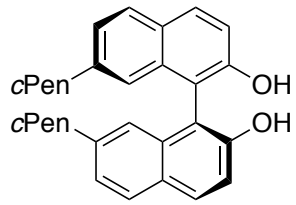
(*S*)-7,7'-Diiodo-[1,1'-binaphthalene]-2,2'-diol (2h): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-iodonaphthalen-2-ol (77.8 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 60 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 4.98 (s, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 1.6, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 1.6, 8.4 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.7, 109.3, 118.6, 128.4, 130.2, 131.9, 132.5, 133.2, 135.0, 153.4. IR (KBr) 3484, 3049, 1609, 1583, 1494, 1443, 1426, 1378, 1328, 1257, 1211, 1162, 1060, 832 cm^{-1}. $[\alpha]_D^{25}$ 207.7º (c 1.09, $CHCl_3$, for *S* enantiomer with 87% ee). HRMS (EI) calcd for $C_{20}H_{12}I_2O_2$ $[M]^+$ 537.8927, found 537.8924.
HPLC analysis; AD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 14.7 min (major), 31.8 min (minor).



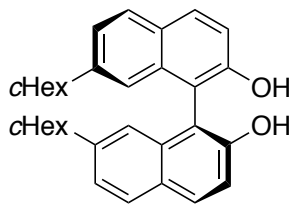
(*S*)-7,7'-Diisopropyl-[1,1'-binaphthalene]-2,2'-diol (2i):[8] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-isopropylnaphthalen-2-ol (53.6 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 1.12 (d, *J* = 6.8 Hz, 6H), 1.13 (d, *J* = 6.8 Hz, 6H), 2.81 (sep, *J* = 6.8 Hz, 2H), 5.01 (s, 2H), 6.98 (s, 2H), 7.30-7.33 (m, 4H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 34.5, 110.8, 117.0, 121.3, 123.3, 128.2, 128.6, 131.1, 133.5, 148.3, 152.9. IR (KBr) 3486, 2959, 2925, 2867, 1622, 1510, 1457, 1385, 1308, 1218, 1192, 1168, 837 cm^{-1}. $[\alpha]_D^{23}$ 118.4º (c 0.76, $CHCl_3$, for *S* enantiomer with 90% ee). HRMS (EI) calcd for $C_{26}H_{26}O_2$ $[M]^+$ 370.1933, found 370.1940.
HPLC analysis; AS-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 6.0 min (major), 11.3 min (minor).



(*S*)-7,7'-Dioctyl-[1,1'-binaphthalene]-2,2'-diol (2j): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-octylnaphthalen-2-ol (73.8 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 24 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 0.85 (t, *J* = 7.0 Hz, 6H), 1.18-1.25 (m, 20H), 1.46-1.49 (m, 4H), 2.50-2.54 (m, 4H), 4.99 (s, 2H), 6.93 (s, 2H), 7.23-7.25 (m, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 29.3, 29.4, 29.5, 31.6, 32.0, 36.3, 110.6, 116.9, 122.9, 125.6, 128.0, 128.4, 131.1, 133.6, 142.6, 152.9. IR (neat) 3489, 2925, 2854, 1623, 1512, 1455, 1381, 1316, 1219, 1172, 1146, 838 cm^{-1}. $[\alpha]_D^{23}$ 115.3º (c 0.54, $CHCl_3$, for *S* enantiomer with 85% ee). HRMS (EI) calcd for $C_{36}H_{46}O_2$ $[M]^+$ 510.3498, found 510.3501.
HPLC analysis; AD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 6.0 min (major), 10.0 min (minor).

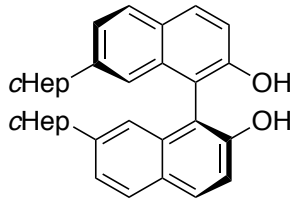


(*S*)-7,7'-Dicyclopentyl-[1,1'-binaphthalene]-2,2'-diol (2k): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-cyclopentylnaphthalen-2-ol (61.1 mg, 0.288 mmol) and $MeNO_2$ (total 600 μL: 300 μL for the preparation of iron complex and 300 μL for the reaction) at 0 ºC for 15 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 1.44-1.62 (m, 8H), 1.67-1.74 (m, 4H), 1.85-1.98 (m, 4H), 2.89 (quin, *J* = 8.6 Hz, 2H), 5.00 (s, 2H), 7.00 (s, 2H), 7.30-7.33 (m, 4H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 34.8, 46.3, 110.7, 116.9, 122.0, 123.8, 128.1, 128.6, 131.1, 133.4, 146.0, 152.9. IR (KBr) 3489, 2951, 2865, 1621, 1509, 1450, 1383, 1364, 1211, 1168, 1124, 837 cm^{-1}. $[\alpha]_D^{25}$ 118.4º (c 1.0, $CHCl_3$, for *S* enantiomer with 86% ee). HRMS (ESI) m/z calcd for $C_{30}H_{30}O_2$ $[M + Na]^+$ 445.2138, found 445.2142.
HPLC analysis; OD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 7.9 min (major), 12.2 min (minor).

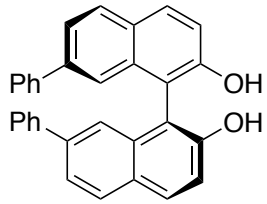


(*S*)-7,7'-Dicyclohexyl-[1,1'-binaphthalene]-2,2'-diol (2l): Procedure for 2.5 mol% of catalyst; Iron(II) complex was prepared according to the *General Procedure* using $Fe(OTf)_2$ (1.3 mg, 0.0036 mmol), **L5** (6.8 mg, 0.00864 mmol) and $MeNO_2$ (150 μL) at room temperature. After being stirred for 1 h, the mixture was passed through grass fiber filter. To the filtrate was added $MeNO_2$ (450 μL) and 7-cyclohexylnaphthalen-2-ol (65.2 mg, 0.288 mmol) at room temperature. After being cooled to 0 ºC, to the mixture was added *t*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol). After 45 h, sat.

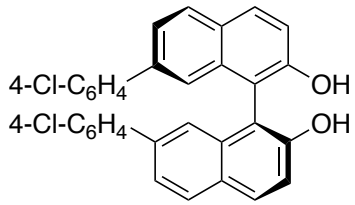
$Na_2S_2O_3$ (0.2 mL) was added to the reaction mixture. It was directly subjected to column chromatography on silica gel (Hexane/AcOEt = 4/1) to give a pure product (59.5 mg, 92%).
^{1}H NMR (400 MHz, CD_3Cl) δ 1.12-1.37 (m, 10H), 1.64-1.74 (m, 10H), 2.38-2.44 (m, 2H), 4.99 (s, 2H), 6.98 (d, *J* = 1.6 Hz, 2H), 7.30 (dd, *J* = 1.6, 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 26.7, 26.8, 34.2, 34.3, 44.9, 110.8, 117.0, 121.6, 123.7, 128.2, 128.5, 131.0, 133.5, 147.5, 152.8. IR (KBr) 3529, 2924, 2849, 1623, 1510, 1448, 1385, 1361, 1217, 1166, 1125, 836 cm^{-1}. $[\alpha]_D^{27}$ 125.4º (c 1.1, $CHCl_3$, for *S* enantiomer with 88% ee). HRMS (EI) calcd for $C_{32}H_{34}O_2$ $[M]^+$ 450.2559, found 450.2558.
HPLC analysis; AD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 16.8 min (major), 33.7 min (minor).



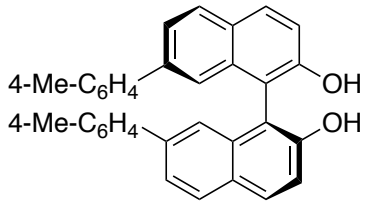
(*S*)-7,7'-Dicycloheptyl-[1,1'-binaphthalene]-2,2'-diol (2m): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-cycloheptylnaphthalen-2-ol (73.3 mg, 0.288 mmol) and $MeNO_2$ (total 600 μL: 300 μL for the preparation of iron complex and 300 μL for the reaction) at 0 ºC for 15 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 1.36-1.82 (m, 24H), 2.51-2.59 (m, 2H), 4.99 (s, 2H), 6.95 (s, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2, 27.3, 27.9(2C), 36.6, 36.7, 47.2, 110.8, 116.9, 121.2, 123.8, 128.0, 128.6, 131.1, 133.5, 149.4, 152.8. IR (KBr) 3529, 2923, 2852, 1622, 1510, 1457, 1385, 1362, 1214, 1171, 1126, 836 cm^{-1}. $[\alpha]_D^{29}$ 120.8º (c 1.0, $CHCl_3$, for *S* enantiomer with 84% ee). HRMS (ESI) m/z calcd for $C_{34}H_{38}O_2$ $[M + Na]^+$ 501.2764, found 501.2774.
HPLC analysis; AD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 10.9 min (major), 34.6 min (minor).



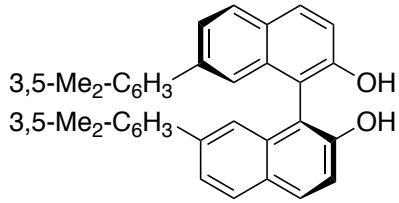
(*S*)-7,7'-Diphenyl-[1,1'-binaphthalene]-2,2'-diol (2n):[15] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-phenylnaphthalen-2-ol (63.4 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 45 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 5.10 (s, 2H), 7.23-7.34 (m, 6H), 7.38-7.44 (m, 8H), 7.63 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.1, 117.9, 122.2, 124.1, 127.5, 127.6, 128.8(2C), 129.1, 131.3, 133.7, 140.5, 141.1, 153.3. IR (KBr) 3496, 3057, 3027, 1619, 1491, 1163, 840, 754, 697 cm^{-1}. $[\alpha]_D^{26}$ 435.1º (c 1.0, $CHCl_3$, for *S* enantiomer with 87% ee). HRMS (ESI) m/z calcd for $C_{32}H_{22}O_2$ $[M + Na]^+$ 461.1512, found 461.1499.
HPLC analysis; OD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 15.4 min (major), 30.3 min (minor).



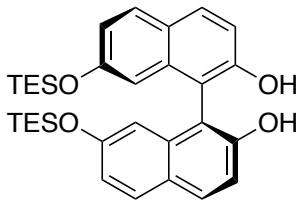
(*S*)-7,7'-Bis(4-chlorophenyl)-[1,1'-binaphthalene]-2,2'-diol (2o): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-(4-chlorophenyl)naphthalen-2-ol (73.4 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 60 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 5.09 (s, 2H), 7.25-7.40 (m, 12H), 7.57 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.0, 118.2, 122.0, 123.8, 128.8, 128.9, 129.0, 129.4, 131.5, 133.6, 133.7, 139.3, 139.5, 153.4. IR (KBr) 3420, 3055, 3019, 1619, 1491, 1164, 1093, 1012, 826 cm^{-1}. $[\alpha]_D^{23}$ 417.4º (c 1.0, $CHCl_3$, for *S* enantiomer with 88% ee). HRMS (EI) calcd for $C_{32}H_{20}Cl_2O_2$ $[M]^+$ 506.0840, found 506.0844.
HPLC analysis; IC, hexane:*i*-PrOH = 19:1, 1.0 mL/min, t_R = 18.8 min (major), 25.6 min (minor).



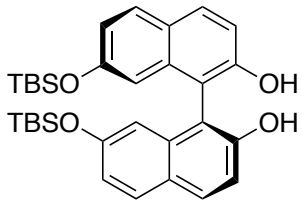
(*S*)-7,7'-Di-*p*-tolyl-[1,1'-binaphthalene]-2,2'-diol (2p): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-(*p*-tolyl)naphthalen-2-ol (73.2 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 60 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 2.30 (s, 6H), 5.08 (s, 2H), 7.11 (d, J = 8.4 Hz, 4H), 7.29-7.37 (m, 8H), 7.60 (dd, J = 1.6, 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 111.0, 117.8, 121.9, 124.0, 127.5, 128.7, 129.1, 129.5, 131.3, 133.8, 137.4, 138.3, 140.5, 153.3. IR (KBr) 3447, 2913, 2850, 1542, 1507, 1457, 1164, 820 cm^{-1}. $[\alpha]_D^{25}$ 420.7º (c 1.0, $CHCl_3$, for *S* enantiomer with 88% ee). HRMS (ESI) m/z calcd for $C_{34}H_{26}O_2$ $[M + Na]^+$ 489.1825, found 489.1804.
HPLC analysis; IC, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 8.6 min (major), 10.2 min (minor).



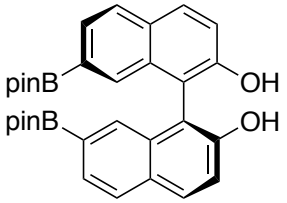
(*S*)-7,7'-Bis(3,5-dimethylphenyl)-[1,1'-binaphthalene]-2,2'-diol (2q): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-(3,5-dimethylphenyl)naphthalen-2-ol (71.5 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 45 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 2.27 (s, 12H), 5.08 (s, 2H), 6.91 (s, 2H), 7.02 (s, 4H), 7.35 (d, J = 1.6 Hz, 2H), 7.39 (d, J = 9.0 Hz, 2H), 7.60 (dd, J = 1.6, 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 9.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 111.1, 117.8, 122.2, 124.4, 125.6, 128.8, 129.9, 129.1, 131.4, 133.7, 138.3, 140.9, 141.3, 153.3. IR (KBr) 3489, 2918, 2855, 1601, 1509, 1457, 1367, 1194, 1156, 1131, 1036, 846 cm^{-1}. $[\alpha]_D^{25}$ 368.2º (c 0.34, $CHCl_3$, for *S* enantiomer with 89% ee). HRMS (EI) calcd for $C_{36}H_{30}O_2$ $[M]^+$ 494.2246, found 494.2241.
HPLC analysis; IA-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 14.6 min (major), 27.6 min (minor).



(*S*)-7,7'-bis((triethylsilyl)oxy)-[1,1'-binaphthalene]-2,2'-diol (2r): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-(triethylsilyl)oxy)naphthalen-2-ol (79.0 mg, 0.288 mmol) and $MeNO_2$ (total 600 μL: 300 μL for the preparation of iron complex and 300 μL for the reaction) at 0 ºC for 48 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 0.49 (q, *J* = 8.0 Hz, 12H), 0.77 (t, *J* = 8.0 Hz, 18H), 5.06 (s, 2H), 6.46 (d, *J* = 2.4 Hz, 2H), 6.95 (dd, *J* = 2.4, 9.2 Hz, 2H), 7.22 (d, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9, 6.5, 109.9, 111.5, 115.3, 119.7, 125.1, 129.9, 131.0, 135.1, 153.3, 155.2. IR (neat) 3481, 2956, 2912, 2876, 1619, 1509, 1455, 1365, 1270, 1222, 1178, 834 cm^{-1}. $[\alpha]_D^{28}$ 172.7º (c 1.0, $CHCl_3$, for *S* enantiomer with 90% ee). HRMS (ESI) m/z calcd for $C_{32}H_{42}O_4Si_2$ $[M + H]^+$ 547.2694, found 547.2703.
HPLC analysis; OD-3, hexane:*i*-PrOH = 19:1, 1.0 mL/min, t_R = 10.1 min (major, *S*), 14.6 min (minor, *R*).



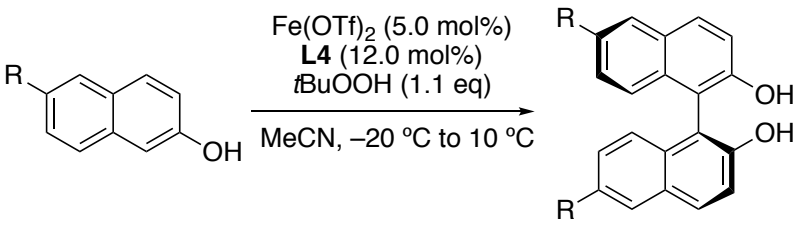
(*S*)-7,7'-Bis((*tert*-butyldimethylsilyl)oxy)-[1,1'-binaphthalene]-2,2'-diol (2s): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L5** (13.5 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-ol (79.0 mg, 0.288 mmol) and $MeNO_2$ (total 1200 μL: 300 μL for the preparation of iron complex and 900 μL for the reaction) at 0 ºC for 45 h.
^{1}H NMR (400 MHz, CD_3Cl) δ –0.06 (s, 6H), –0.04 (s, 6H), 0.83 (s, 18H), 5.05 (s, 2H), 6.46 (d, *J* = 2.4 Hz, 2H), 6.94 (dd, *J* = 2.4, 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.48, 18.3, 25.8, 109.8, 111.7, 115.3, 119.9, 125.1, 129.9, 131.1, 134.9, 153.3, 155.3. IR (KBr) 3483, 2955, 2929, 2858, 1619, 1509, 1458, 1364, 1269, 1227, 1166, 836, 781 cm^{-1}. $[\alpha]_D^{23}$ 166.1º (c 1.0, $CHCl_3$, for *S* enantiomer with 92% ee). HRMS (ESI) m/z calcd for $C_{32}H_{42}O_4Si_2$ $[M + Na]^+$ 569.2514, found 569.2498.
HPLC analysis; OD-3, hexane:*i*-PrOH = 99:1, 1.0 mL/min, t_R = 23.3 min (major, *S*), 52.2 min (minor, *R*).



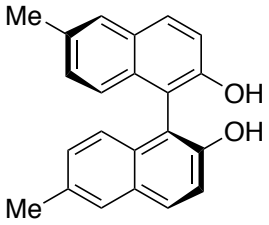
(*S*)-7,7'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-binaphthalene]-2,2'-diol (2t): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 7-(2,4,4,5,5-pentamethyl-1,3,2λ4-dioxaborolan-2-yl) naphthalen-2-ol (82.1 mg, 0.288 mmol) and $MeNO_2$ (300 μL) at –10 ºC for 45 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 1.23 (s, 12H), 1.25 (s, 12H), 4.95 (s, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.69 (s, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 24.9, 25.0, 83.9, 111.6, 119.2, 127.7, 129.2, 131.3, 131.4,131.8(2C), 132.7, 152.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.8. IR (KBr) 3422, 2979, 2928, 2855, 1604, 1458, 1372, 1344, 1306, 1146, 1086, 846 cm^{-1}. $[\alpha]_D^{26}$ 32.8º (c 1.0, $CHCl_3$, for *S* enantiomer with 81% ee). HRMS (ESI) m/z calcd for $C_{32}H_{36}B_2O_6$ $[M + Na]^+$ 561.2590, found 561.2587.
HPLC analysis; IA-3, hexane:*i*-PrOH = 19:1, 1.0 mL/min, t_R = 31.2 min (major, *S*), 45.6 min (minor, *R*).

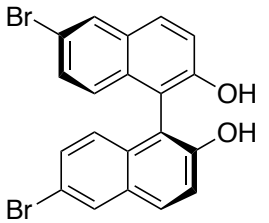
5. General procedure for enantioselective oxidative coupling of 6-substituted 2-naphthols.



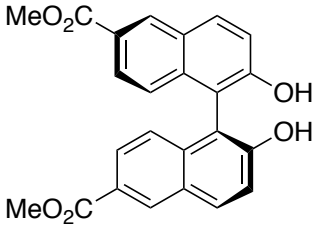
A well-dried 5 mL vial was charged with $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol) and MeCN (300 μL) at room temperature. After being stirred for 1 h, the mixture was passed through grass fiber filter. To the filtrate was added MeCN (500 μL) and 6-substituted 2-naphthol derivatives (0.288 mmol) at room temperature. To the mixture was added *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol). After completion of the reaction (monitored by TLC), sat. $Na_2S_2O_3$ (0.2 mL) was added to the reaction mixture. It was directly subjected to column chromatography on silica gel (Hexane/AcOEt = 4/1) to give a pure product.



(*S*)-6,6'-Dimethyl-[1,1'-binaphthalene]-2,2'-diol (2u):[16] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 6-methylnaphthalen-2-ol (45.6 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at –20 ºC for 96 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 2.47 (s, 6H), 4.96 (s, 2H), 7.05 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.66 (s, 2H), 7.88 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 21.3, 114.9, 119.4, 125.5, 127.9, 129.1, 129.8, 130.1, 132.8, 133.6, 153.8. IR (KBr) 3479, 3007, 2916, 2857, 1599, 1474, 1381, 1354, 1310, 1214, 1185, 1145, 822 cm^{-1}. $[\alpha]_D^{29}$ 27.2º (c 1.0, $CHCl_3$, for *S* enantiomer with 60% ee). HRMS (EI) calcd for $C_{22}H_{18}O_2$ $[M]^+$ 314.1307, found 314.1302.
HPLC analysis; OD-3, hexane:*i*-PrOH = 9:1, 1.0 mL/min, t_R = 9.6 min (major, *S*), 17.7 min (minor, *R*).



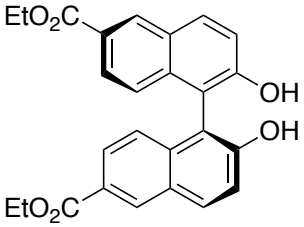
(*S*)-6,6'-Dibromo-[1,1'-binaphthalene]-2,2'-diol (2v):[15] Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 6-bromonaphthalen-2-ol (64.2 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at –10 ºC for 96 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 5.03 (brs, 2H), 6.96 (d, J = 8.6 Hz, 2H), 7.35-7.40 (m, 4H), 7.89 (d, J = 8.6 Hz, 2H), 8.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.8, 118.1, 119.1, 126.0, 130.6, 130.7, 130.8, 131.0, 132.0, 153.1. IR (KBr) 3453, 3062, 2922, 1586, 1501, 1382, 1350, 1215, 1146, 1066, 930 cm^{-1}. $[\alpha]_D^{27}$ 92.4º (c 1.0, $CHCl_3$, for *S* enantiomer with 74% ee).
HPLC analysis; AS-3, hexane:*i*-PrOH =9:1, 1.0 mL/min, t_R = 15.3 min (major), 22.2 min (minor).



Dimethyl (*S*)-2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-dicarboxylate (2w): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), methyl-6-hydroxy-2-naphthoate (58.2 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at 10 ºC for 96 h.

^{1}H NMR (400 MHz, acetone-d_6) δ 3.90 (s, 6H), 7.12 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.78 (dd, J = 1.6, 9.2 Hz, 2H), 8.13 (d, J = 9.2 Hz, 2H), 8.62 (d, J = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 52.2, 115.0, 120.5, 125.5(2C), 126.4, 128.9, 131.9, 132.4, 137.8, 156.9, 167.4. IR (KBr) 3397, 2951, 1917, 2849, 1699, 1618, 1475, 1438, 1382, 1286, 1200, 1100, 814 cm^{-1}. $[\alpha]_D^{24}$ 44.0º (c 0.50, acetone, for *S* enantiomer with 85% ee). HRMS (ESI) m/z calcd for $C_{24}H_{18}O_6$ $[M + Na]^+$ 425.0996, found 425.0996.

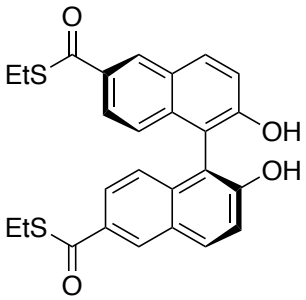
HPLC analysis; OD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 10.2 min (major, *S*), 16.3 min (minor, *R*)



Diethyl (*S*)-2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-dicarboxylate (2x): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), ethyl-6-hydroxy-2-naphthoate (62.3 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at 0 ºC for 96 h.

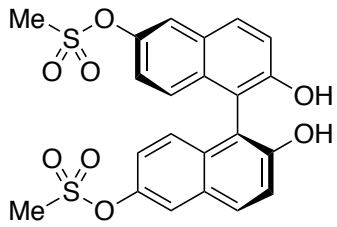
^{1}H NMR (400 MHz, acetone-d_6) δ 1.37 (t, J = 7.2 Hz, 6H), 4.36 (q, J = 7.2 Hz, 4H), 7.12 (d, J = 9.2, 2H), 7.45 (d, J = 9.2 Hz, 2H), 7.79 (dd, J = 1.6, 8.8 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 8.52 (br, 2H), 8.62 (d, J = 1.6 Hz, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 14.7, 61.3, 115.1, 120.5, 125.5, 125.8, 126.5, 128.9, 131.8, 132.3, 137.8, 156.8, 167.0. IR (KBr) 3393, 2976, 2926, 2855, 1705, 1688, 1475, 1383, 1364, 1288, 1193, 755 cm^{-1}. $[\alpha]_D^{28}$ 57.6º (c 1.0, acetone, for *S* enantiomer with 81% ee). HRMS (ESI) m/z calcd for $C_{26}H_{22}O_6$ $[M + Na]^+$ 453.1309, found 453.1314.

HPLC analysis; OD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 8.1 min (major, *S*), 13.4 min (minor, *R*).



***S*,*S*-Diethyl (*S*)-2,2'-dihydroxy-[1,1'-binaphthalene]-6,6'-bis(carbothioate) (2y):** Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), *S*-ethyl-6-hydroxynaphthalene-2-carbothioate

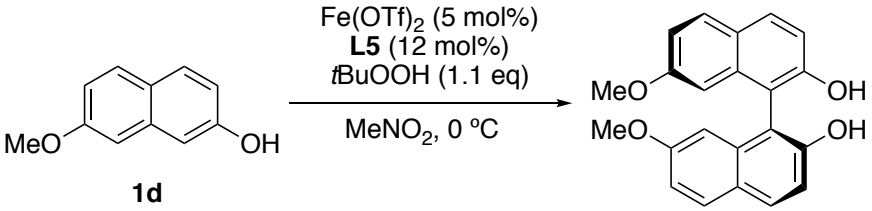
(67.1 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at 0 ºC for 96 h.
^{1}H NMR (400 MHz, acetone-d_6) δ 1.29 (t, *J* = 7.4 Hz, 6H), 3.05 (q, *J* = 7.4 Hz, 4H), 7.11 (d, *J* = 9.2, 2H), 7.45 (d, *J* = 9.2 Hz, 2H), 7.72 (dd, *J* = 2.0, 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 8.55 (d, *J* = 2.0 Hz, 2H), 8.55 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 23.7, 115.1, 120.8, 124.3, 125.8, 128.8, 129.5, 132.7(2C), 138.1, 157.1, 191.4. IR (KBr) 3387, 2964, 2928, 2871, 1639, 1613, 1469, 1280, 1227, 1158, 813 cm^{-1}. $[\alpha]_D^{29}$ 125.4º (c 1.0, acetone, for *S* enantiomer with 80% ee). HRMS (ESI) m/z calcd for $C_{26}H_{22}O_4S_2$ $[M + Na]^+$ 485.0852, found 485.0852.
HPLC analysis; OD-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 8.6 min (major, *S*), 15.5 min (minor, *R*).



(*S*)-2,2'-Dihydroxy-[1,1'-binaphthalene]-6,6'-diyl dimethanesulfonate (2z): Prepared according to the *General Procedure* using $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol), **L4** (12.6 mg, 0.0173 mmol), *tert*-butyl hydroperoxide (5.5 *M* in nonane, 28.8 μL, 0.158 mmol), 6-hydroxynaphthalen-2-yl methanesulfonate (68.6 mg, 0.288 mmol) and MeCN (total 800 μL: 300 μL for the preparation of iron complex and 500 μL for the reaction) at 0 ºC for 96 h.
^{1}H NMR (400 MHz, CD_3Cl) δ 3.19 (s, 6H), 5.08 (s, 2H), 7.13 (d, *J* = 9.2 Hz, 2H), 7.22 (dd, *J* = 2.0, 9.2 Hz, 2H), 7.44 (d, *J* = 9.2 Hz, 2H), 7.82 (d, *J* = 2.0 Hz, 2H), 7.98 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 111.4, 119.5, 120.4, 122.3, 126.6, 129.5, 131.3, 132.3, 145.4, 153.3. IR (KBr) 3449, 3029, 2936, 2854, 1604, 1509, 1459, 1362, 1273, 1216, 1177, 1117, 836 cm^{-1}. $[\alpha]_D^{29}$ 40.0º (c 1.0, $CHCl_3$, for *S* enantiomer with 81% ee). HRMS (ESI) m/z calcd for $C_{22}H_{18}O_8S_2$ $[M + Na]^+$ 497.0335, found 497.0340.
HPLC analysis; ID-3, hexane:*i*-PrOH = 4:1, 1.0 mL/min, t_R = 52.4 min (major, *S*), 61.1 min (minor, *R*).

6. Non-linear effect.

The non-linear effect in the oxidative coupling reaction of 7-methoxy-2-naphthol **1d** was examined with the use of 5 mol% of $Fe(OTf)_2$ and 12 mol% of **L5**. On the relationship between the ee of **L5** and the ee of **2d**, positive non-linear effect was observed (Figure S1).



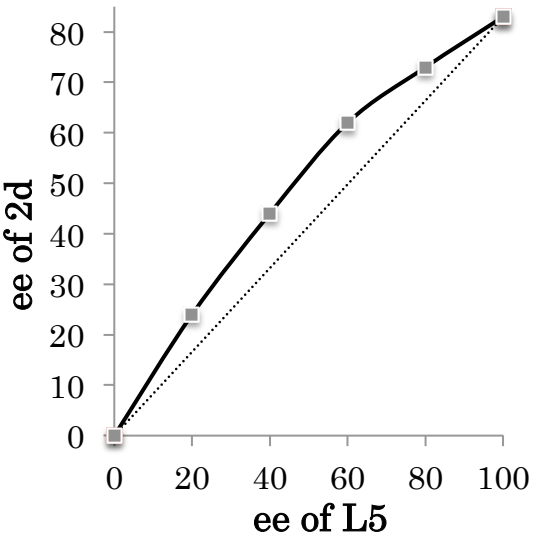


Figure S1. Relationship between the ee of **L5** and the ee of **2d**.

7. ESI-MS analysis of iron complex.

To a solution of $Fe(OTf)_2$ (2.5 mg, 0.0072 mmol) in MeCN (300 μL) was added **L5** (13.5 mg, 0.0173 mmol) in a well-dried 5 mL vial. After 1 h, 10 μL of the resulting mixture was diluted with MeCN (10 mL) in a well-dried 5 mL vial (final concentration: 2.4×10^{-5} *M*), and passed through a membrane filter (200 mm mesh) before injection. The spectrum is shown in Figure S2 and Figure S3.

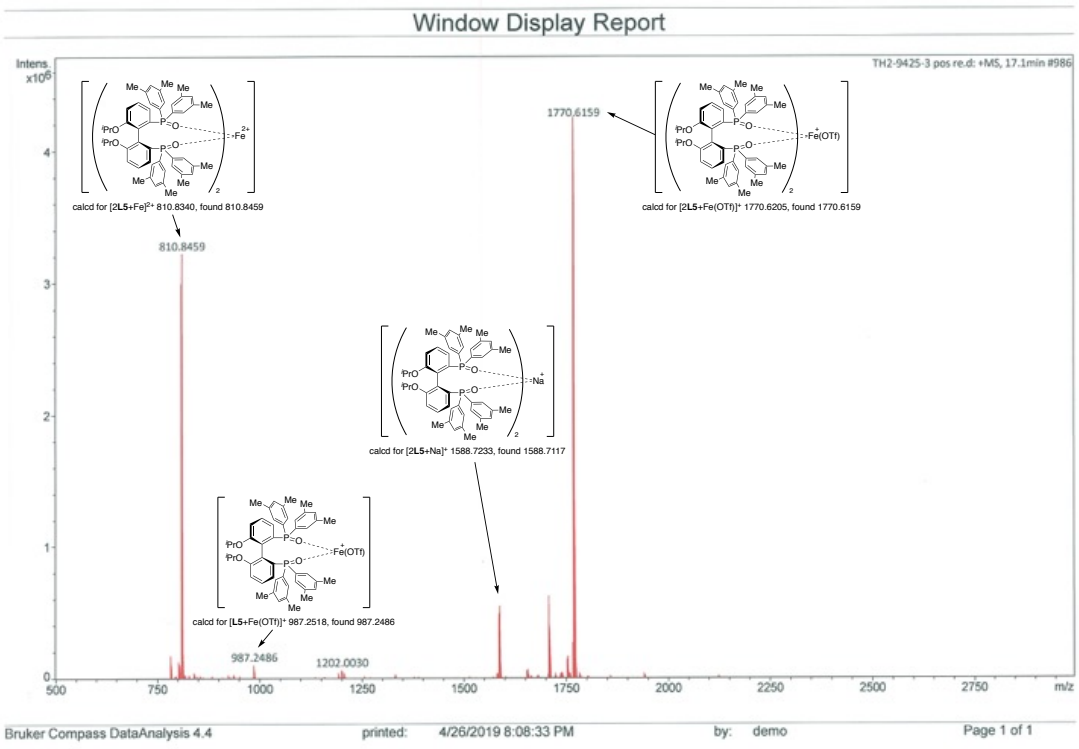


Figure S2. ESI-MS spectrum of $Fe(OTf)_2$/**L5** in MeCN (2.4×10^{-5} *M*).

Correlation of theoretical and observed ion distirbution for the peaks *m/z* = 1771 is shown in Figure S3. For *m/z* = 1771, $C_{101}H_{112}F_3FeO_{11}P_4S$ is identified to $\mathbf{L5}_2Fe(OTf)$ as $[M]^+$.

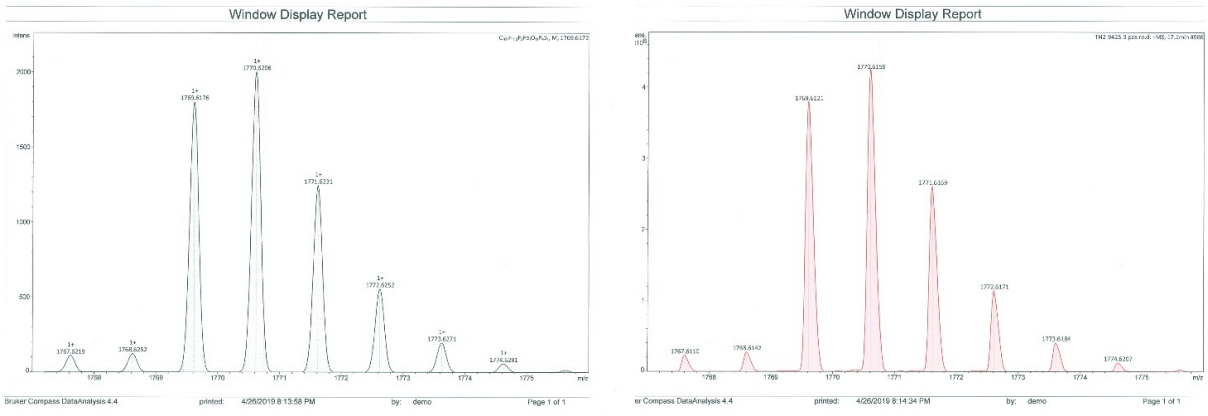
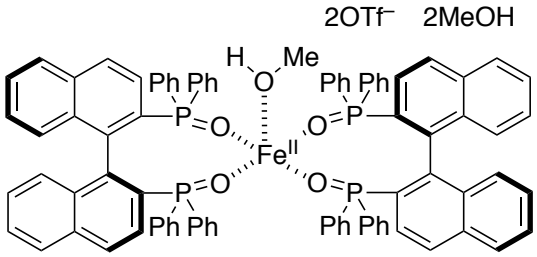


Figure S3. Theoretical ion distribution (left) and observed ion distribution (right) for the peaks *m/z* = 1771 (Zoom-in figure of Figure S2).

8. Isolation of 3.



$FeL1_2(MeOH)(OTf)_2$ (3): A well-dried 5 mL vial was charged with $Fe(OTf)_2$ (3.5 mg, 0.01 mmol), *rac*-BINAP-O **L1** (13.1 mg, 0.02 mmol) and $MeNO_2$ (0.6 mL), and the mixture was stirred at room temperature for 1 h. The mixture was passed through glass fiber and concentrated under reduced pressure. The residue was dissolved in MeOH, and then slow evaporation of the resulting clear solution by nitrogen stream gave a gray crystal of **3**.

Crystal data of 3: Formula $C_{93}H_{76}F_6FeO_{13}P_4S_2$ gray, crystal dimensions 0.240 × 0.100 × 0.010 mm^3, triclinic, space group *P-1*, a = 15.5435(7) Å, b = 15.7355(5) Å, c = 22.4546(8) Å, α = 98.365(3)°, β = 100.634(4)°, γ = 113.523(4)°, V = 4800.6(3) $Å^3$, Z = 2, ρ_{calc} = 1.217 g cm^{-3}, F(000) = 1820.0, μ(MoKα) = 0.335 mm^{-1}, T = 93 K. 87871 reflections collected, 26633 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ =61.506°), and 26633 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.1094 and wR_2 = 0.3485. GOF = 1.056. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1886904. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk; Web page: http://www.ccdc.cam.ac.uk/pages/Home.aspx].

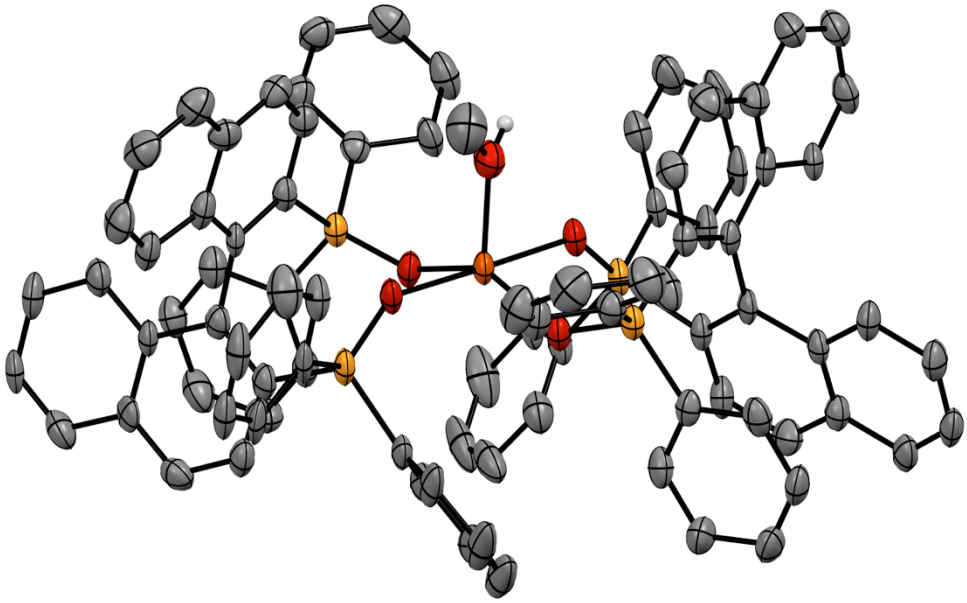


Figure S4. ORTEP drawing of **3**. TfO^-, solvents and hydrogens have been omitted for clarity. (*S*,*S*)-**3** has been shown.

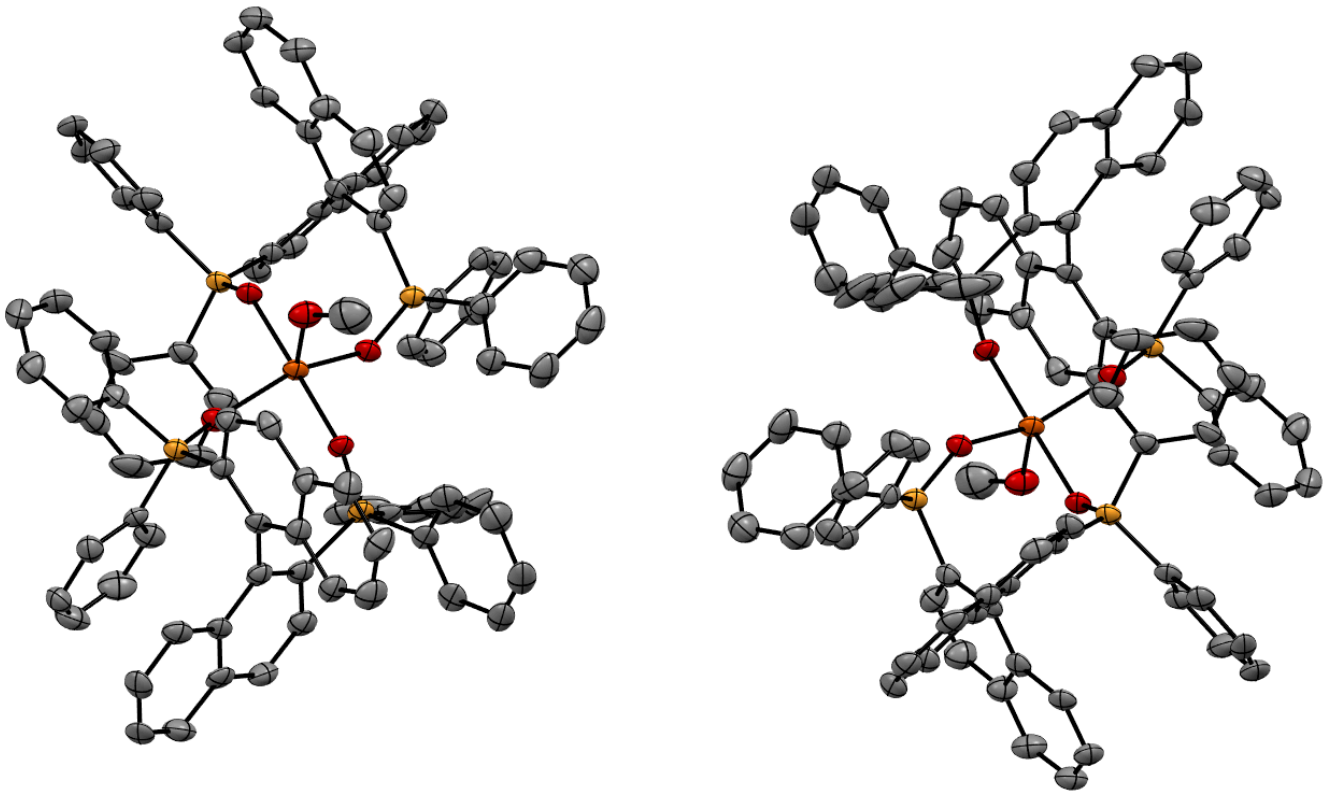
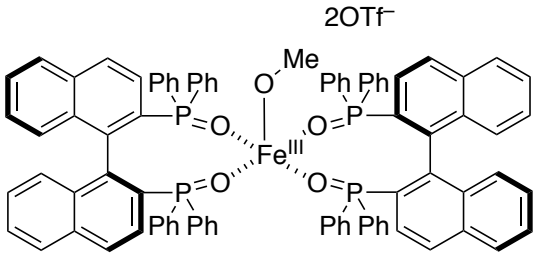


Figure S5. ORTEP drawing of **3**. TfO^-, solvents and hydrogens have been omitted for clarity. Crystal packing of (*S*,*S*)-**3** and (*R*,*R*)-**3** has been shown.

9. Isolation of 4.



Iron(III) complex (4): A well-dried 5 mL vial was charged with $Fe(OTf)_2$ (3.5 mg, 0.01 mmol), *rac*-BINAP-O (13.1 mg, 0.02 mmol) and $MeNO_2$ (0.6 mL), and the mixture was stirred at room temperature for 1 h. The mixture was passed through glass fiber and concentrated under reduced pressure. The residue was dissolved in MeOH, and then *tert*-butyl hydroperoxide (5.5 *M* in nonane, 0.9 μL, 0.005 mmol) was added to the mixture. The mixture was stirred at room temperature for 1 h. The slow evaporation of the resulting brown solution by nitrogen stream gave a gray crystal of **4**.

Crystal data of 4: Formula $C_{91}H_{67}F_6FeO_{11}P_4S_2$, gray, crystal dimensions 0.199 × 0.132 × 0.020 mm^3, triclinic, space group *P-1*, a = 14.7161(6) Å, b = 14.8437(7) Å, c = 20.7334(7) Å, α = 94.995(3)°, β = 98.196(3)°, γ = 116.057(4)°, V = 3969.7(3) $Å^3$, Z = 2, ρ_{calc} = 1.417 g cm^{-3}, F(000) = 1746.0, μ(MoKα) = 0.400 mm^{-1}, T = 93 K. 55878 reflections collected, 26633 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 61.448°), and 21488 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0765 and wR_2 = 0.2349. GOF = 0.996. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1886905. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk; Web page: http://www.ccdc.cam.ac.uk/pages/Home.aspx].

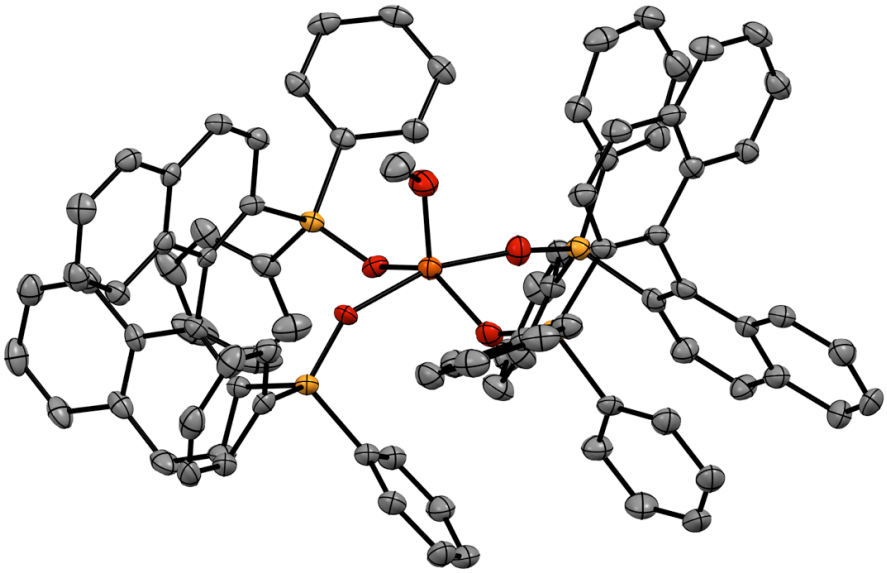


Figure S6. ORTEP drawing of **4**. TfO^- and hydrogens have been omitted for clarity. (*S*,*S*)-**4** has been shown.

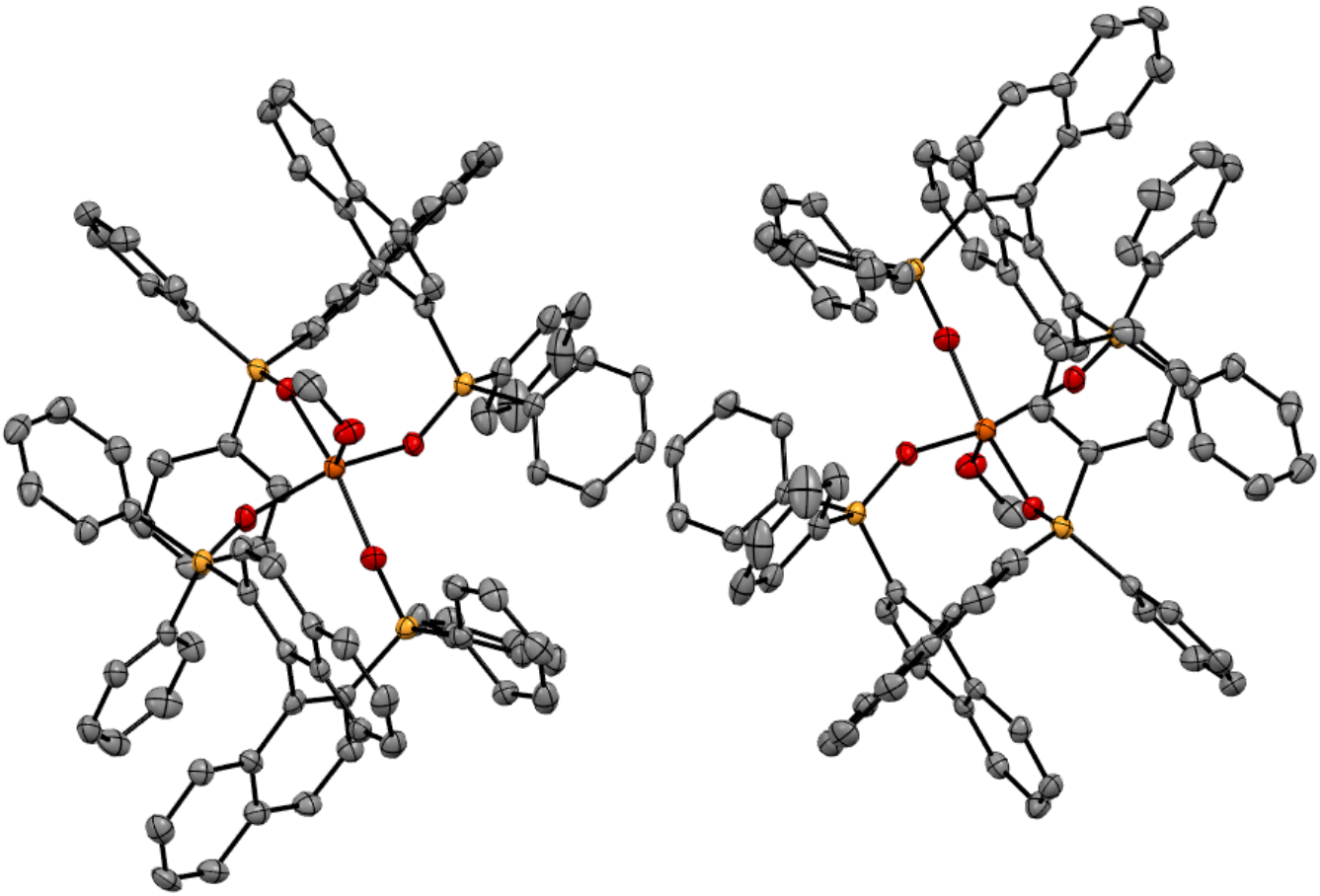
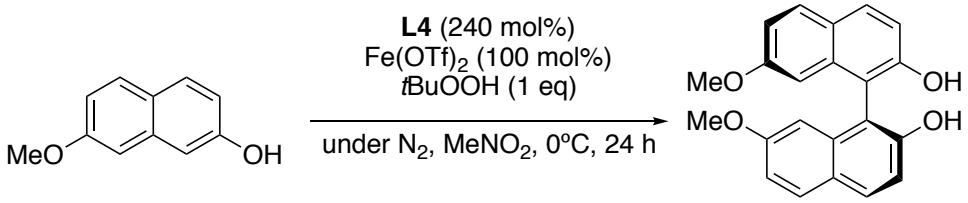


Figure S7. ORTEP drawing of **4**. TfO^- and hydrogens have been omitted for clarity. Crystal packing of (*S*,*S*)-**4** and (*R*,*R*)-**4** has been shown.

10. Oxidative coupling using stoichiometric amount of $Fe(OTf)_2$ with ligand.



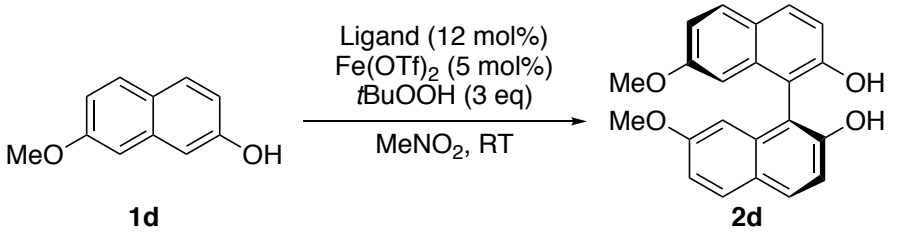
1d **2d**

A well-dried Schlenk flask with magnetic stir bar was charged with $Fe(OTf)_2$ (38.3 mg, 0.108 mmol), **L4** (188.4 mg, 0.259 mmol) and degassed $MeNO_2$ (300 μL) at room temperature under N_2 atmosphere. After being stirred for 1 h, degassed $MeNO_2$ (600 μL) and 7-methoxy-2-naphthol (37.6 mg, 0.216 mmol) and *tert*-butyl hydroperoxide (5.5 *M* in nonane, 19.6 μL, 0.108 mmol) was added to the mixture at 0 ºC. After 24 h, sat. $Na_2S_2O_3$ (1.0 mL) was added to the reaction mixture. It was directly subjected to column chromatography on silica gel (Hexane/AcOEt = 4/1) to give a crude product. After being concentrated under reduced pressure, the crude product was further purified by column chromatography on silica gel (Hexane/AcOEt = 6/1) to give the analytically pure product. Isolated 17.6mg (0.051 mmol, 47% yield)

11. Effect of chiral BINAP-oxide derivatives.

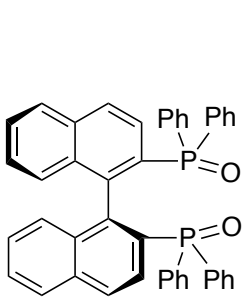
Effect of aryl substituent of diphosphine oxide ligand was examined (Table S1) in oxidative coupling reaction of **1d** in $MeNO_2$ with the use of 12 mol% of ligand and 5 mol% of $Fe(OTf)_2$. After screening chiral diphosphine oxide from commercially available BINAP derivatives, 3,5-xylyl substituent was found to be the most effective with regard to both yield and enantioselectivity.

Table S1. Effect of Aryl Group on Diphosphine Oxide in Oxidative Coupling Reaction

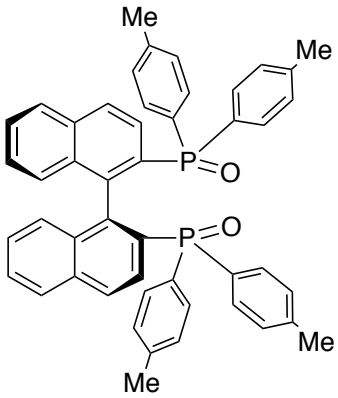


1d **2d**

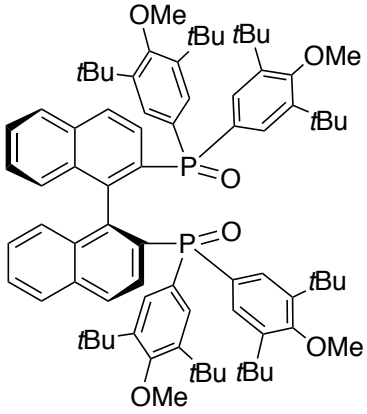
Ligand, yield and enatioselectivity



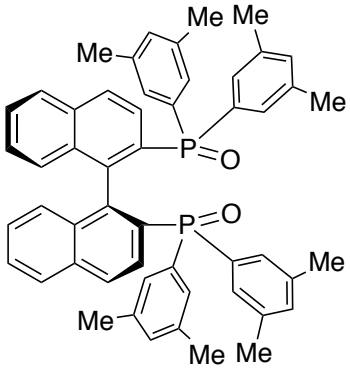
42%, 17% ee



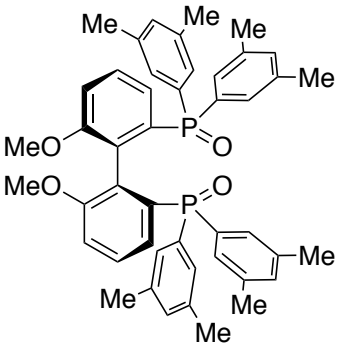
48%, 38% ee



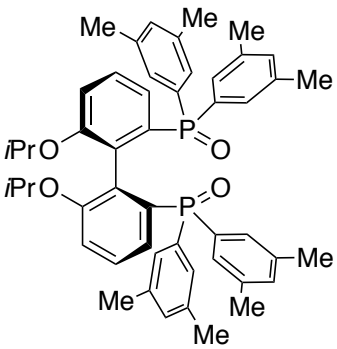
33%, 2% ee



91%, 72% ee[a)]
97%, 76% ee[a,b)]



98%, 76% ee[a,b)]



93%, 84% ee[a,b)]

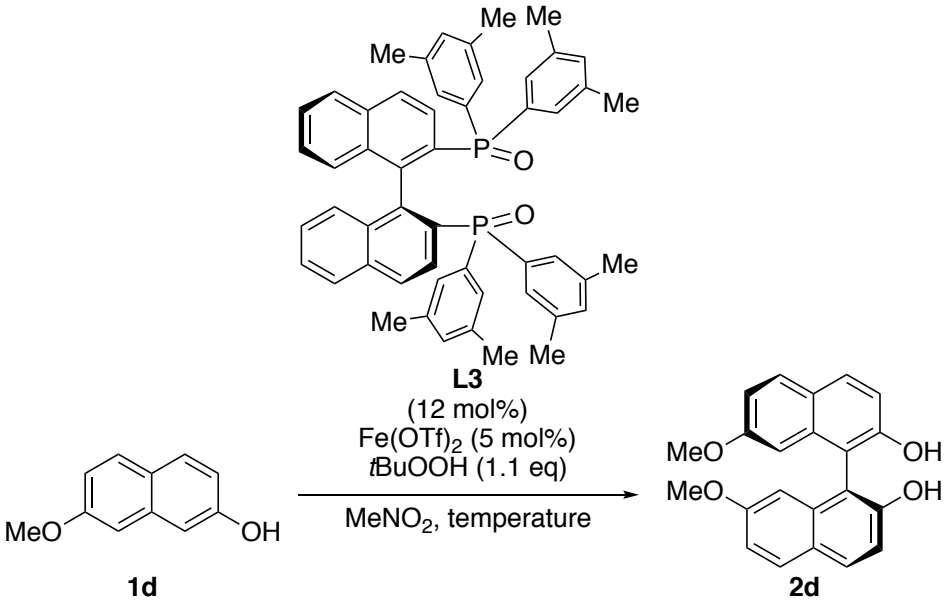
[a)] 1.1 eq of *t*BuOOH was used.
[b)] reaction was conducted at 0 ºC

12. Effect of temperature.

Effect of temperature was examined (Table S2) in oxidative coupling reaction of **1d** in $MeNO_2$ with the use of 12 mol% of (*S*)-xyl-BINAP-oxide and 5 mol% of $Fe(OTf)_2$.

Low temperature was effective for slightly improving the enantioselectivity of **2d**. In contrast, when the reaction was conducted at 40ºC, the enantioselectivity of **2d** was slightly decreased.

Table S2. Effect of Temperature



1d **2d**

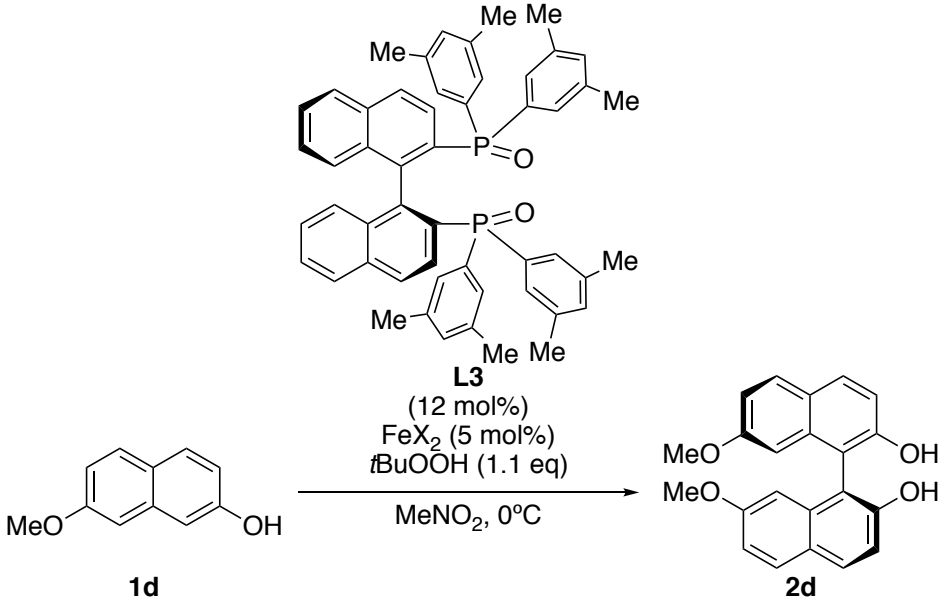
entry	Temperature	yield[a] [%]	ee [%]
1	−20 ºC	63	76
2	0 ºC	97	76
3	Room temperature	91	72
4	40 ºC	94	69

a) The yield was determined by ^1H NMR analysis using 1,3-dinitrobenzene as an internal standard

13. Effect of counter anion.

Effect of a counter anion of iron(II) salt was examined (Table S3) in oxidative coupling reaction of **1d** in $MeNO_2$ with the use of 12 mol% of (*S*)-xyl-BINAP-oxide with 5 mol% of iron(II) salt. Similar reactivities and selectivities were observed when non-coordinating counteranions, such as $Fe(SbF_6)_2$, $Fe(NTf_2)_2$ and $Fe(ClO_4)_2$, were used (entries 2–4). In contrast, relatively coordinating anion, such as $Fe(BF_4)_2$, $Fe(OCOCF_3)_2$ and $Fe(NO_3)_2$, dramatically decreased the yield of **2d** (entries 5–7).

Table S3. Effect of Counteranion



1d **2d**

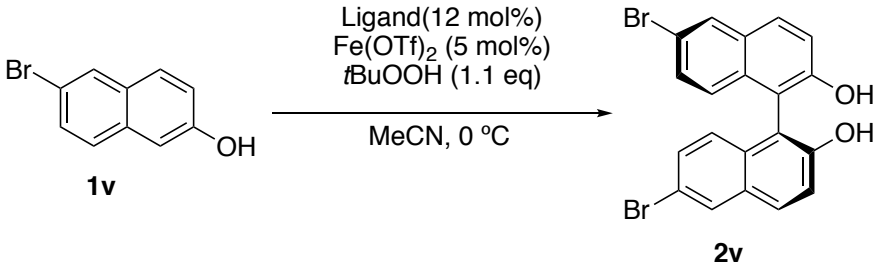
entry	FeX_2	yield [%][a]	ee [%]
1	$Fe(OTf)_2$	97	76
2	$Fe(SbF_6)_2$	92	73
3	$Fe(NTf_2)_2$	94	72
4	$Fe(ClO_4)_2$	97	73
5	$Fe(BF_4)_2$	4	67
6	$Fe(OCOCF_3)_2$	34	64
7	$Fe(NO_3)_2$	<5	–

a) The yield was determined by ^{1}H NMR analysis using 1,3-dinitrobenzene as an internal standard.

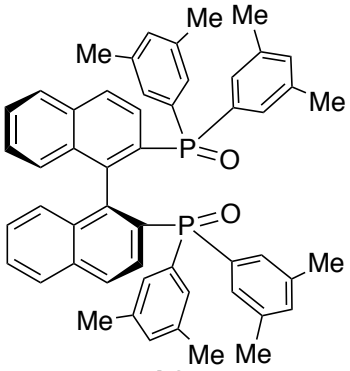
14. Effect of ligand for 6-substituted naphthol.

Effect of ligand for 6-bromonaphthalen-2-ol was examined (Table S4) in oxidative coupling reaction in $MeNO_2$ with the use of 12 mol% of ligand with 5 mol% of iron(II) salt. After screening chiral diphosphine oxide **L3**–**L5**, **L4** was found to be the most effective with regard to both yield and enantioselectivity.

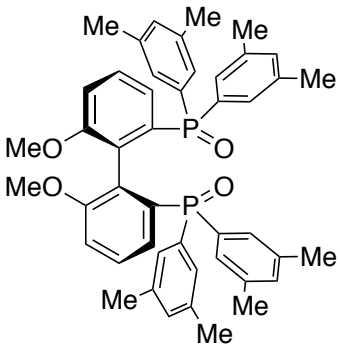
Table S4. Effect of Ligand for 6-Substituted Naphthol



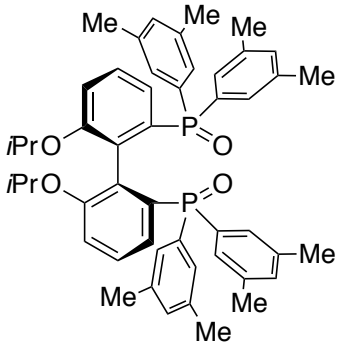
Ligand, yield and enatioselectivity



L3
98%, 55% ee[a)]



L4
89%, 68% ee
72%,74% ee[b)]



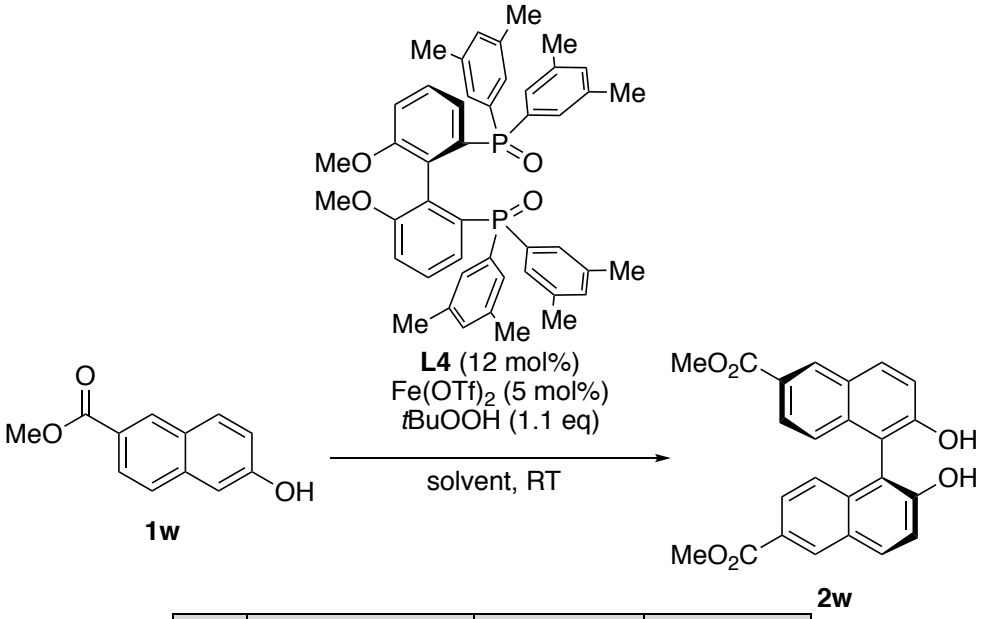
L5
96%, 49% ee

[a)] $MeNO_2$ was used as a solvent
[b)] reaction was conducted at –10 ºC

15. Effect of solvent for 6-substituted naphthol.

Effect of a solvent for methyl 6-hydroxy-2-naphthoate was examined (Table S5) in oxidative coupling reaction in $MeNO_2$ with the use of 12 mol% of **L4** with 5 mol% of iron(II) salt. Whereas $MeNO_2$, CH_2Cl_2, THF and EtOAc afforded the corresponding product with moderate selectivities (entries 1–4), MeCN improved the enantioselectivity (entries 5 and 6).

Table S5. Effect of Solvent for 6-Substituted Naphthol



entry	Solvent	yield [%][a]	ee [%]
1	$MeNO_2$	83	66
2	CH_2Cl_2	10[b]	45
3	THF	22[b]	65
4	EtOAc	32	65
5	MeCN	60	80
6	MeCN	93[c]	85

a) The yield was determined by ^{1}H NMR analysis using 1,3-dinitrobenzene as an internal standard. b) 0 ºC. c) 5 ºC.

16. References.

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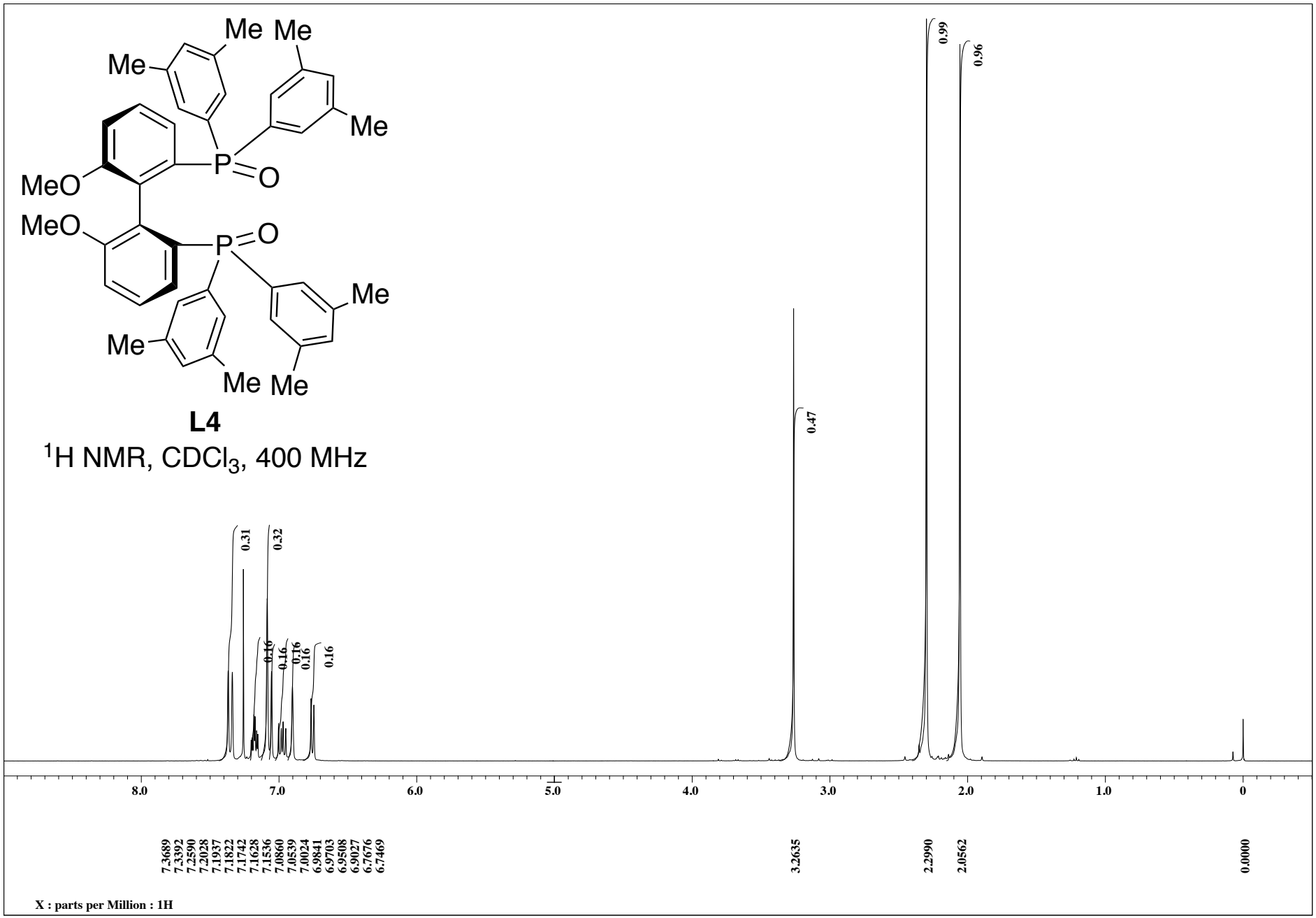
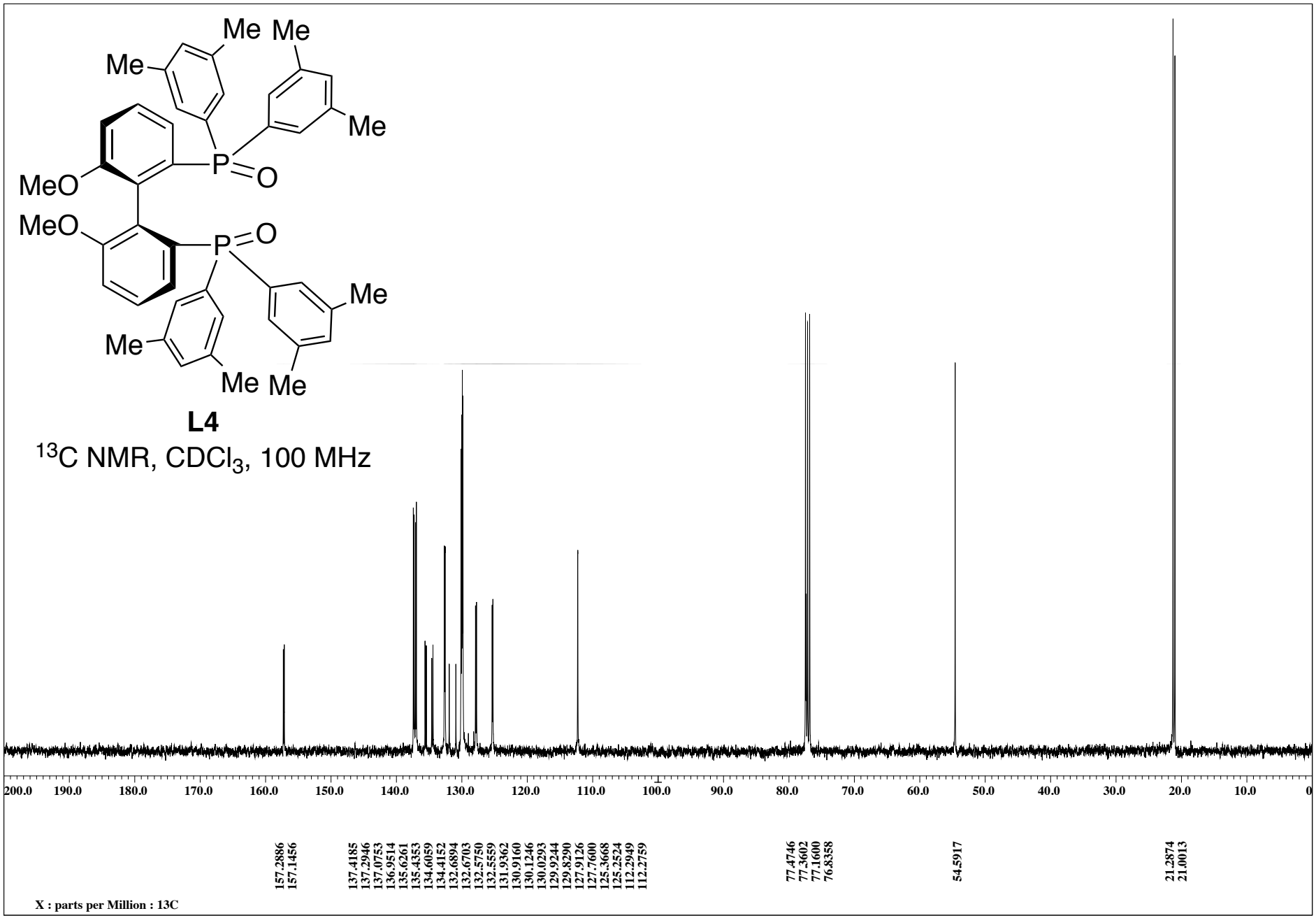
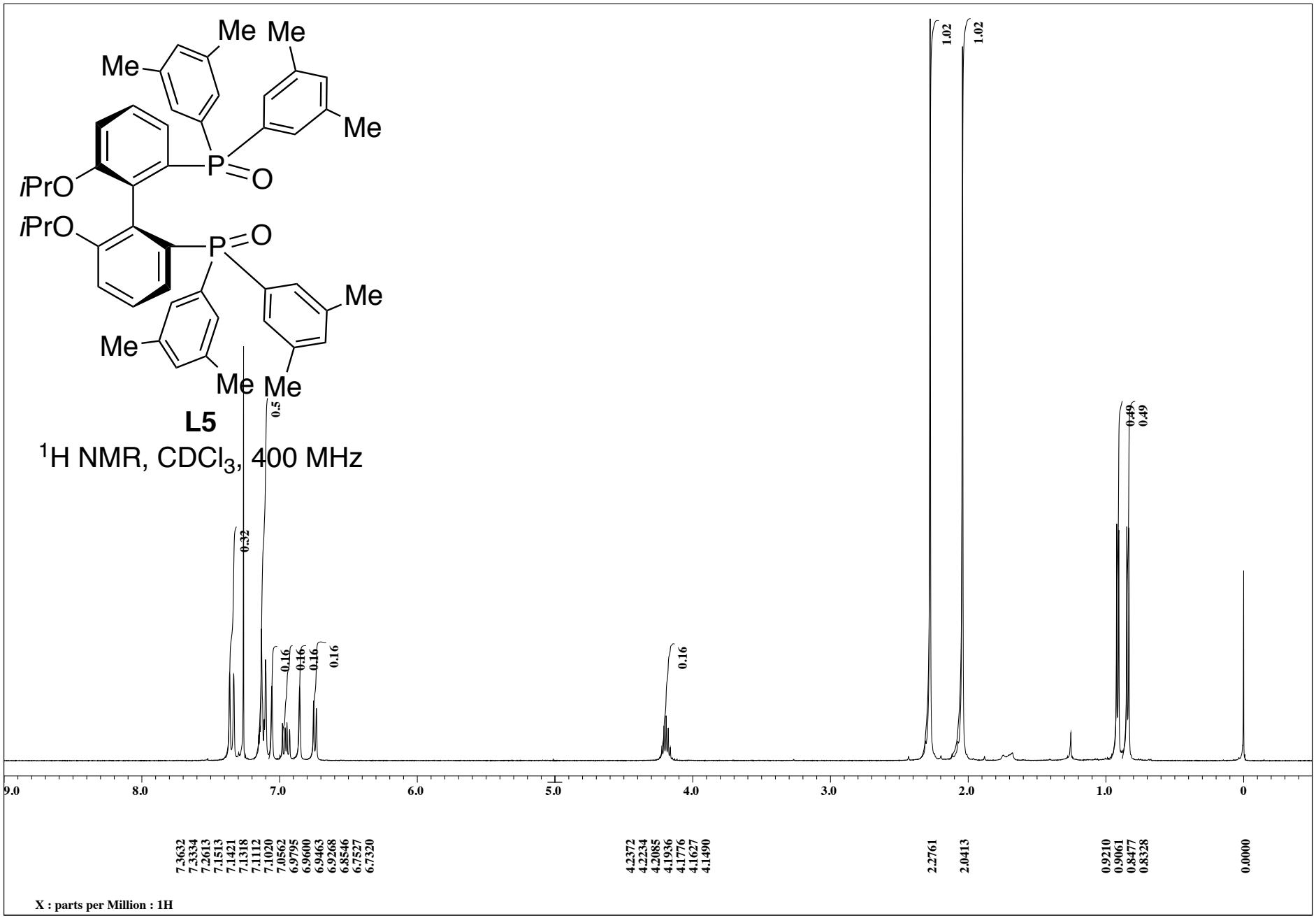


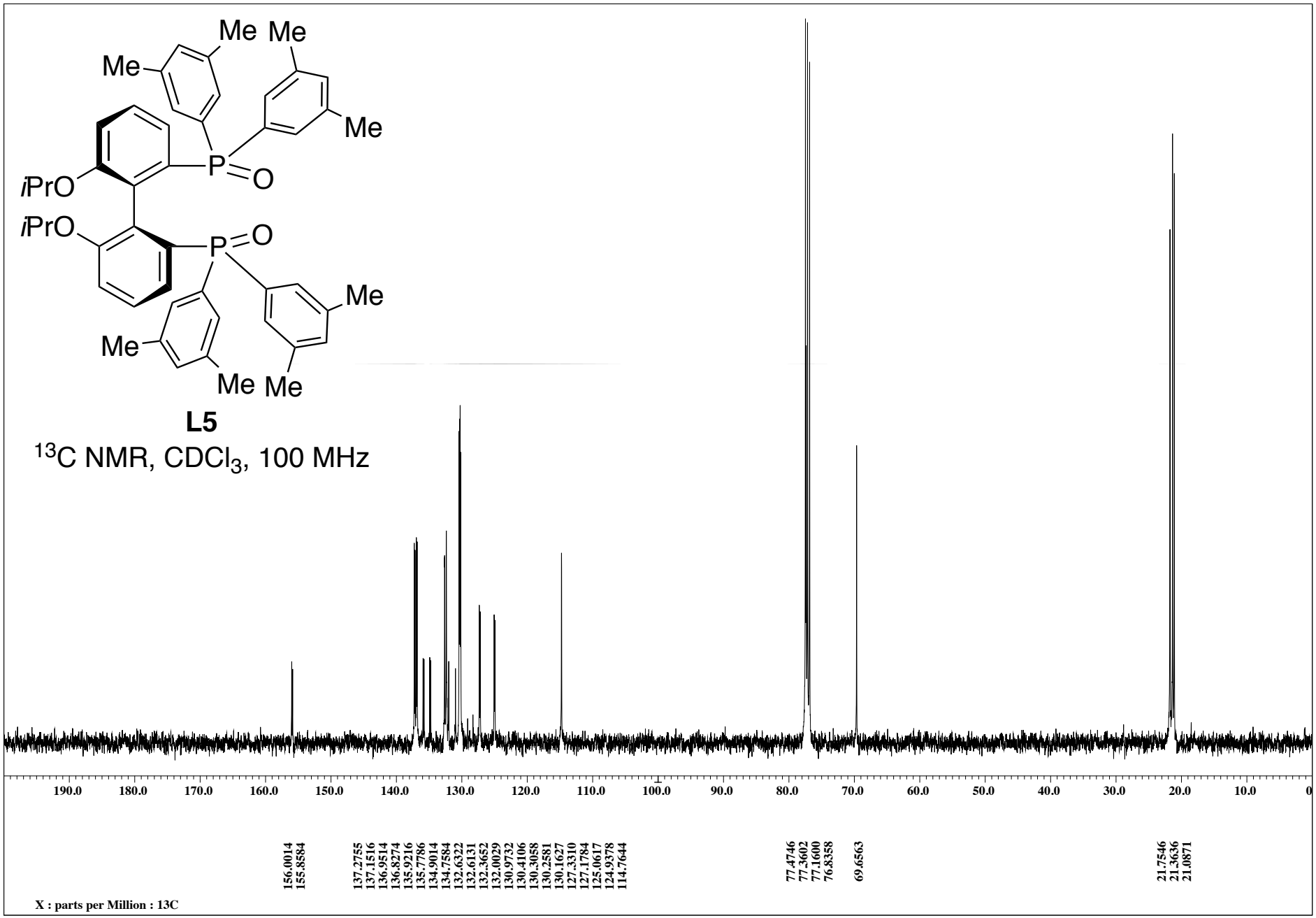
^{1}H NMR spectrum of **L4** ($CDCl_3$, 400 MHz)



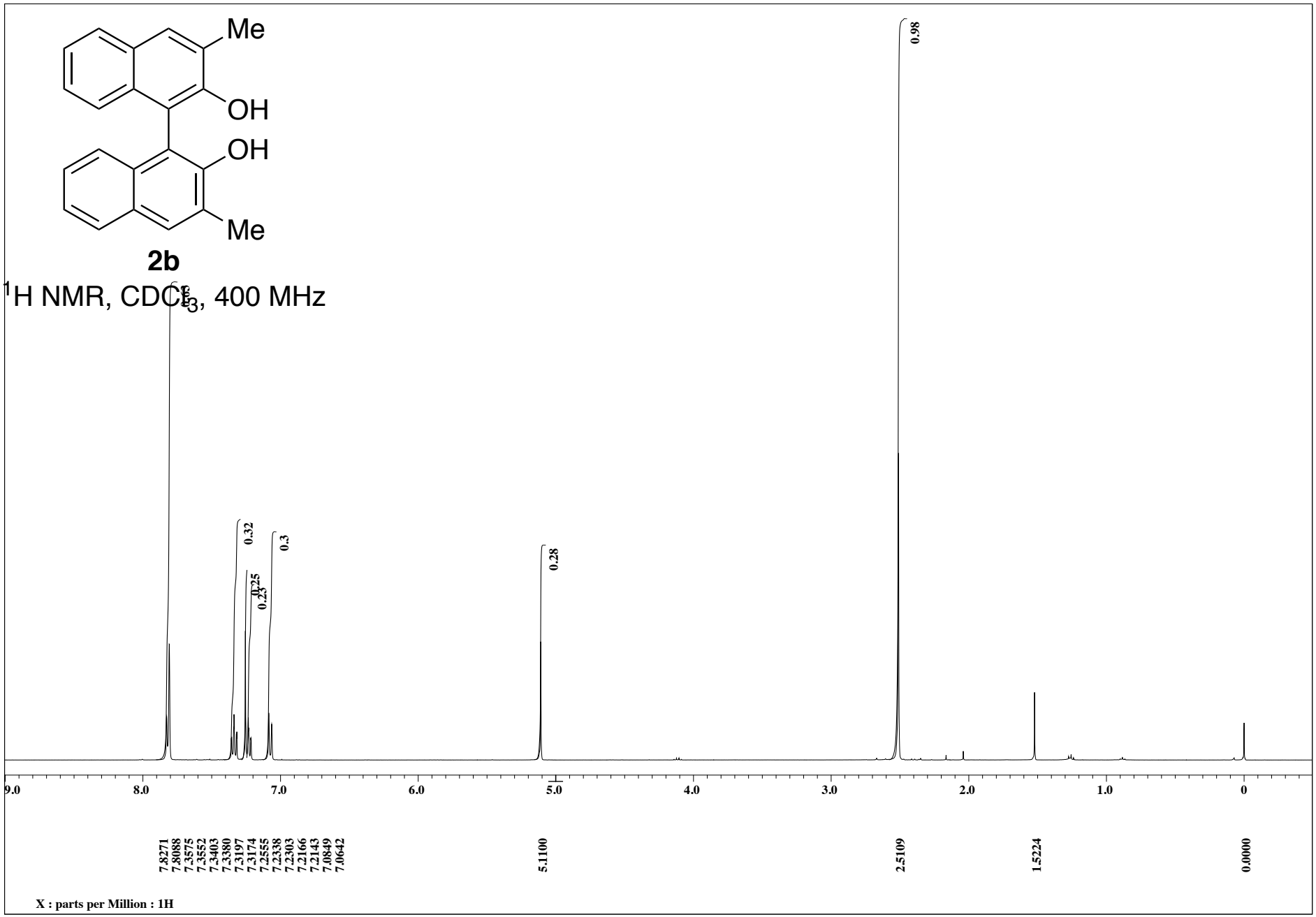
^{13}C NMR spectrum of **L4** ($CDCl_3$, 100 MHz)



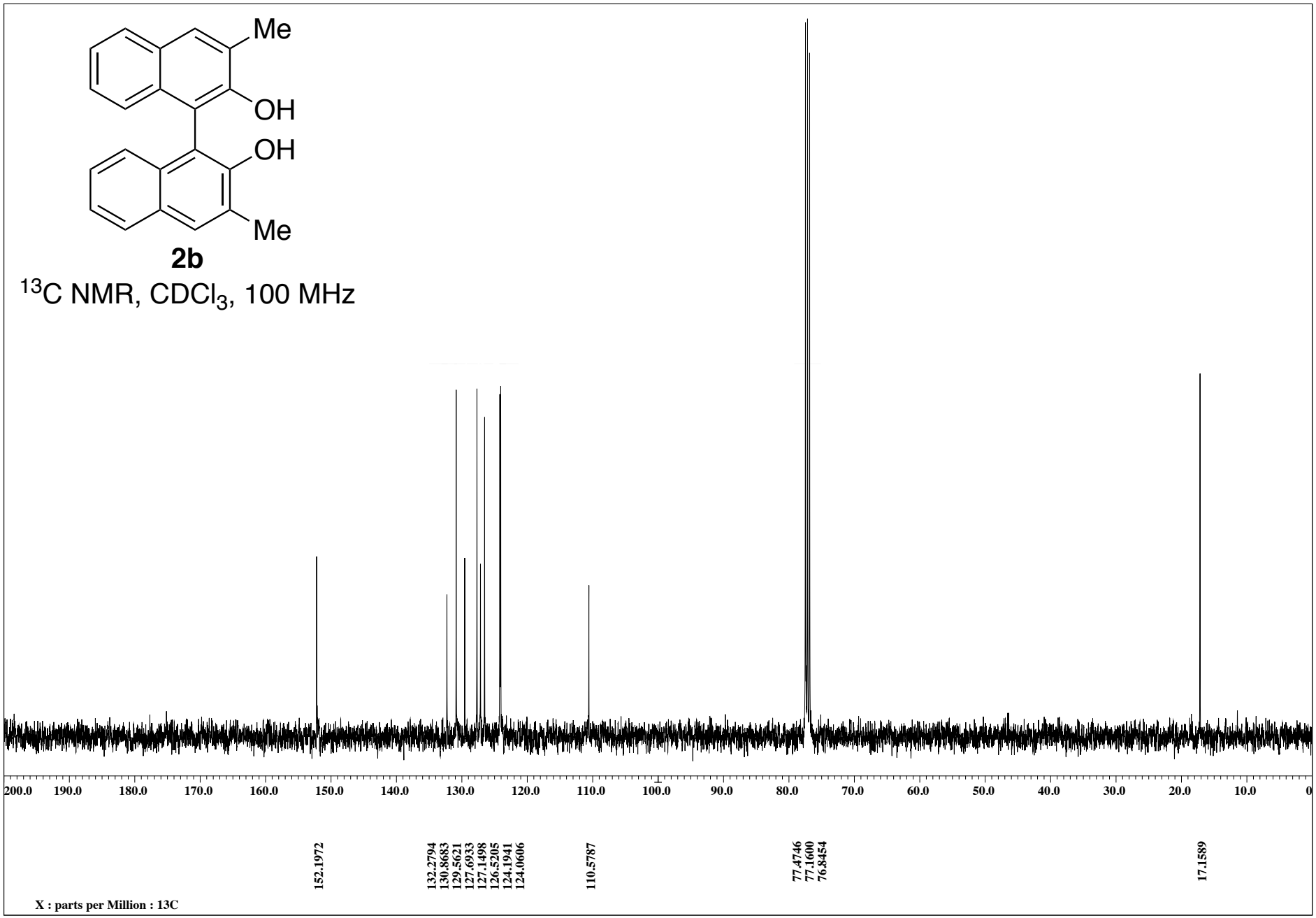
^{1}H NMR spectrum of **L5** ($CDCl_3$, 400 MHz)



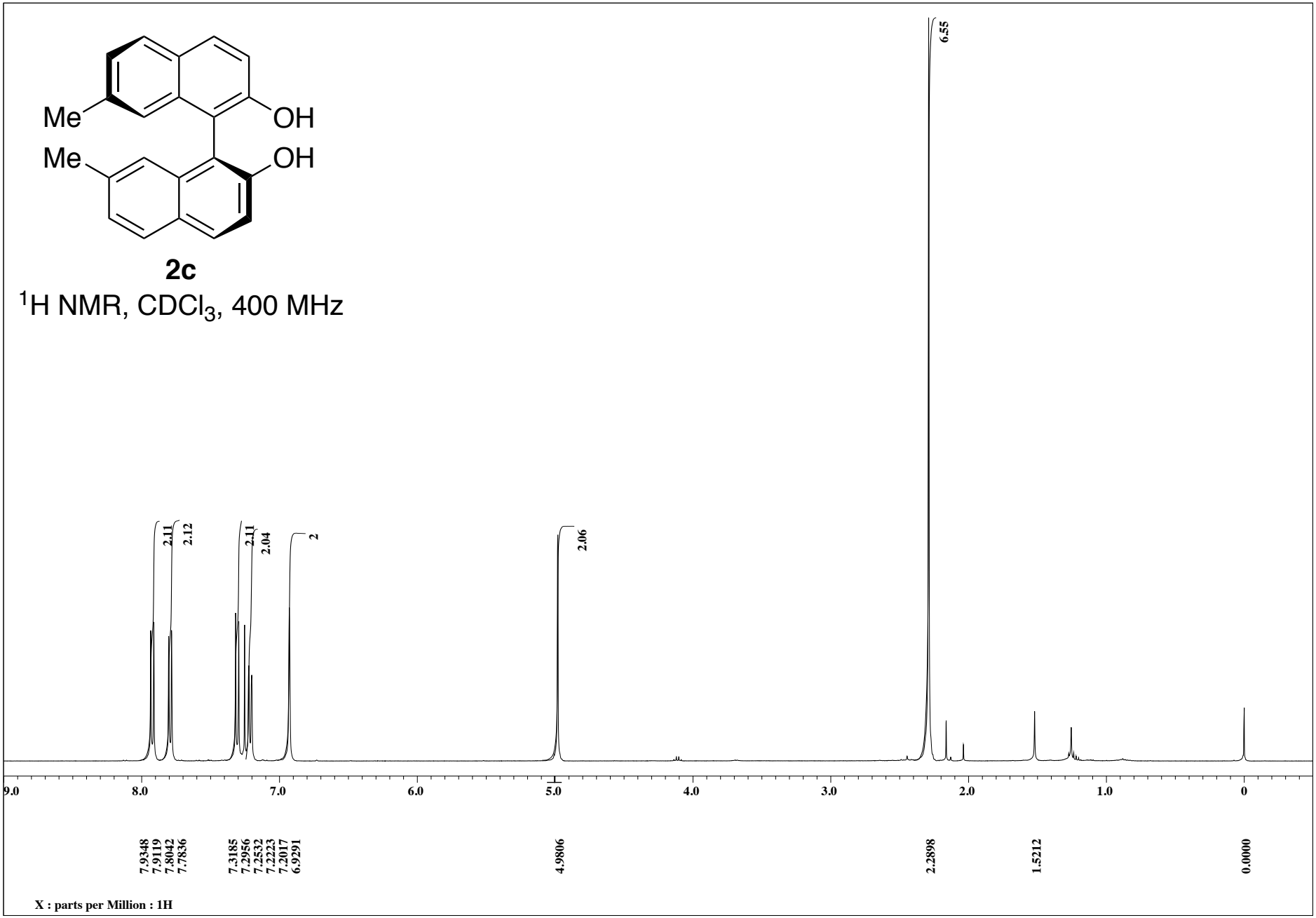
^{13}C NMR spectrum of **L5** ($CDCl_3$, 100 MHz)



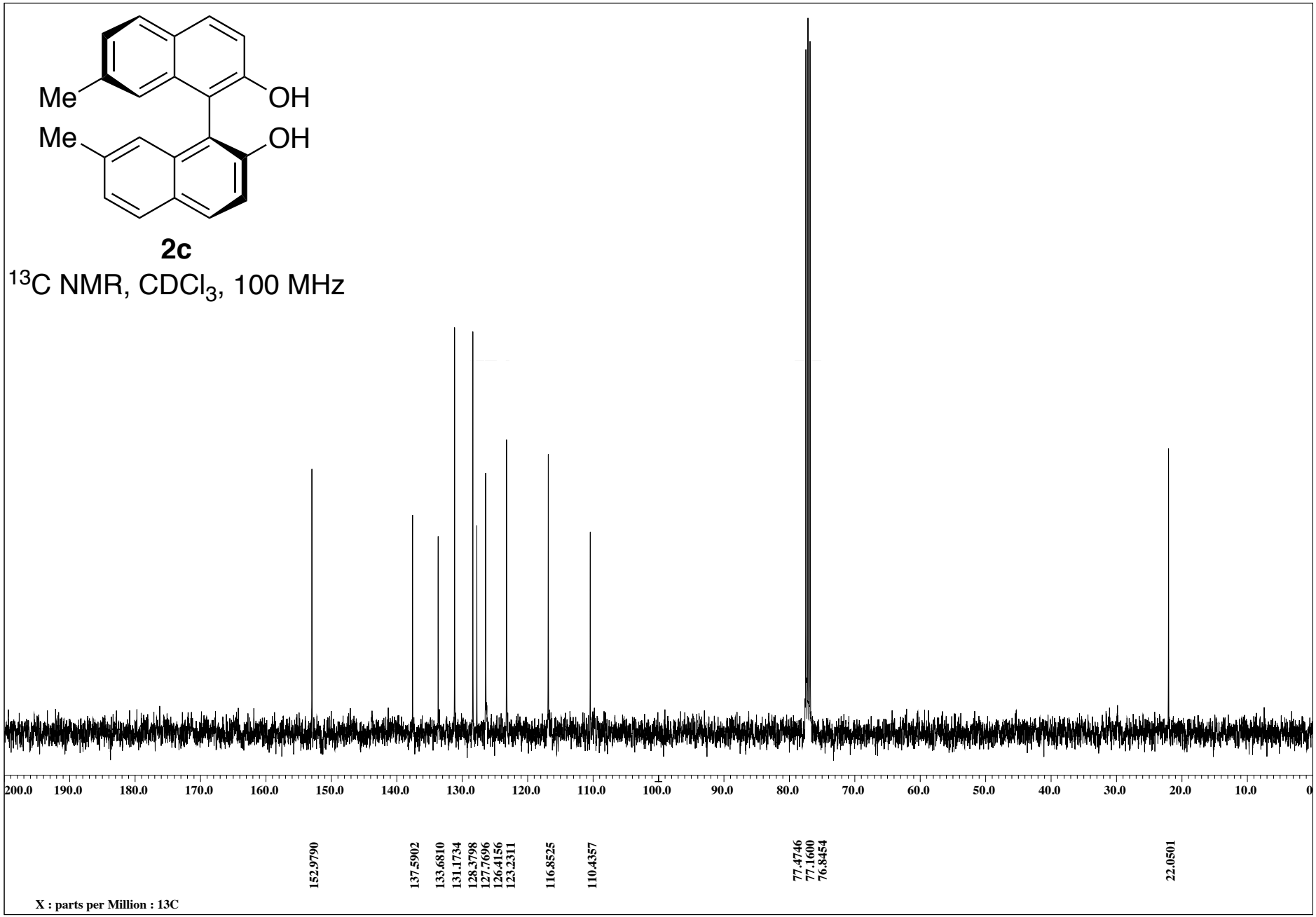
^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz)



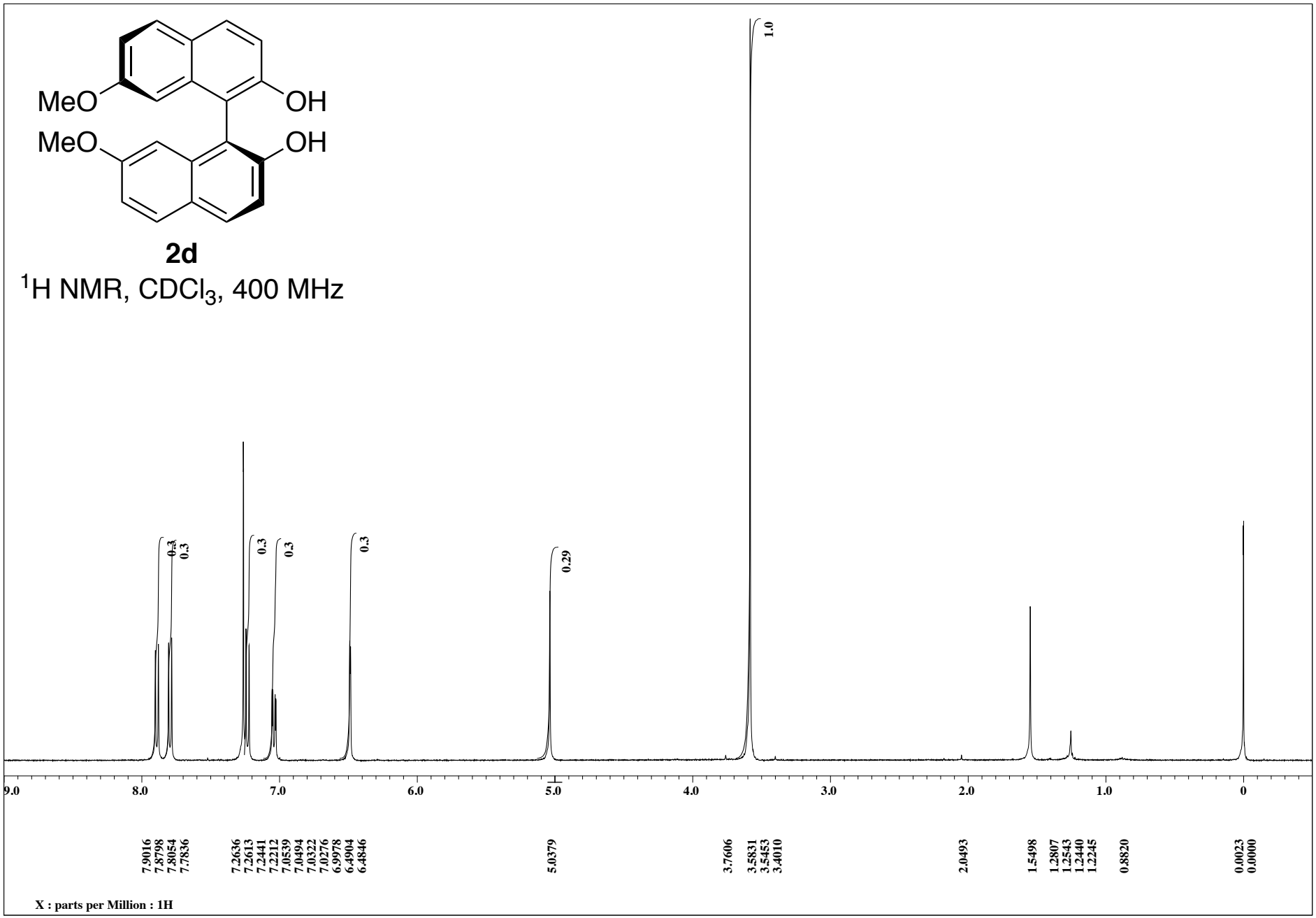
^{13}C NMR spectrum of **2b** ($CDCl_3$, 100 MHz)



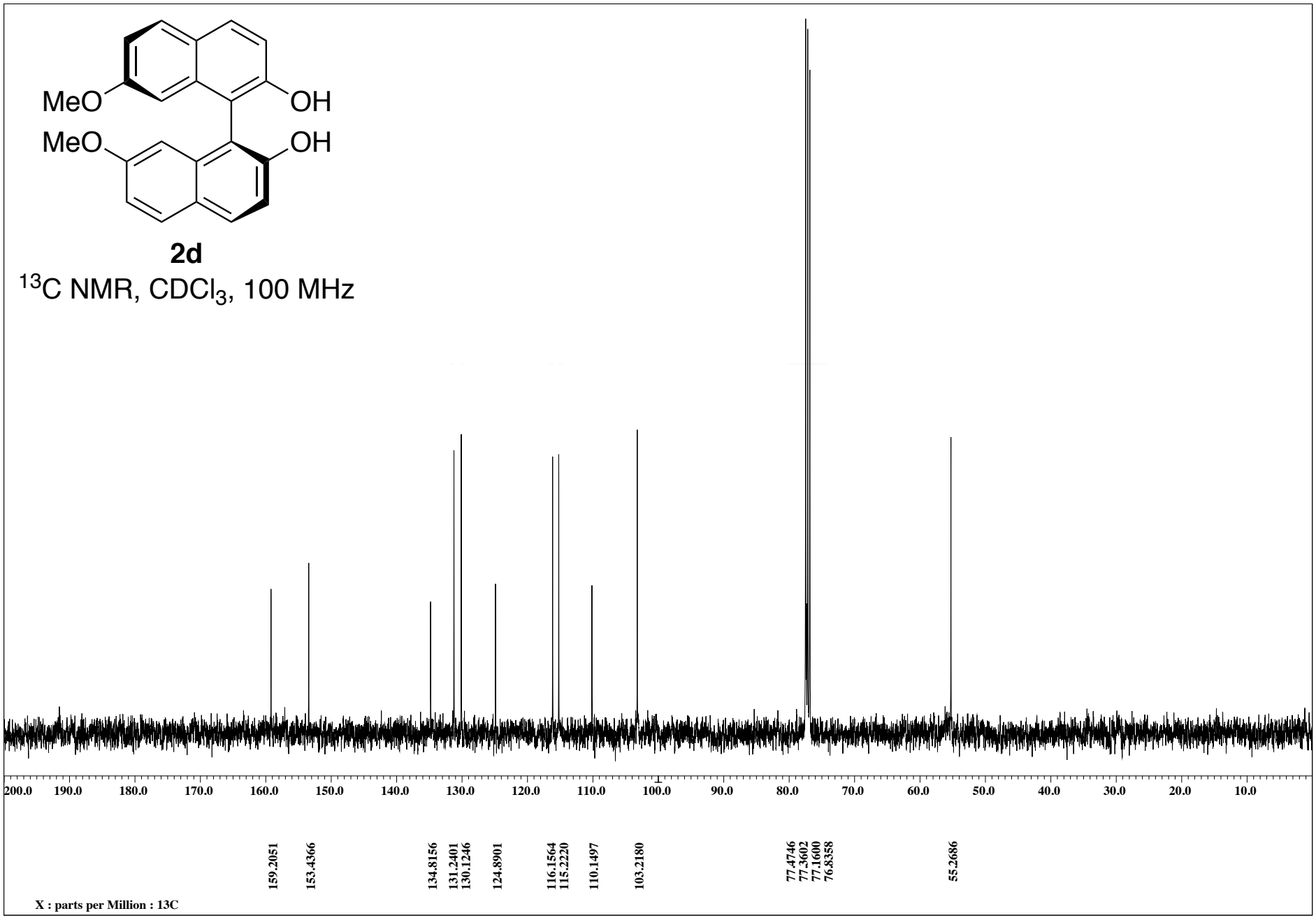
^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz)



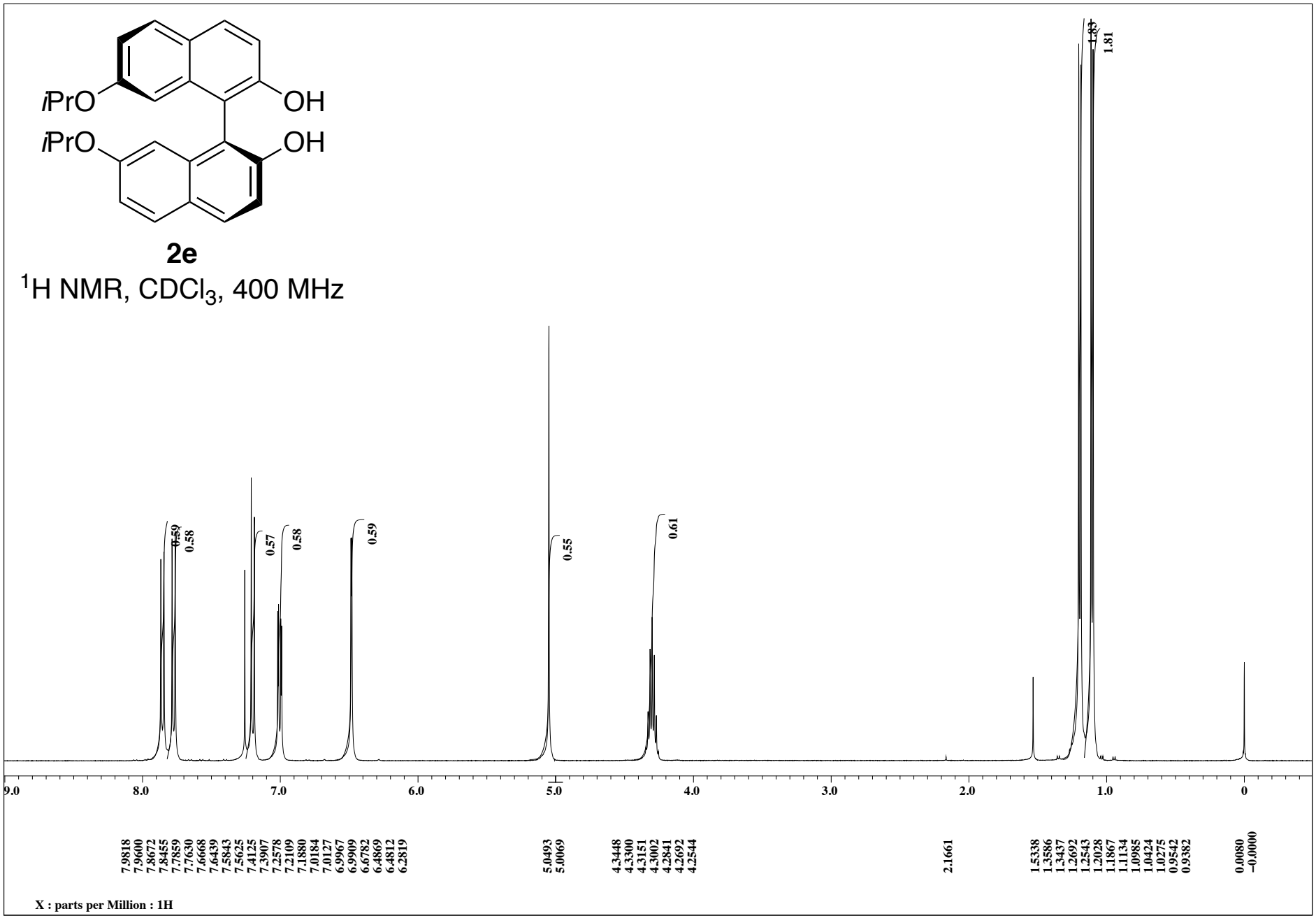
^{13}C NMR spectrum of **2c** ($CDCl_3$, 100 MHz)



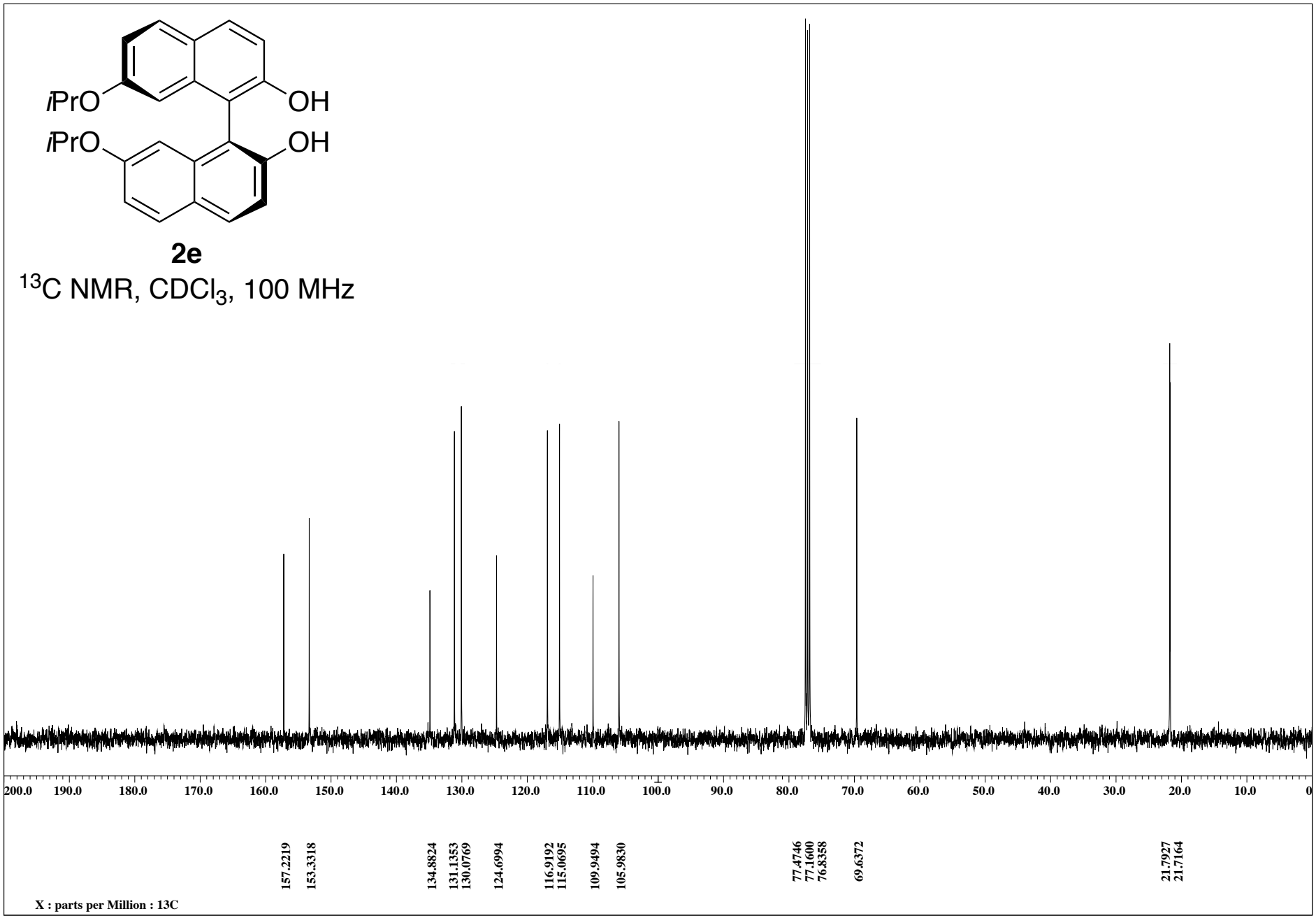
^{1}H NMR spectrum of **2d** ($CDCl_3$, 400 MHz)



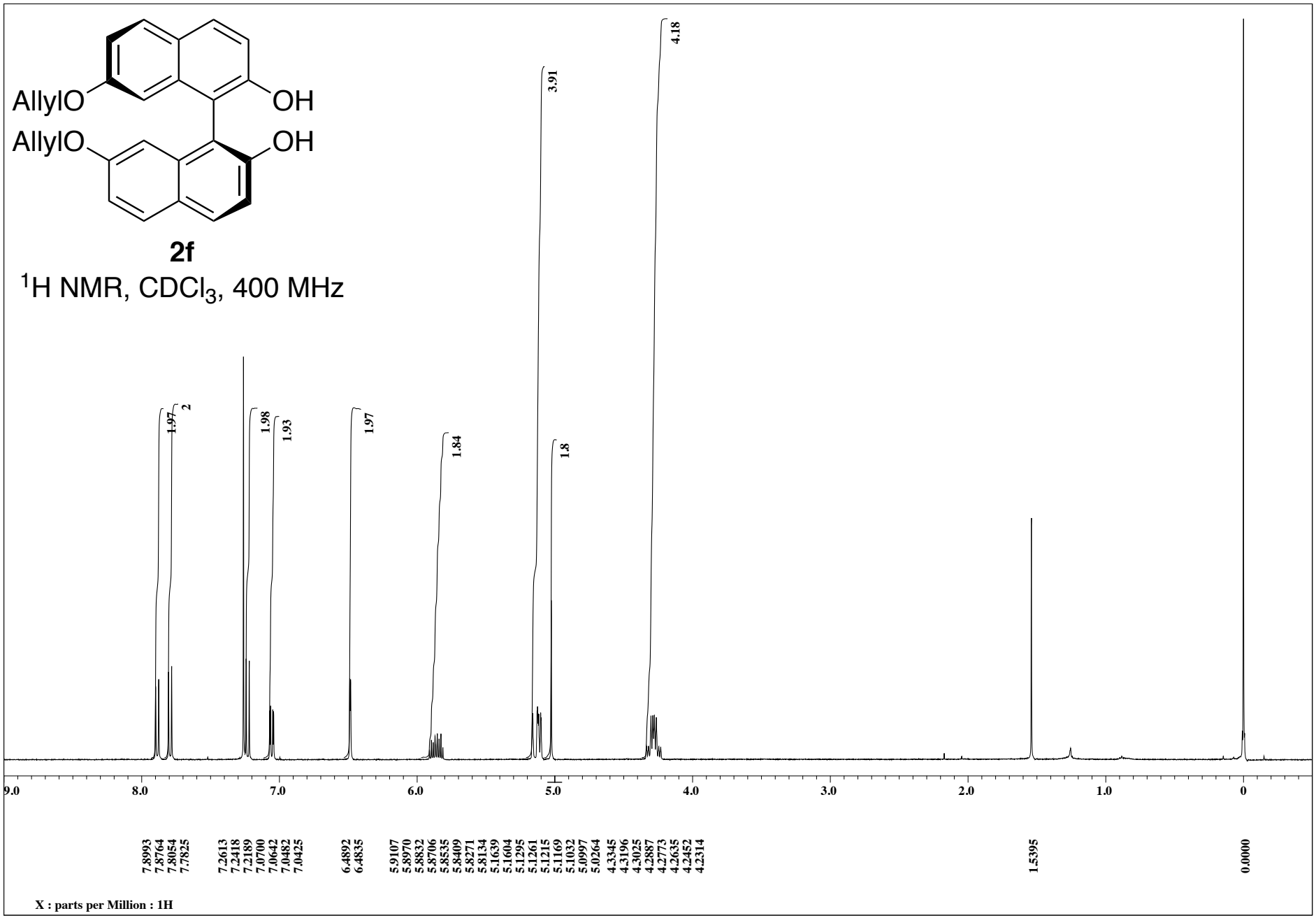
^{13}C NMR spectrum of **2d** ($CDCl_3$, 100 MHz)



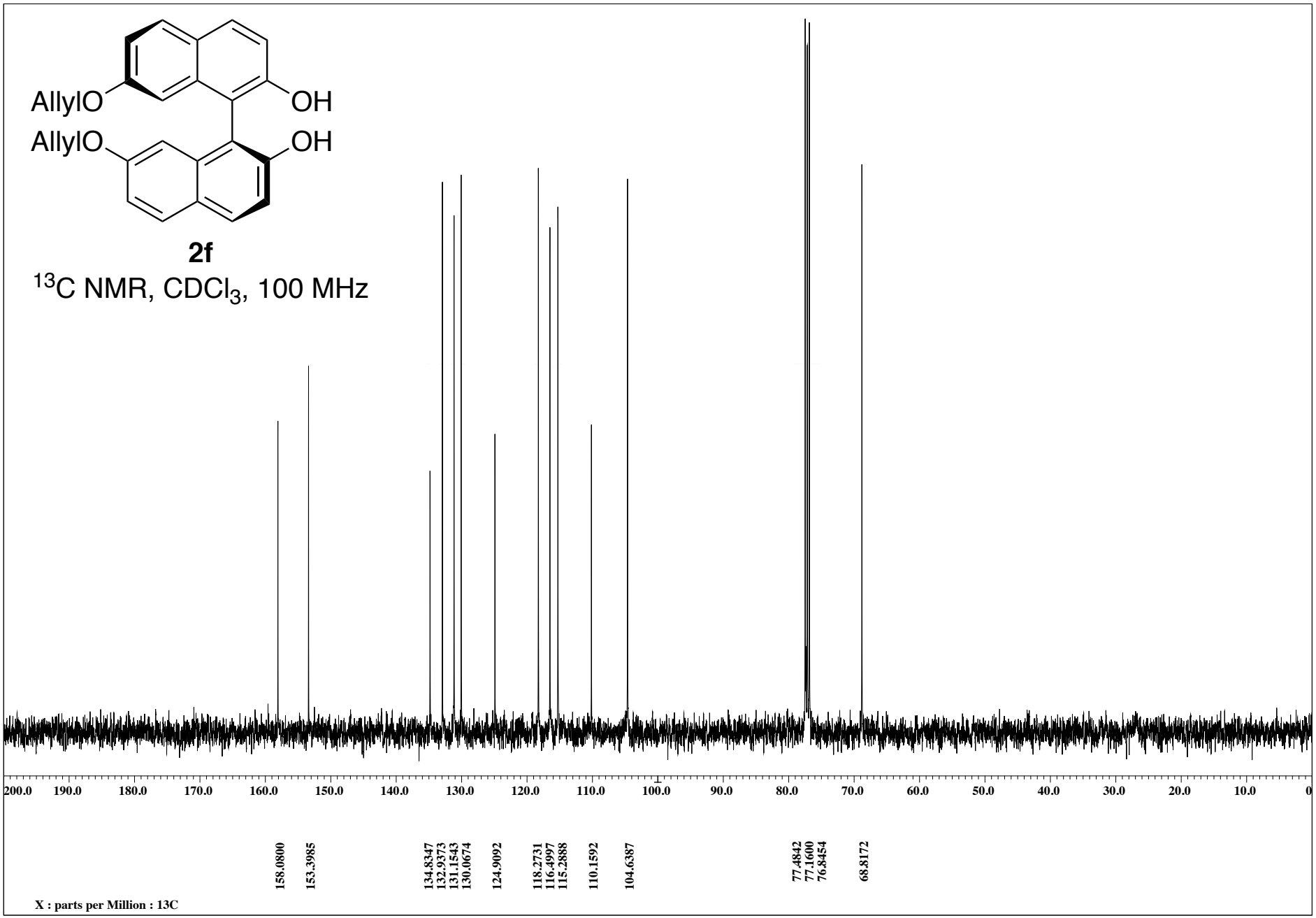
^{1}H NMR spectrum of **2e** ($CDCl_3$, 400 MHz)



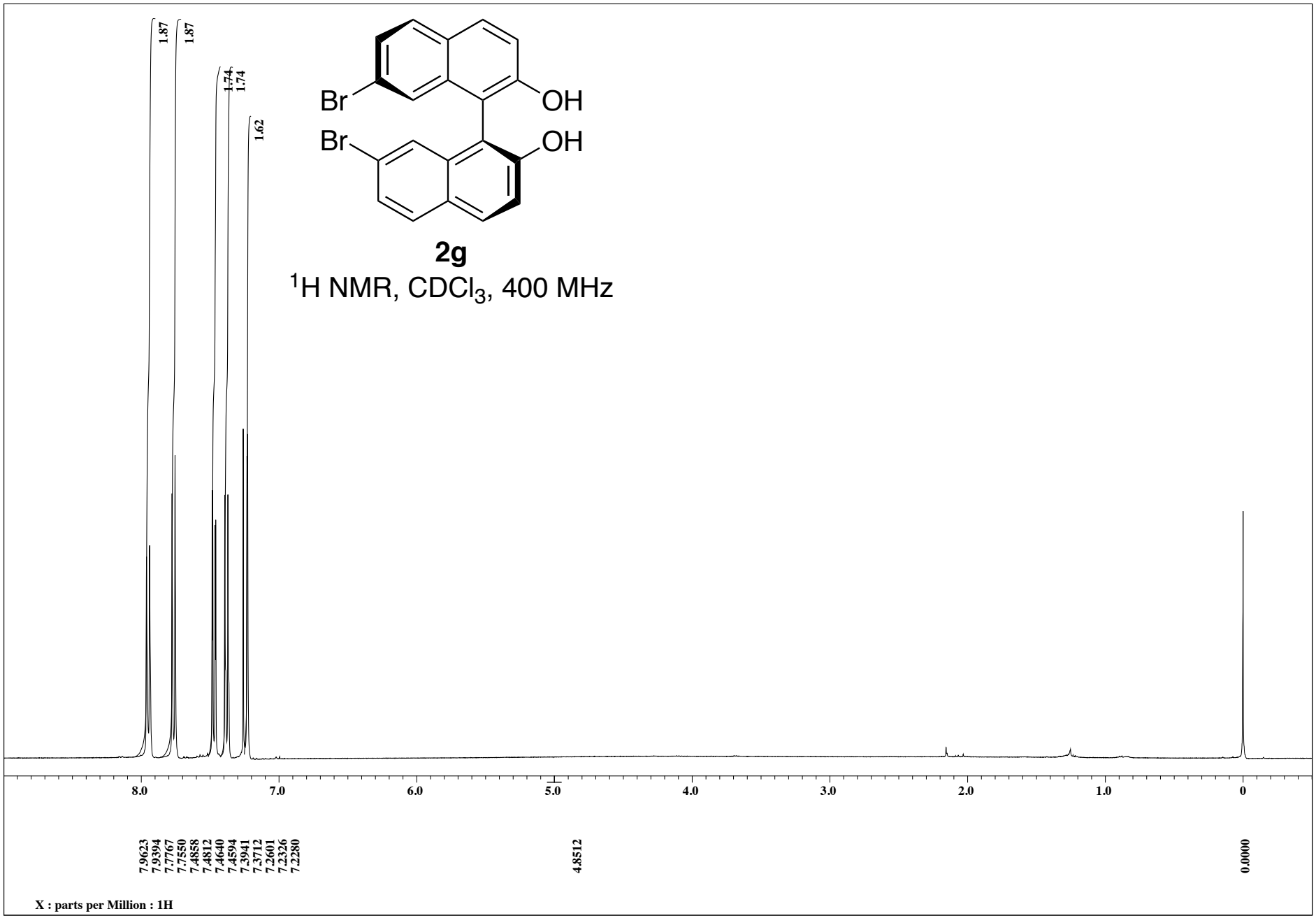
^{13}C NMR spectrum of **2e** ($CDCl_3$, 100 MHz)



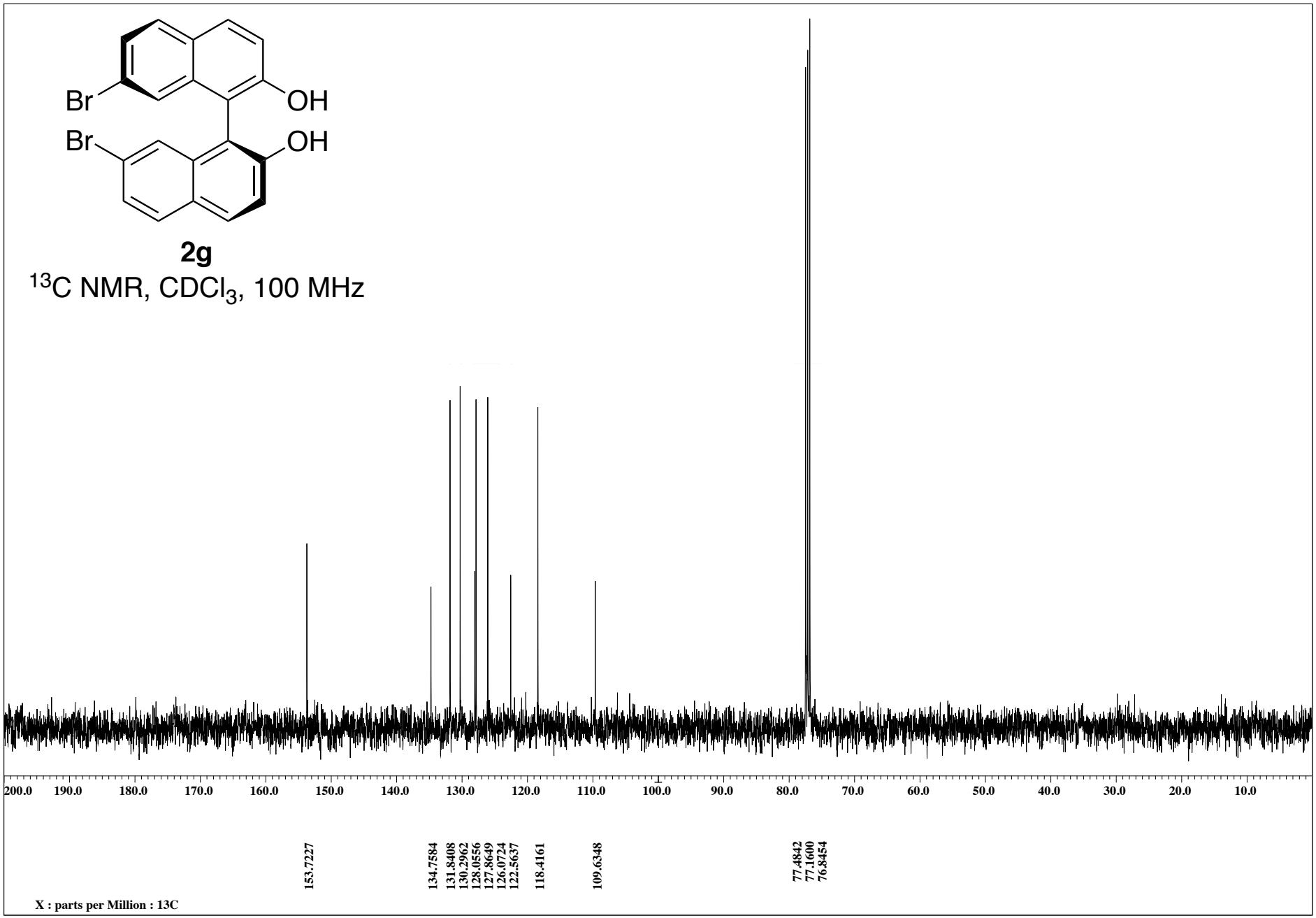
^{1}H NMR spectrum of **2f** ($CDCl_3$, 400 MHz)



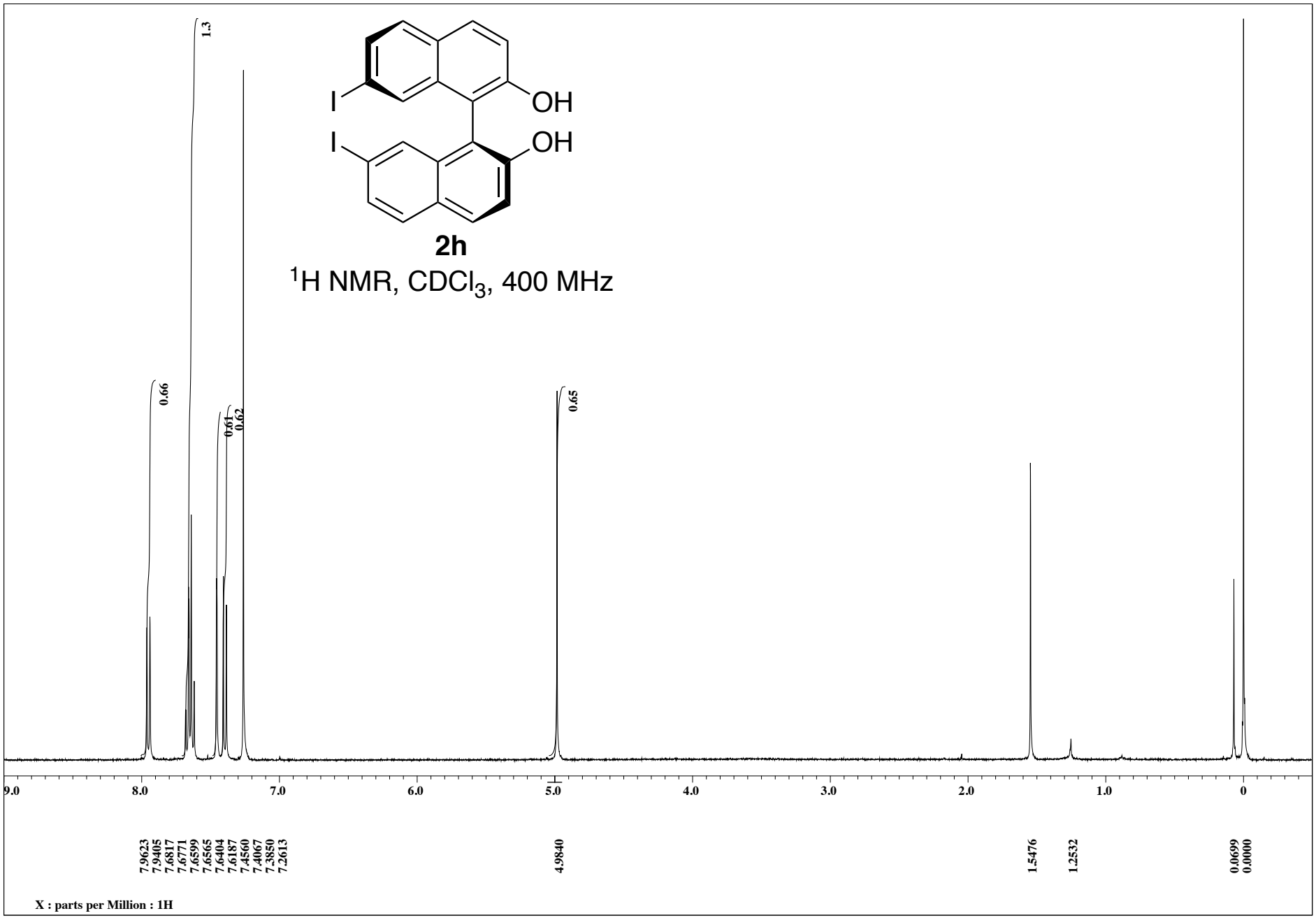
^{13}C NMR spectrum of **2f** ($CDCl_3$, 100 MHz)



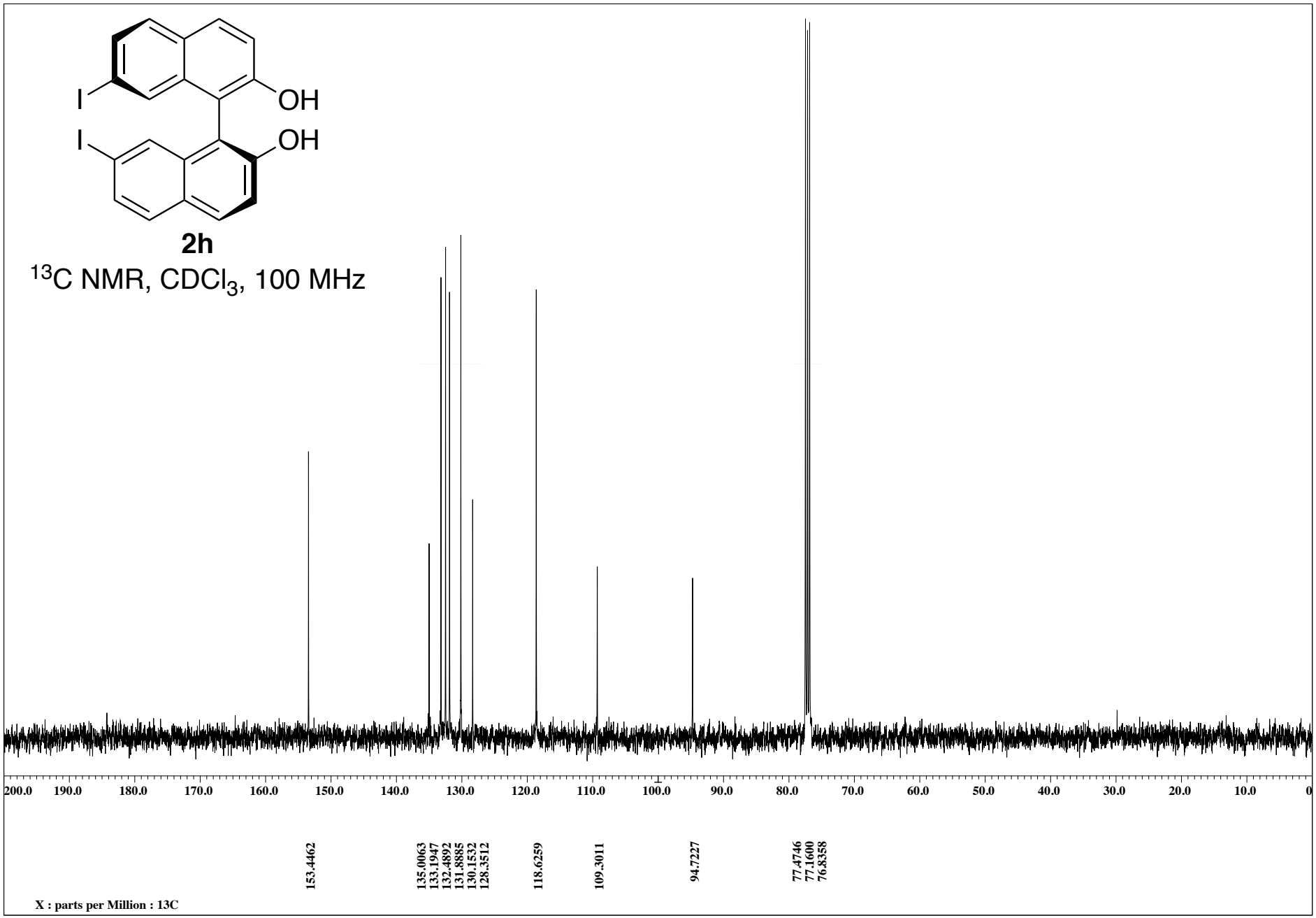
^{1}H NMR spectrum of **2g** ($CDCl_3$, 400 MHz)



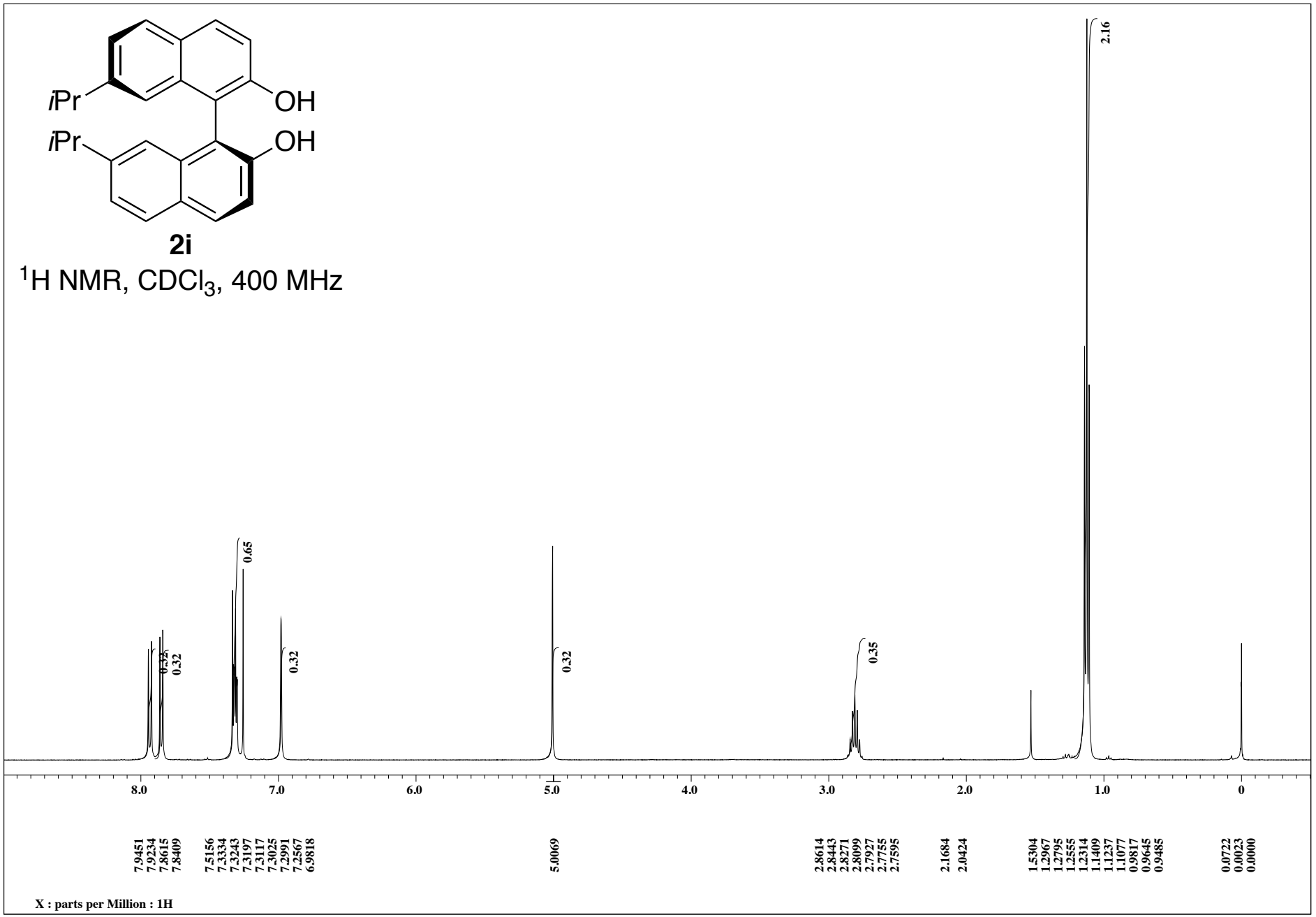
^{13}C NMR spectrum of **2g** ($CDCl_3$, 100 MHz)



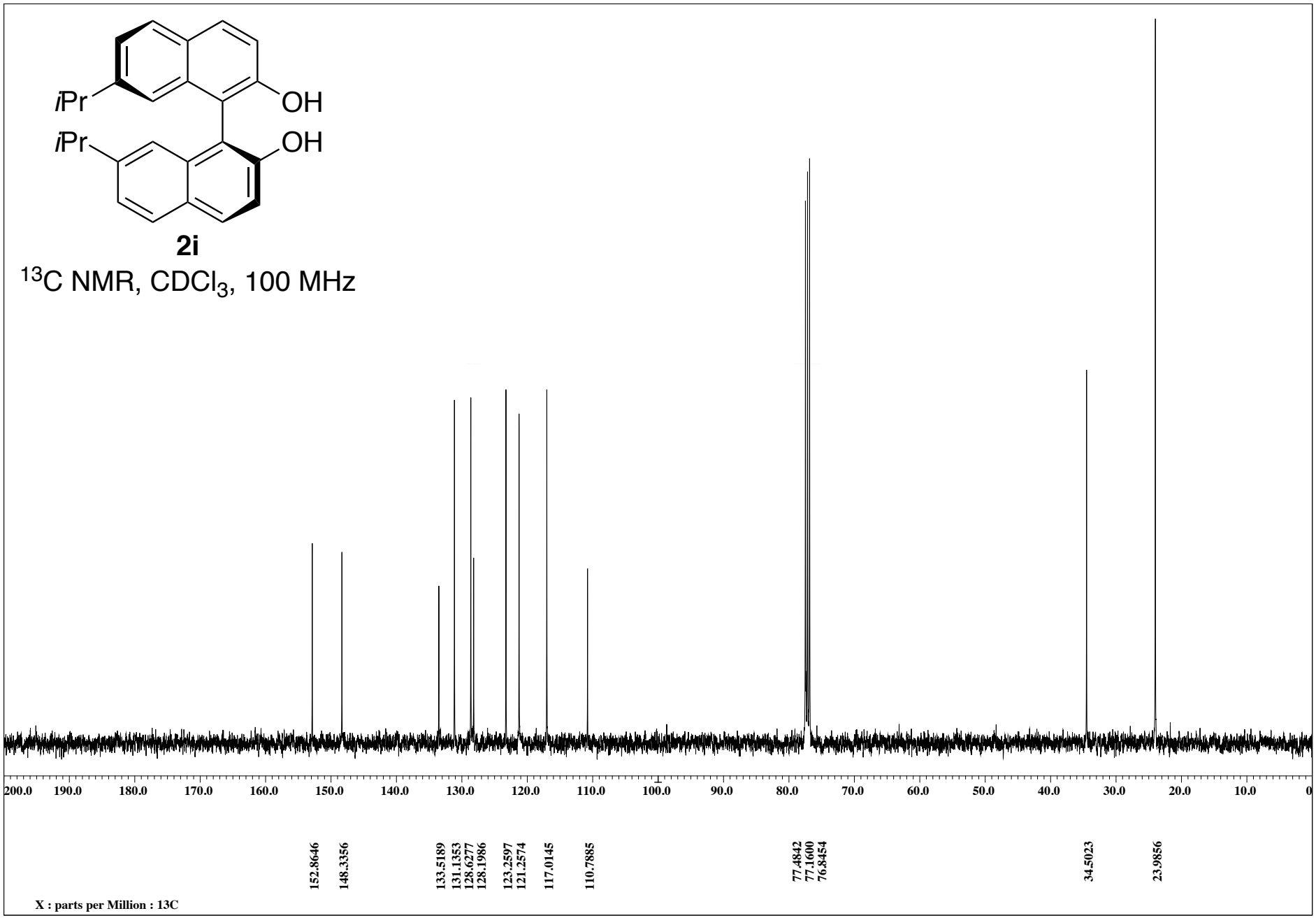
^{1}H NMR spectrum of **2h** ($CDCl_3$, 400 MHz)



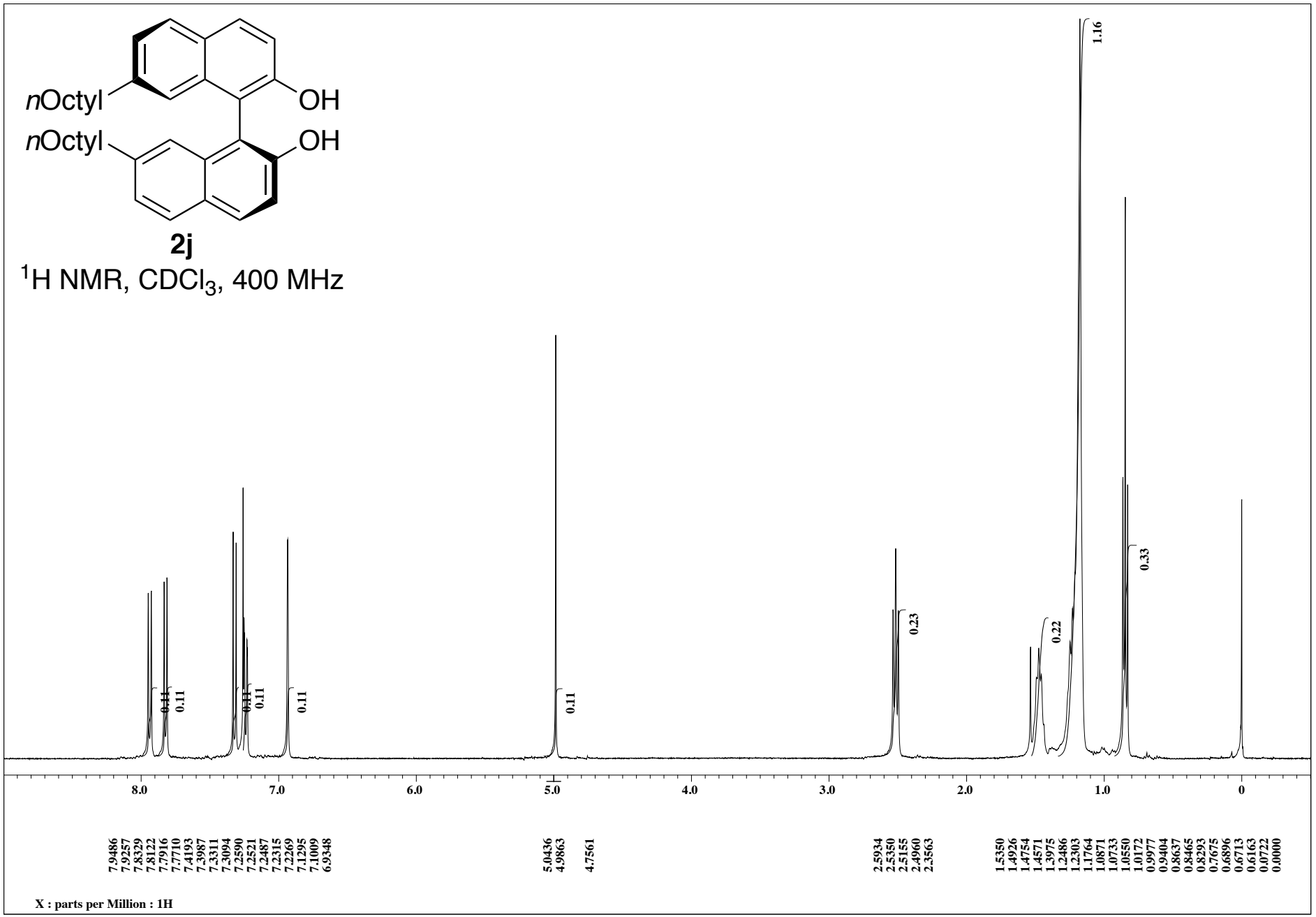
^{13}C NMR spectrum of **2h** ($CDCl_3$, 100 MHz)



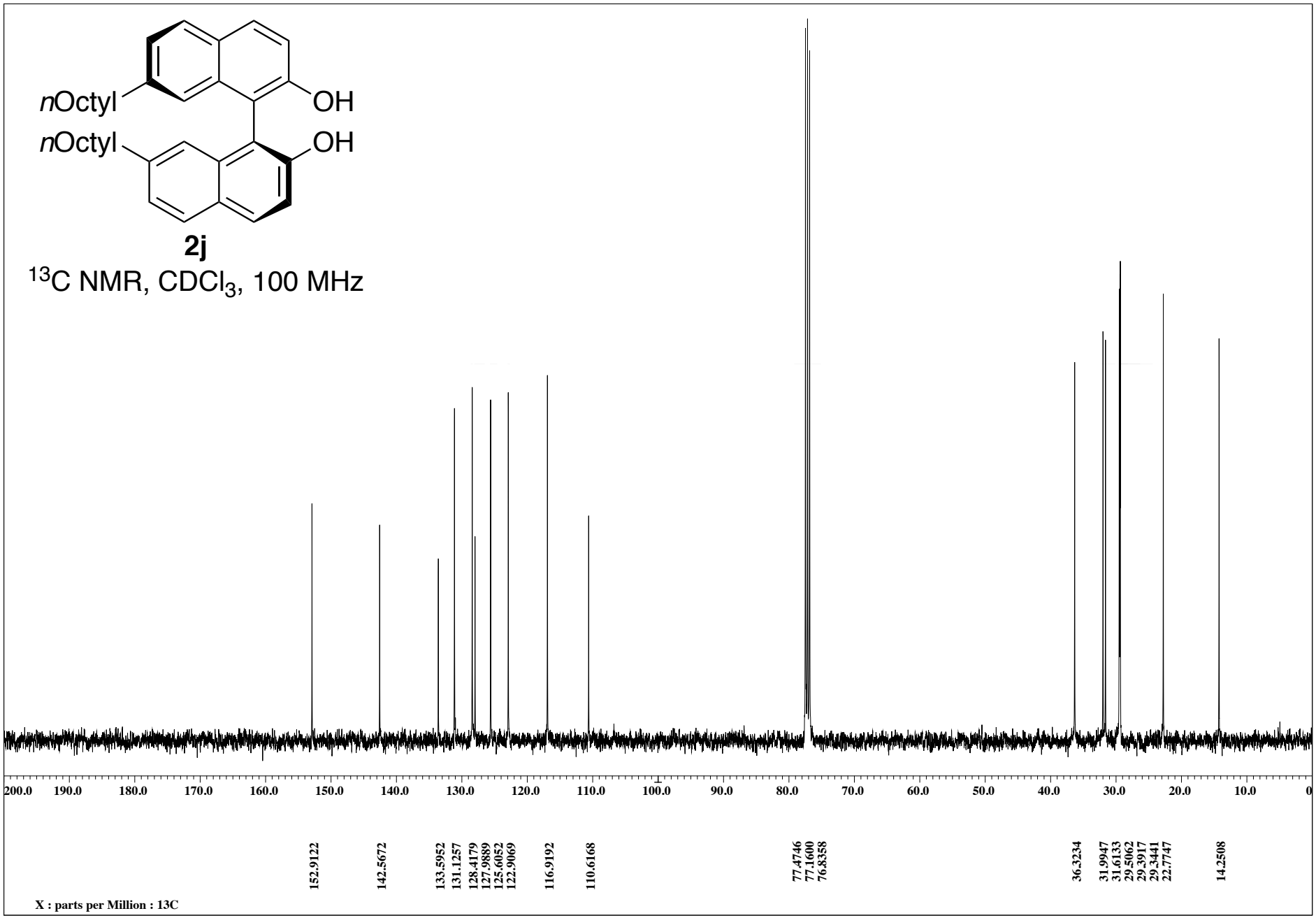
^{1}H NMR spectrum of **2i** ($CDCl_3$, 400 MHz)



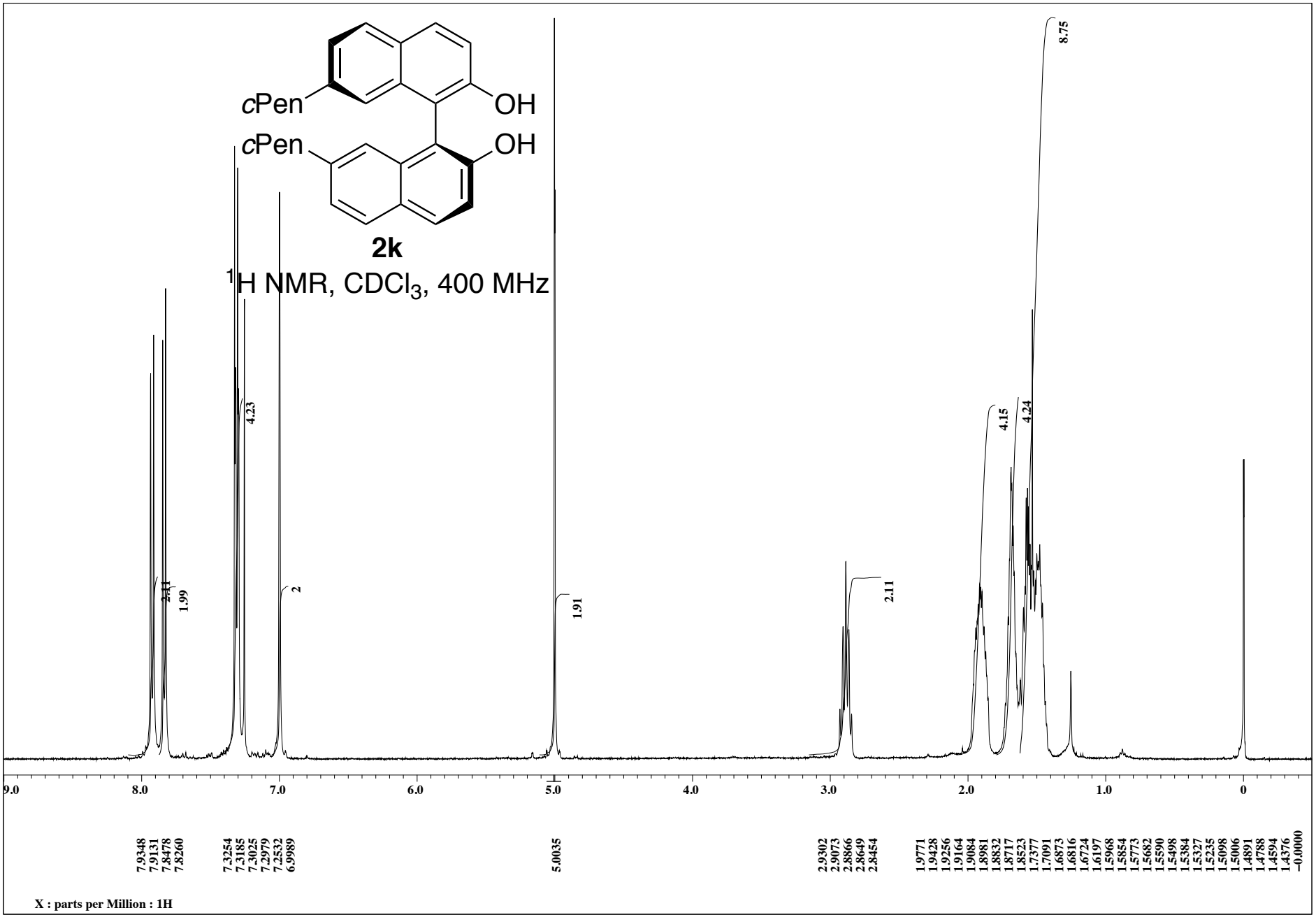
^{13}C NMR spectrum of **2i** ($CDCl_3$, 100 MHz)



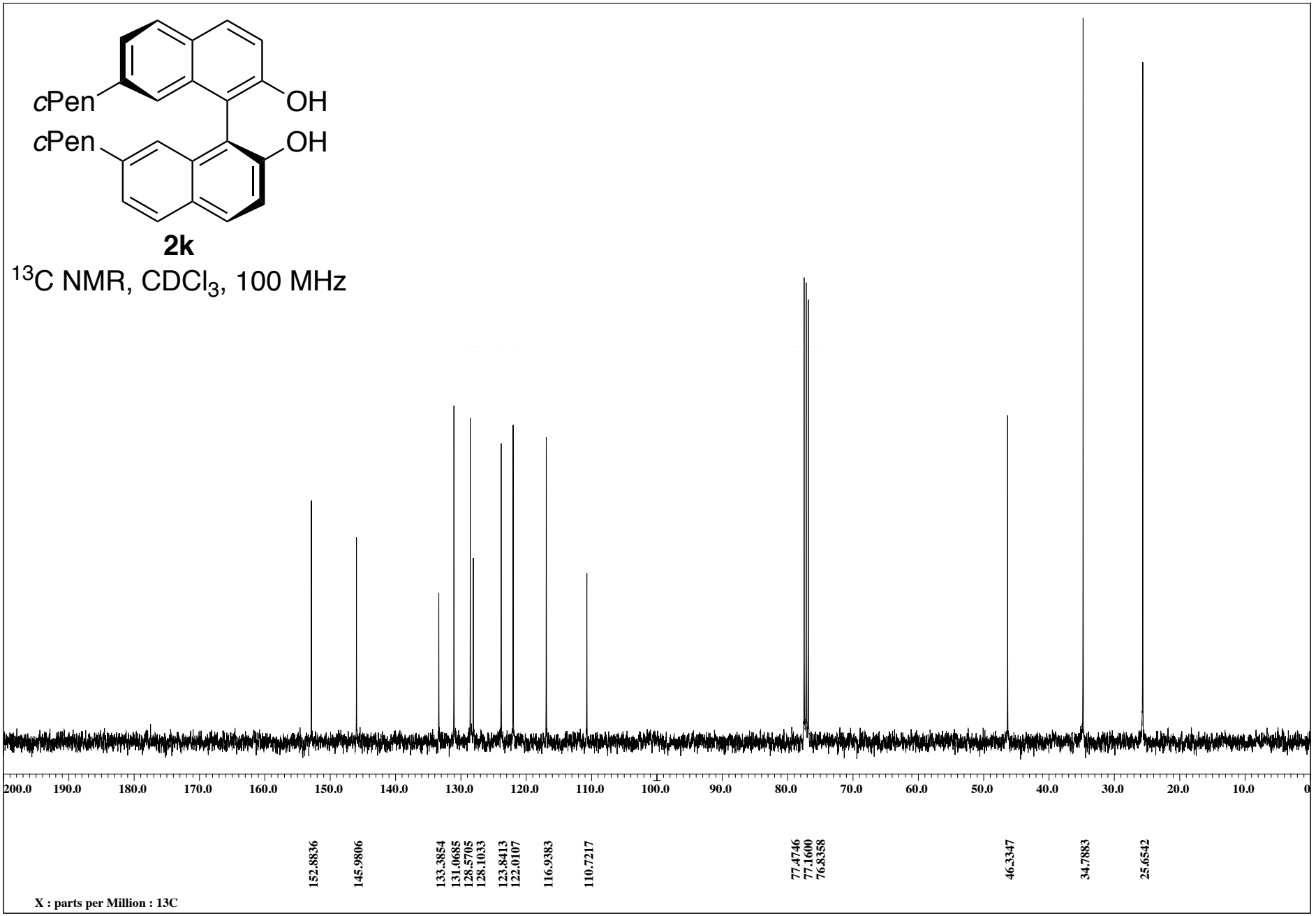
^{1}H NMR spectrum of **2j** ($CDCl_3$, 400 MHz)



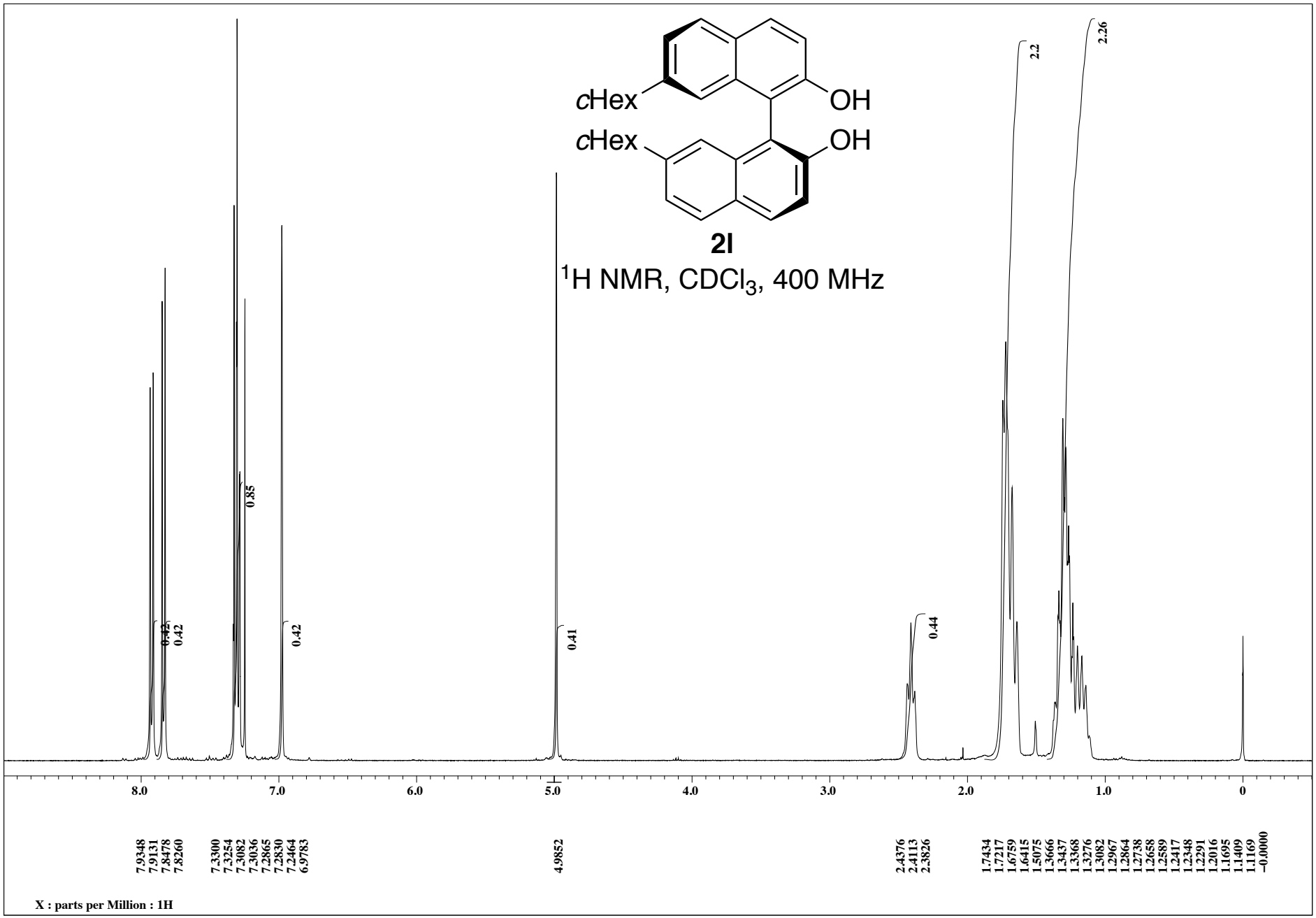
^{13}C NMR spectrum of **2j** ($CDCl_3$, 100 MHz)



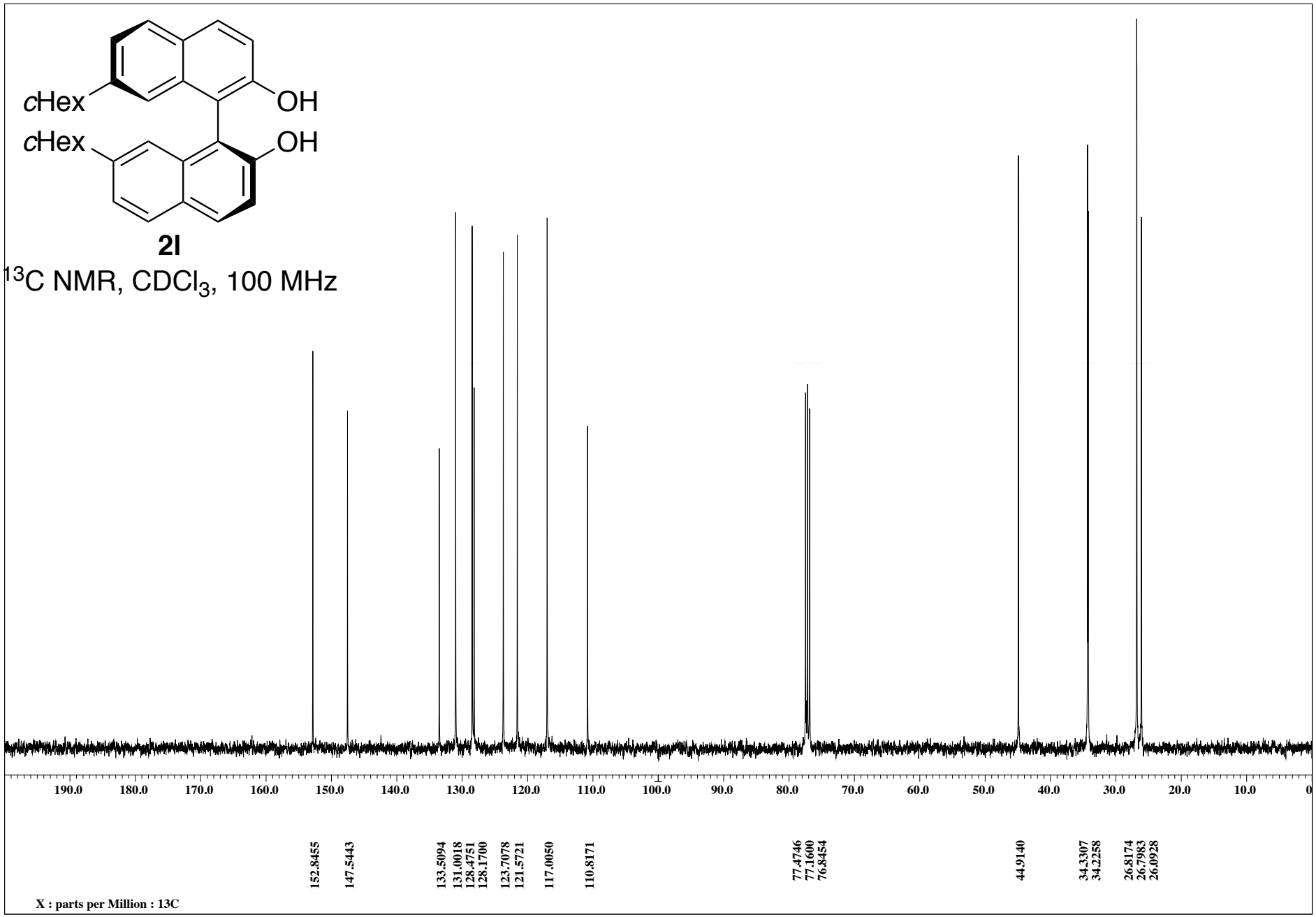
^{1}H NMR spectrum of **2k** ($CDCl_3$, 400 MHz)



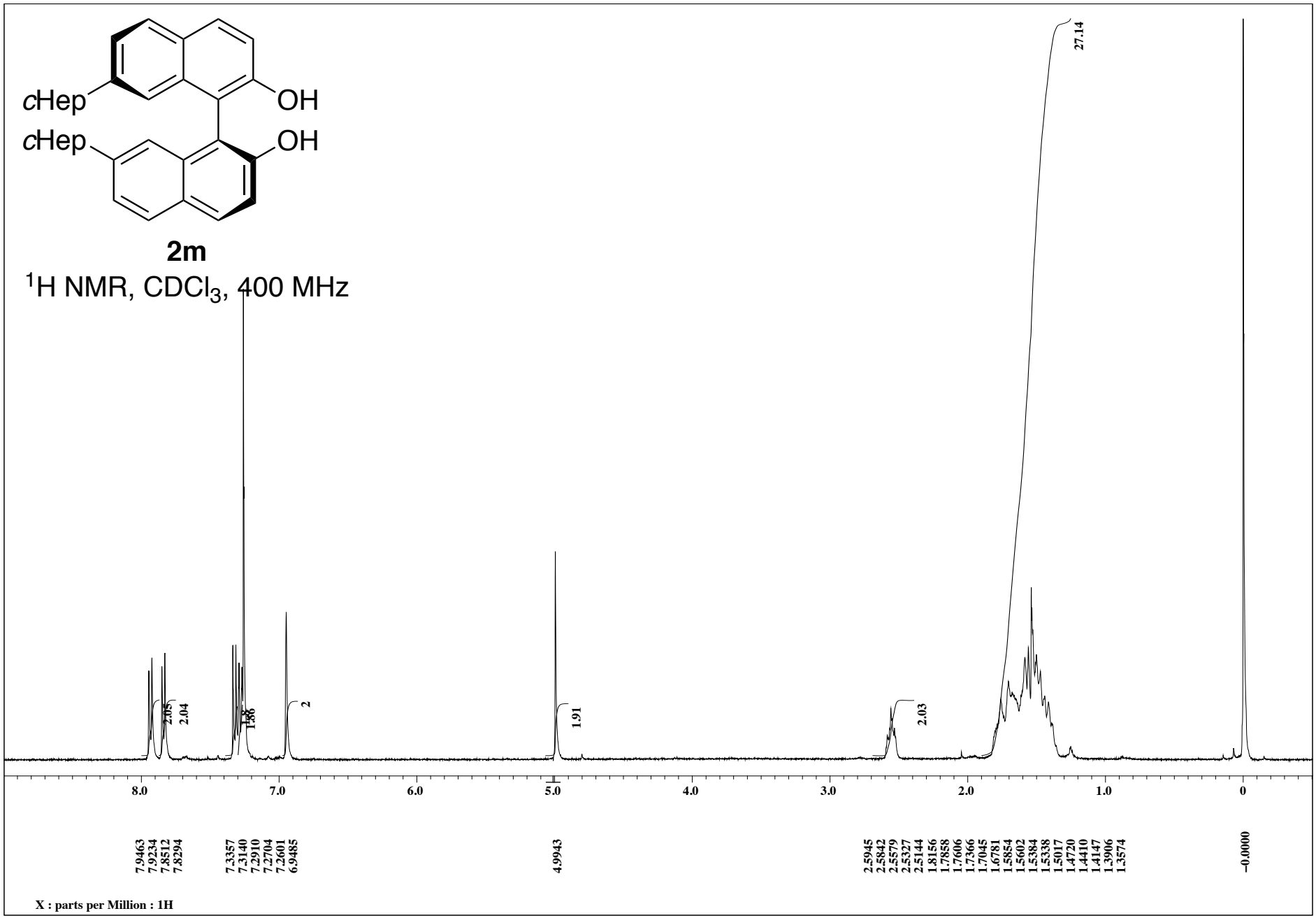
^{13}C NMR spectrum of **2k** ($CDCl_3$, 100 MHz)



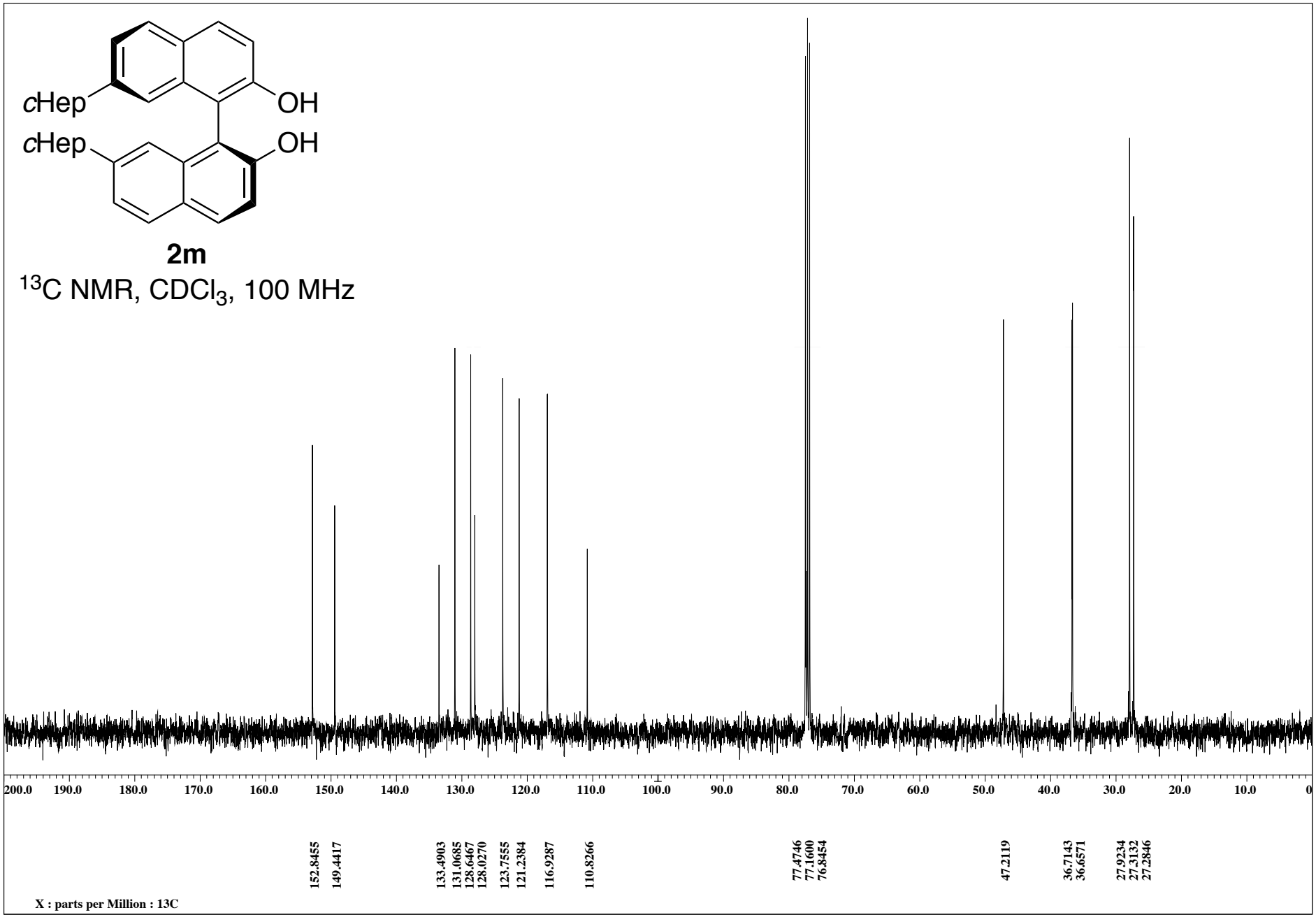
^{1}H NMR spectrum of **2l** ($CDCl_3$, 400 MHz)



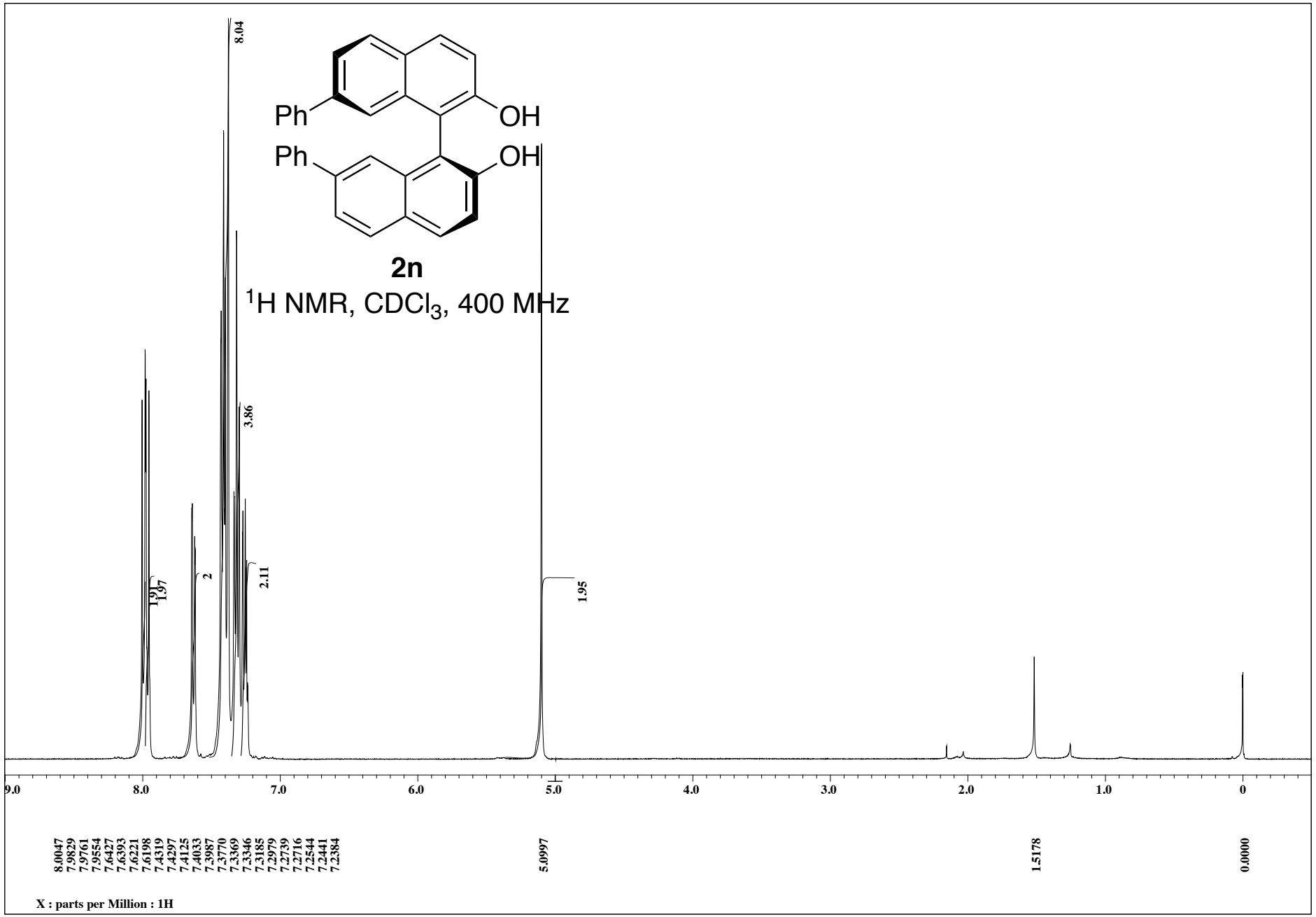
^{13}C NMR spectrum of **2l** ($CDCl_3$, 100 MHz)



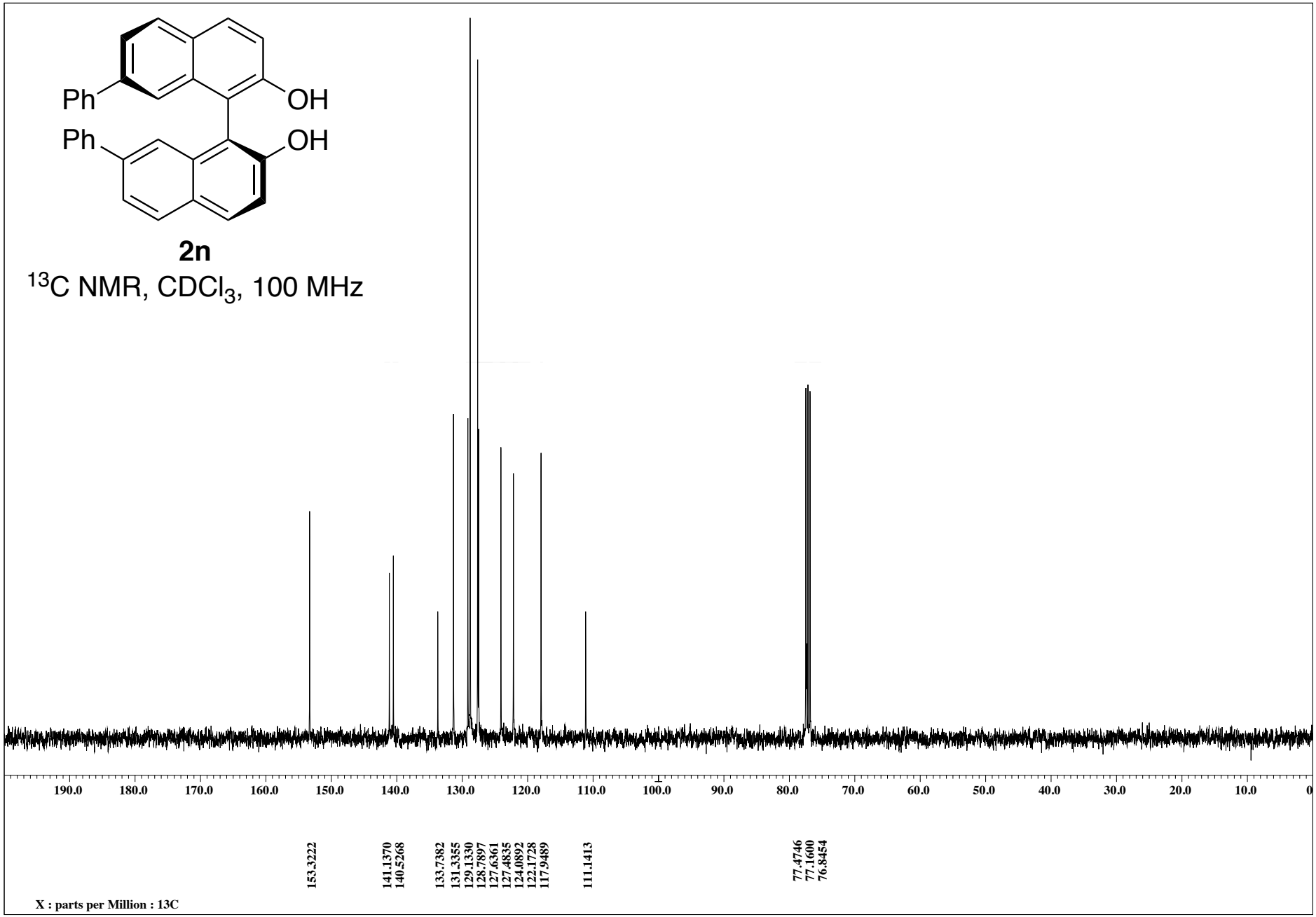
^{1}H NMR spectrum of **2m** ($CDCl_3$, 400 MHz)



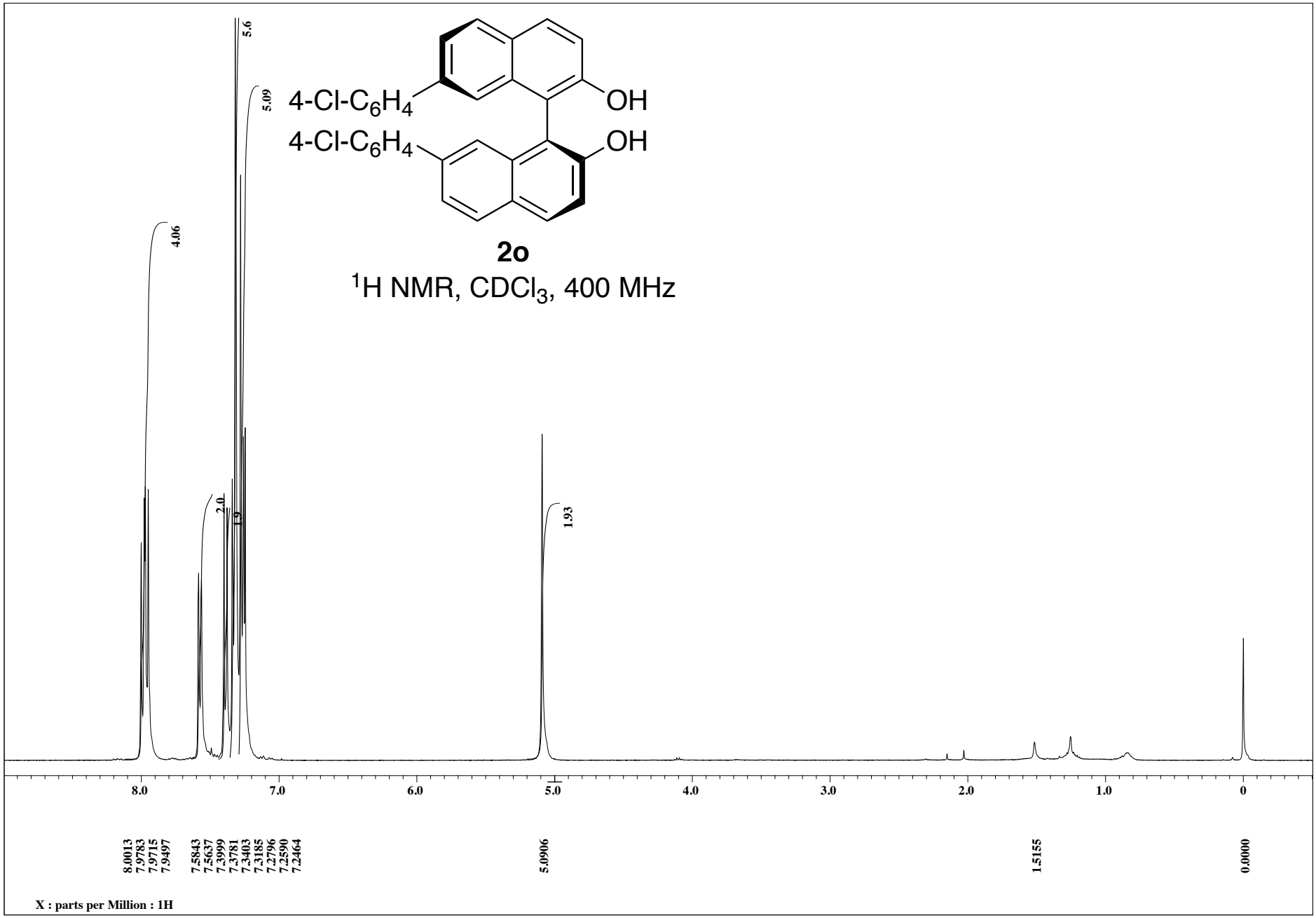
^{13}C NMR spectrum of **2m** ($CDCl_3$, 100 MHz)



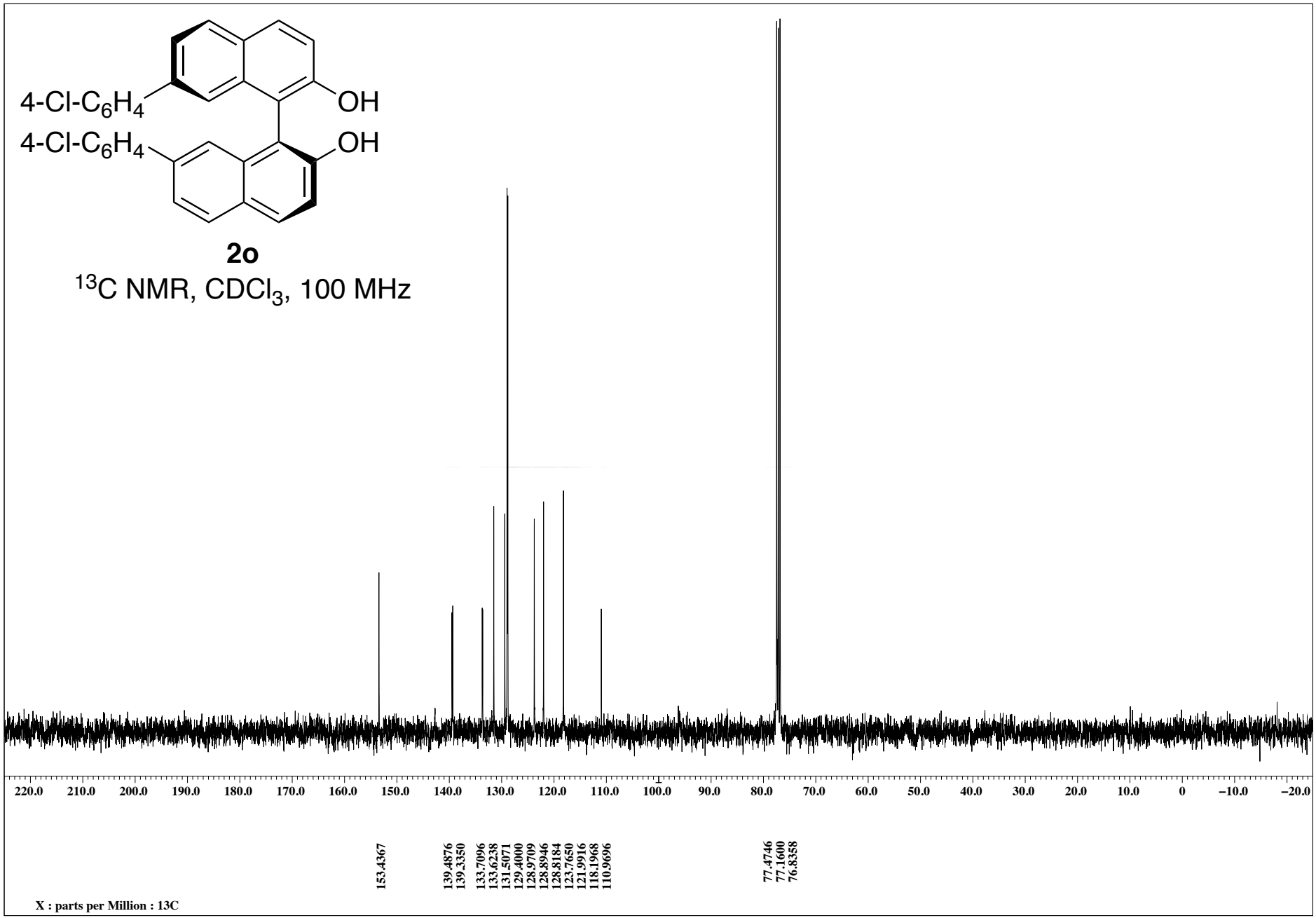
^{1}H NMR spectrum of **2n** ($CDCl_3$, 400 MHz)



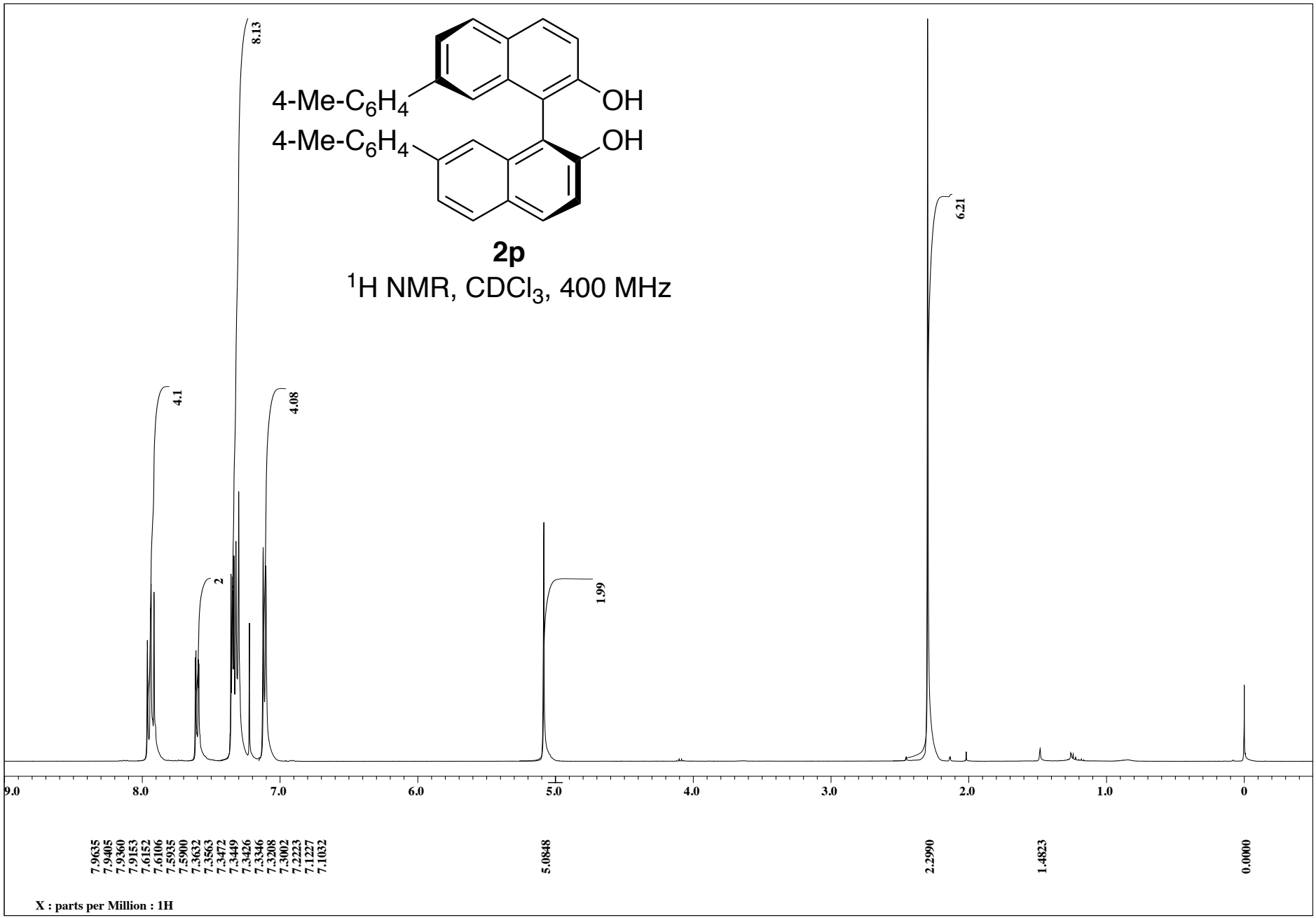
^{13}C NMR spectrum of **2n** ($CDCl_3$, 100 MHz)



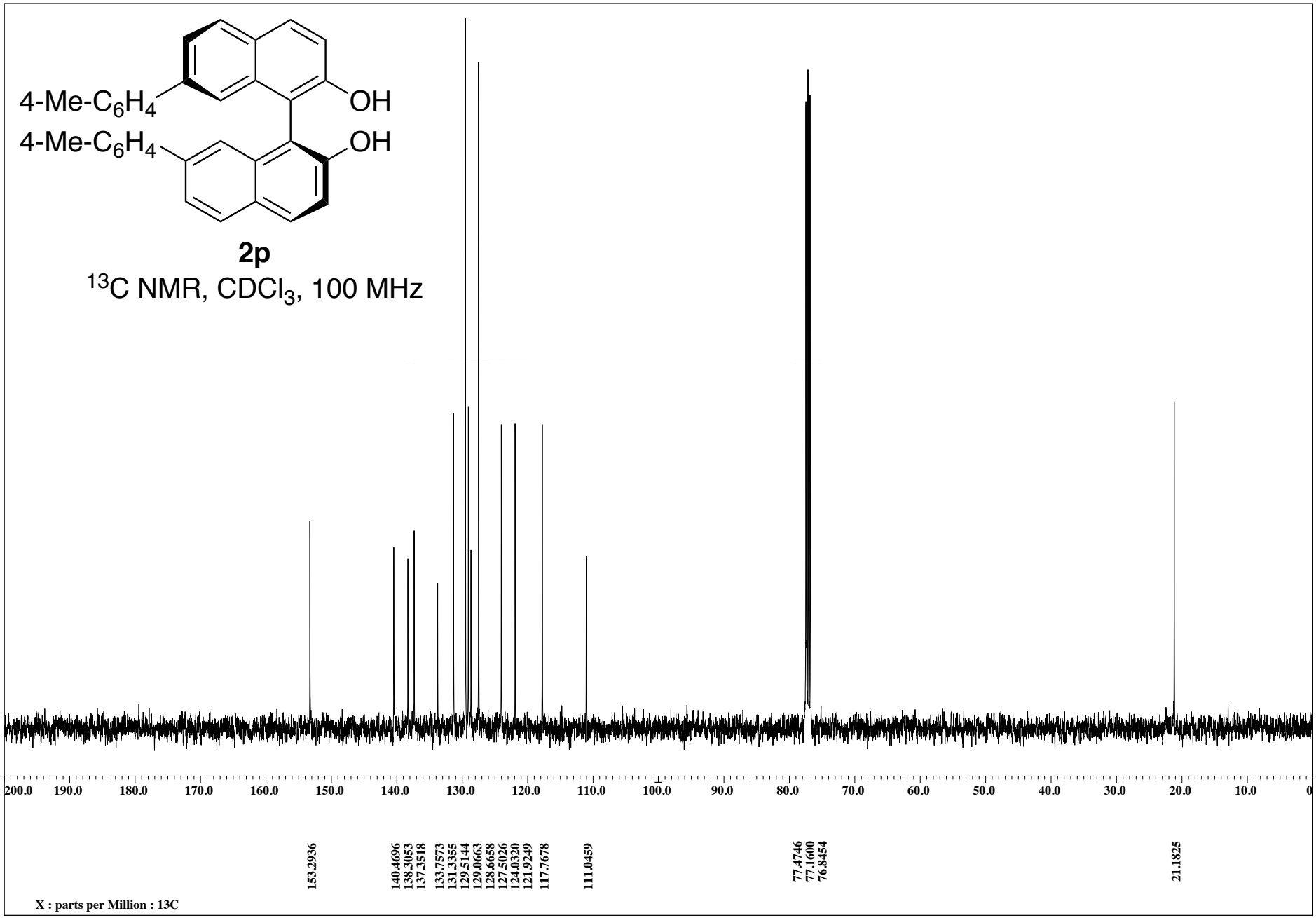
^{1}H NMR spectrum of **2o** ($CDCl_3$, 400 MHz)



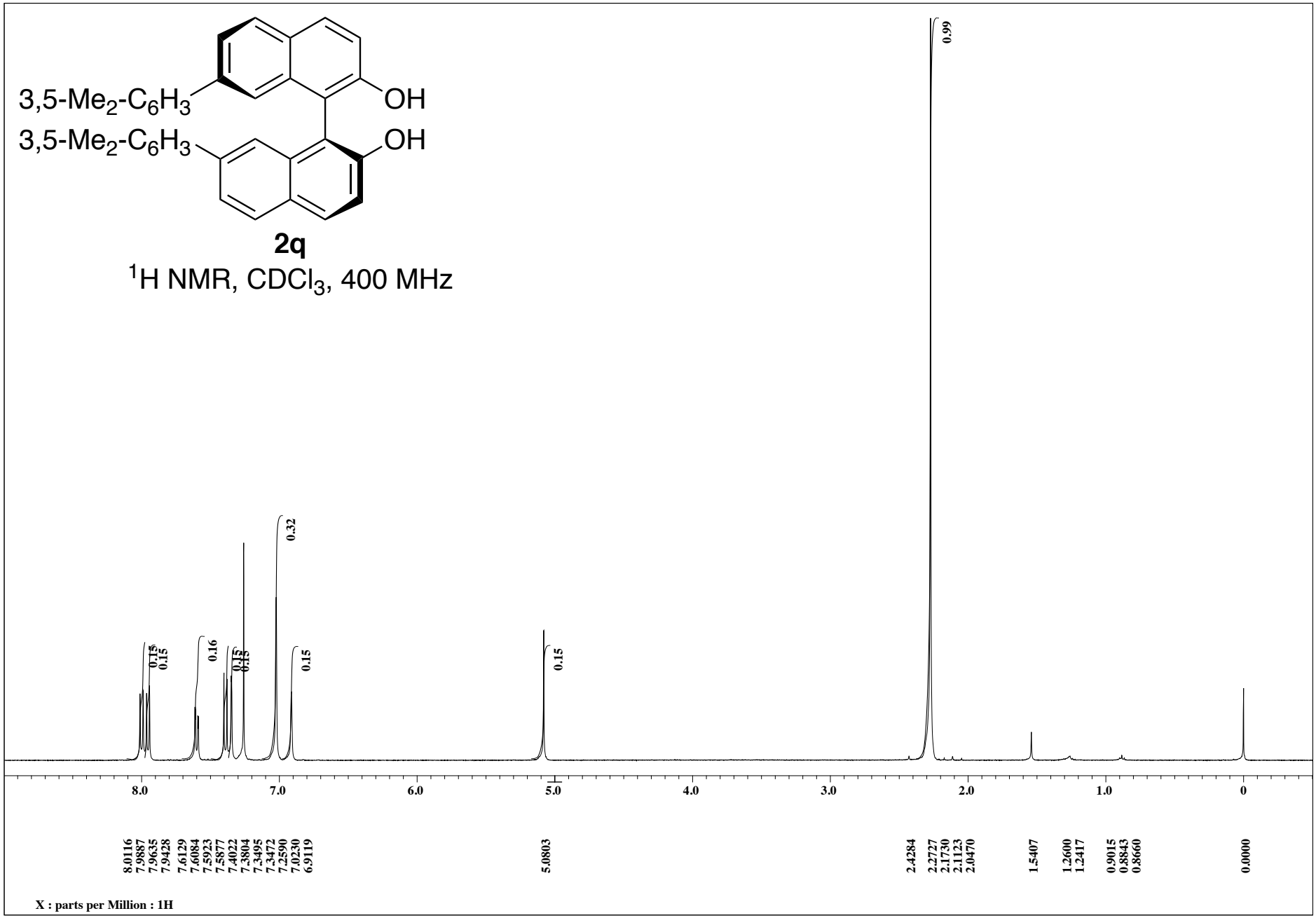
^{13}C NMR spectrum of **2o** ($CDCl_3$, 100 MHz)



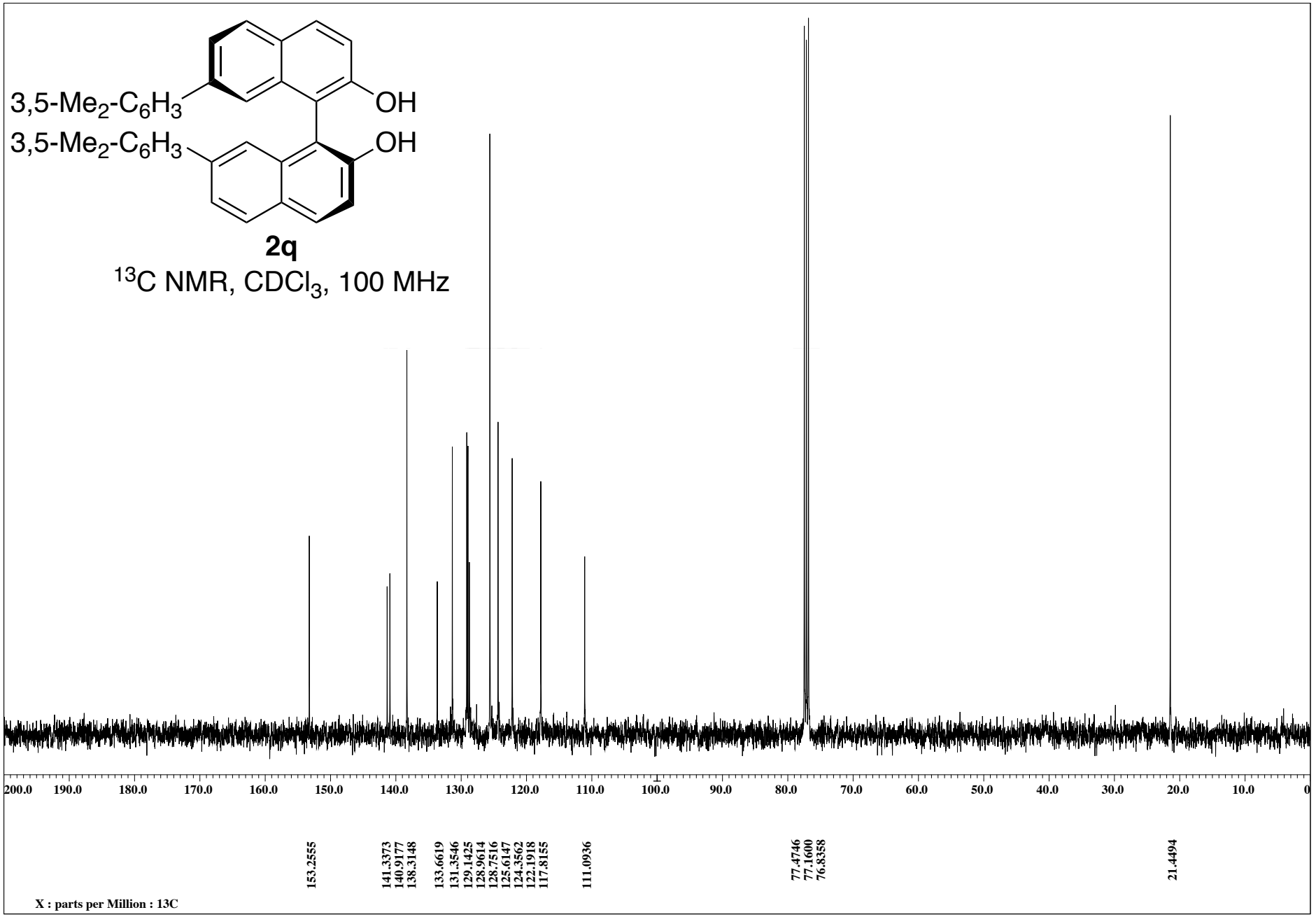
^{1}H NMR spectrum of **2p** ($CDCl_3$, 400 MHz)



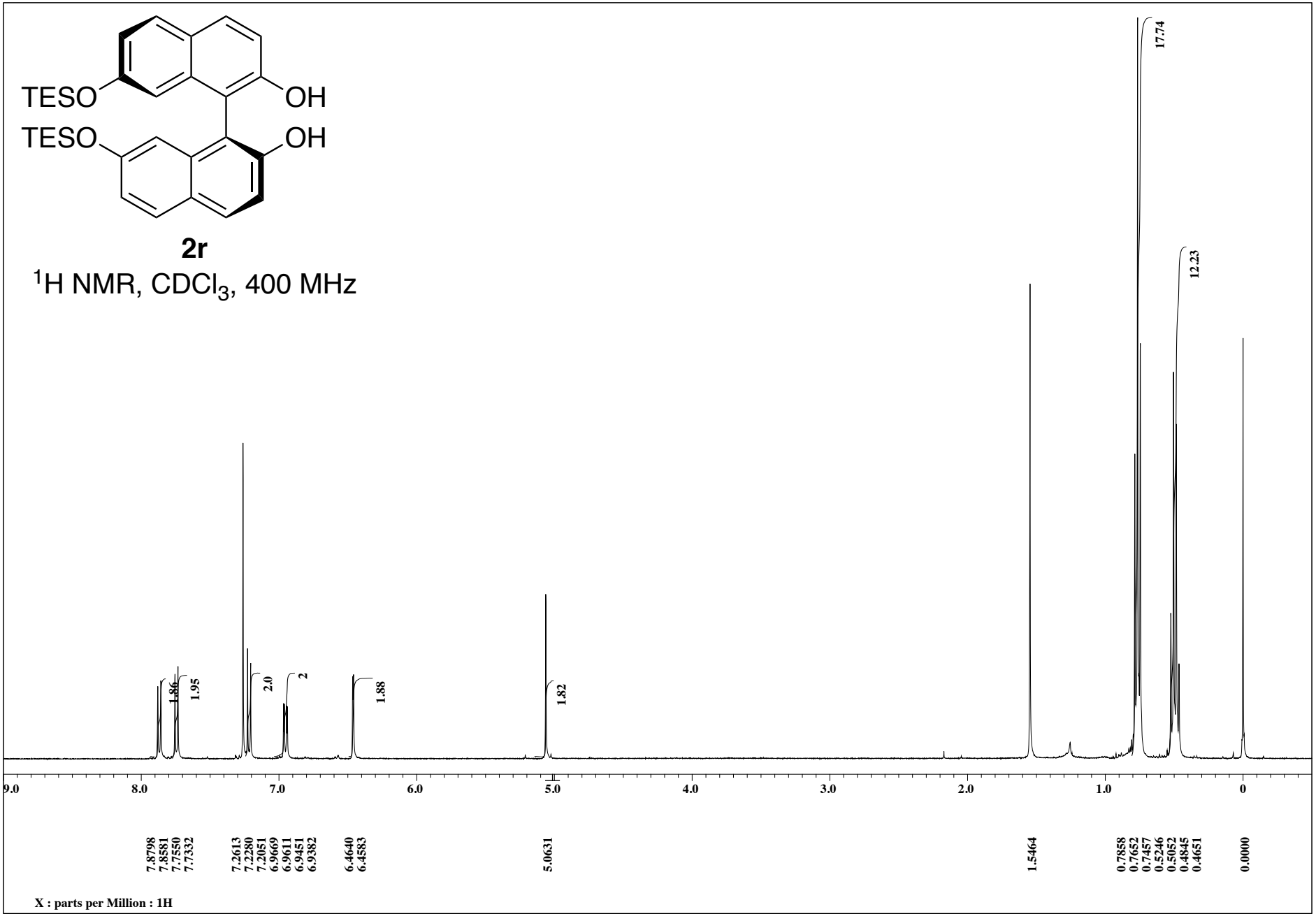
^{13}C NMR spectrum of **2p** ($CDCl_3$, 100 MHz)



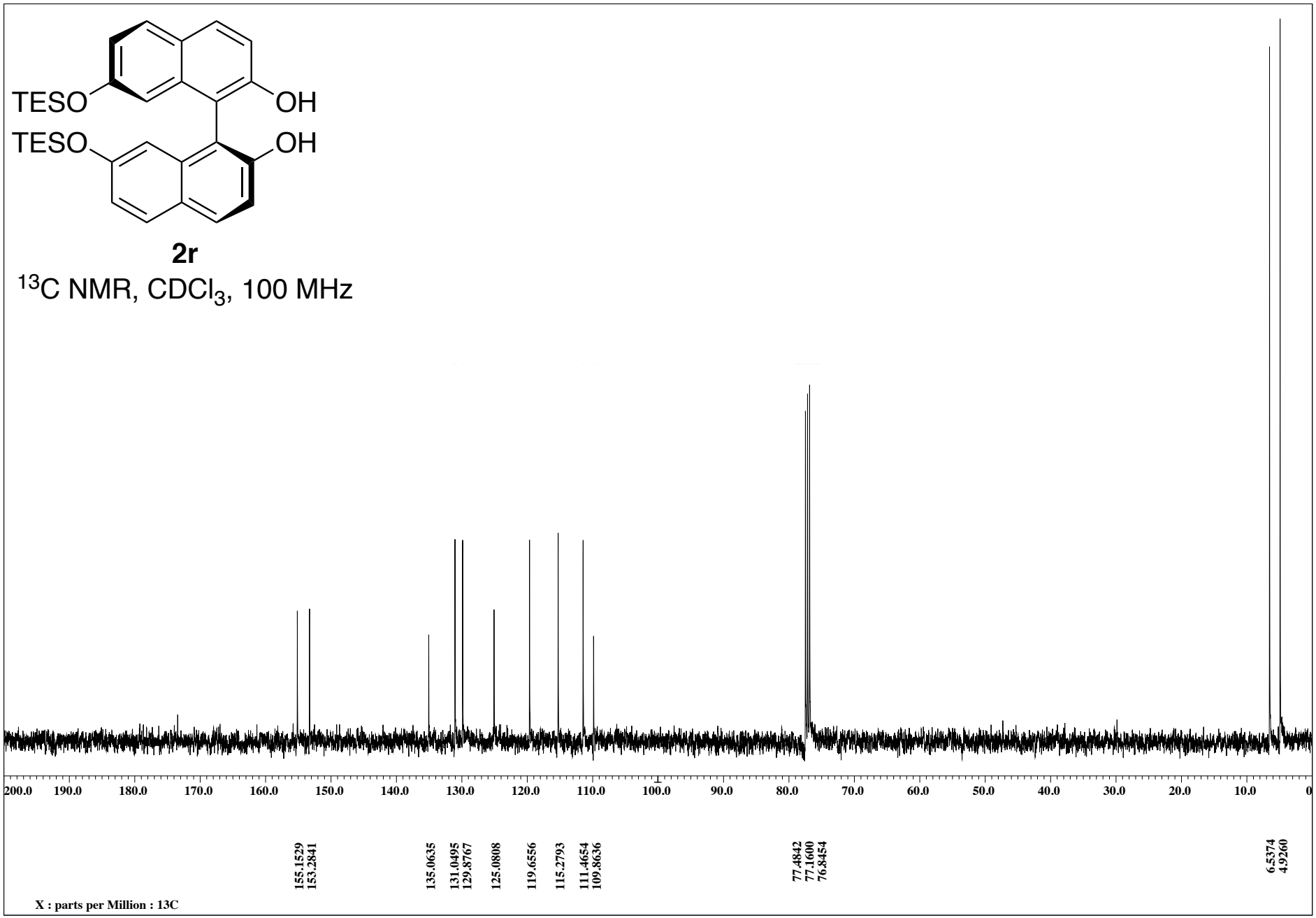
^{1}H NMR spectrum of **2q** ($CDCl_3$, 400 MHz)



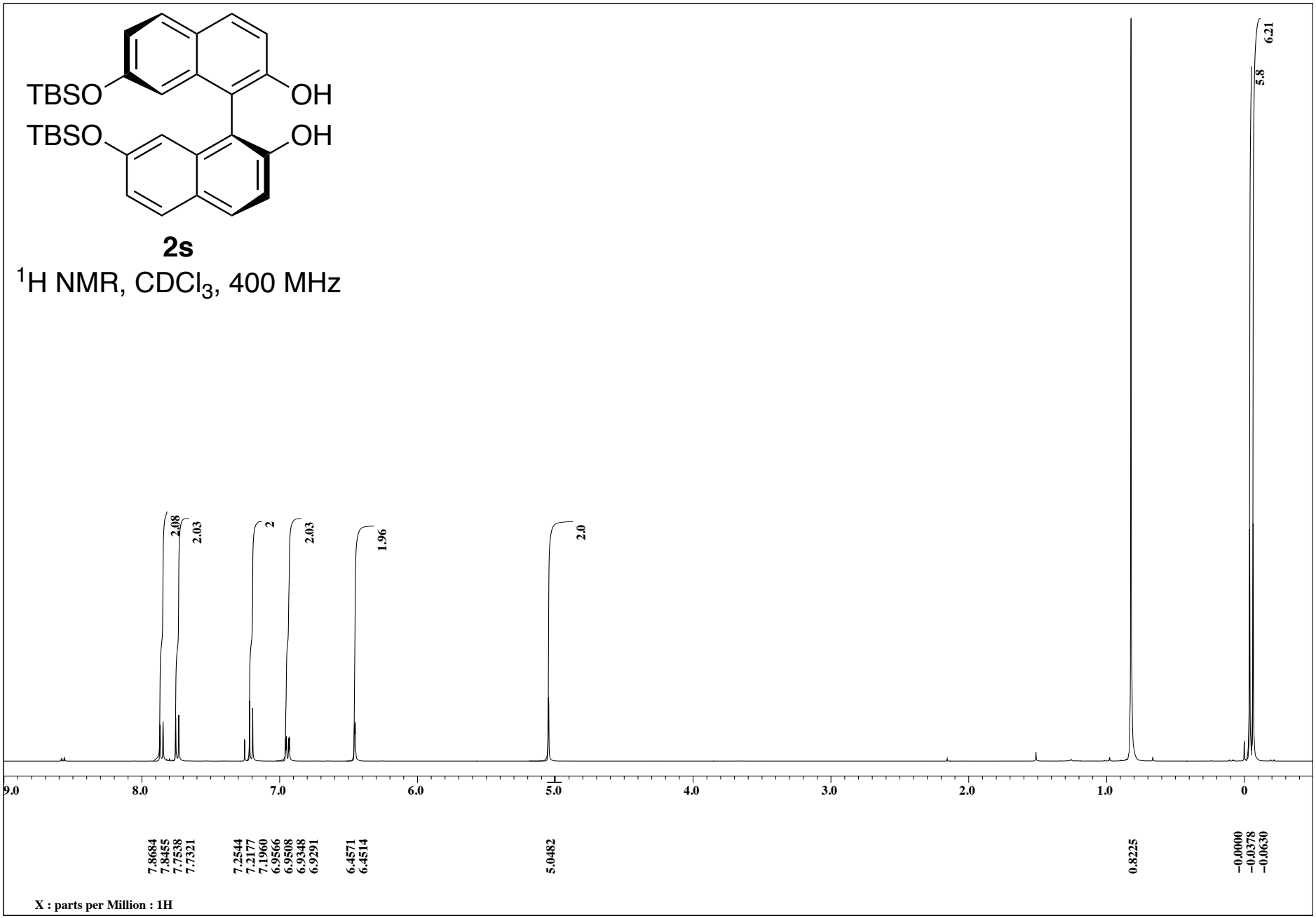
^{13}C NMR spectrum of **2q** ($CDCl_3$, 100 MHz)



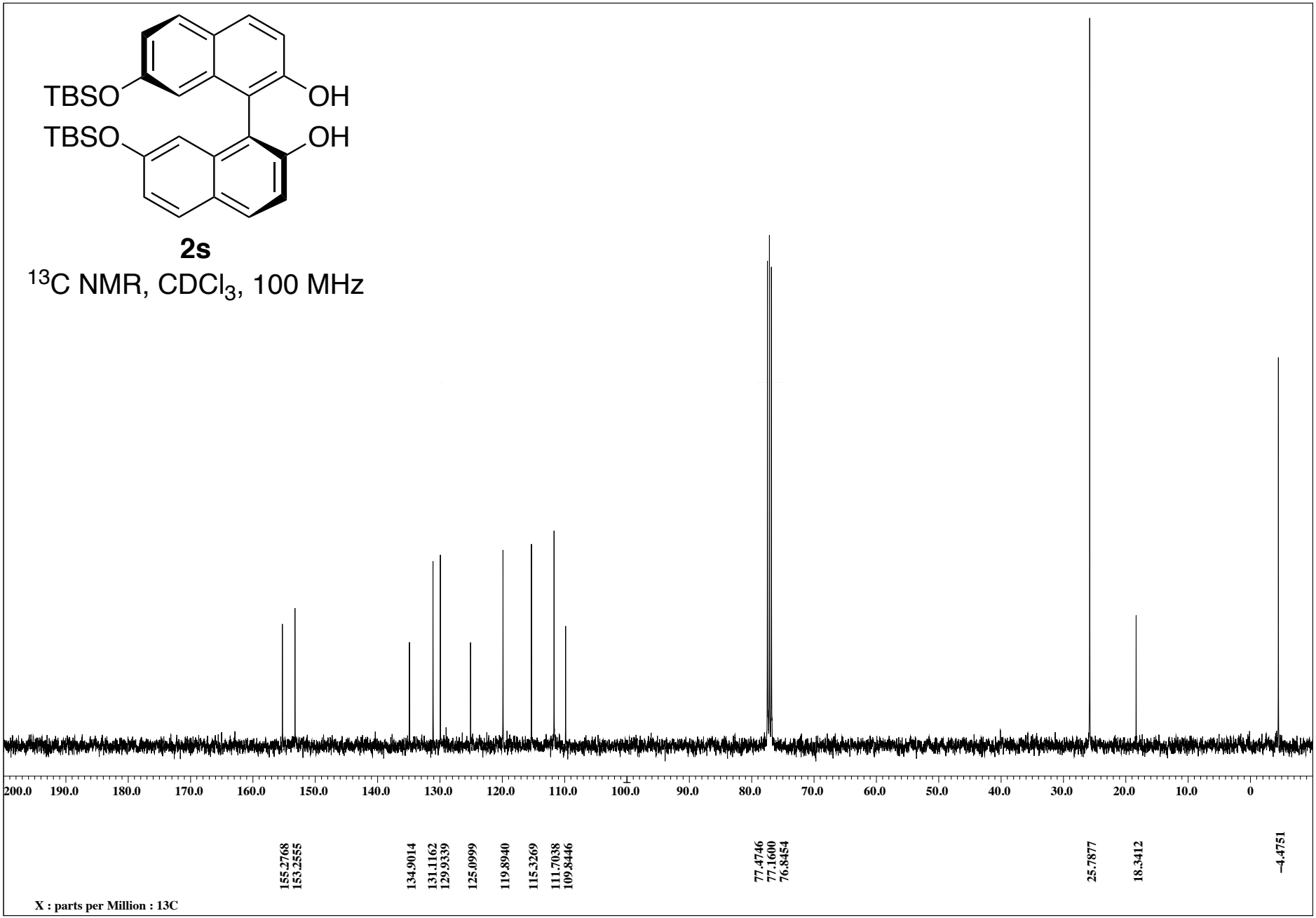
^{1}H NMR spectrum of **2r** ($CDCl_3$, 400 MHz)



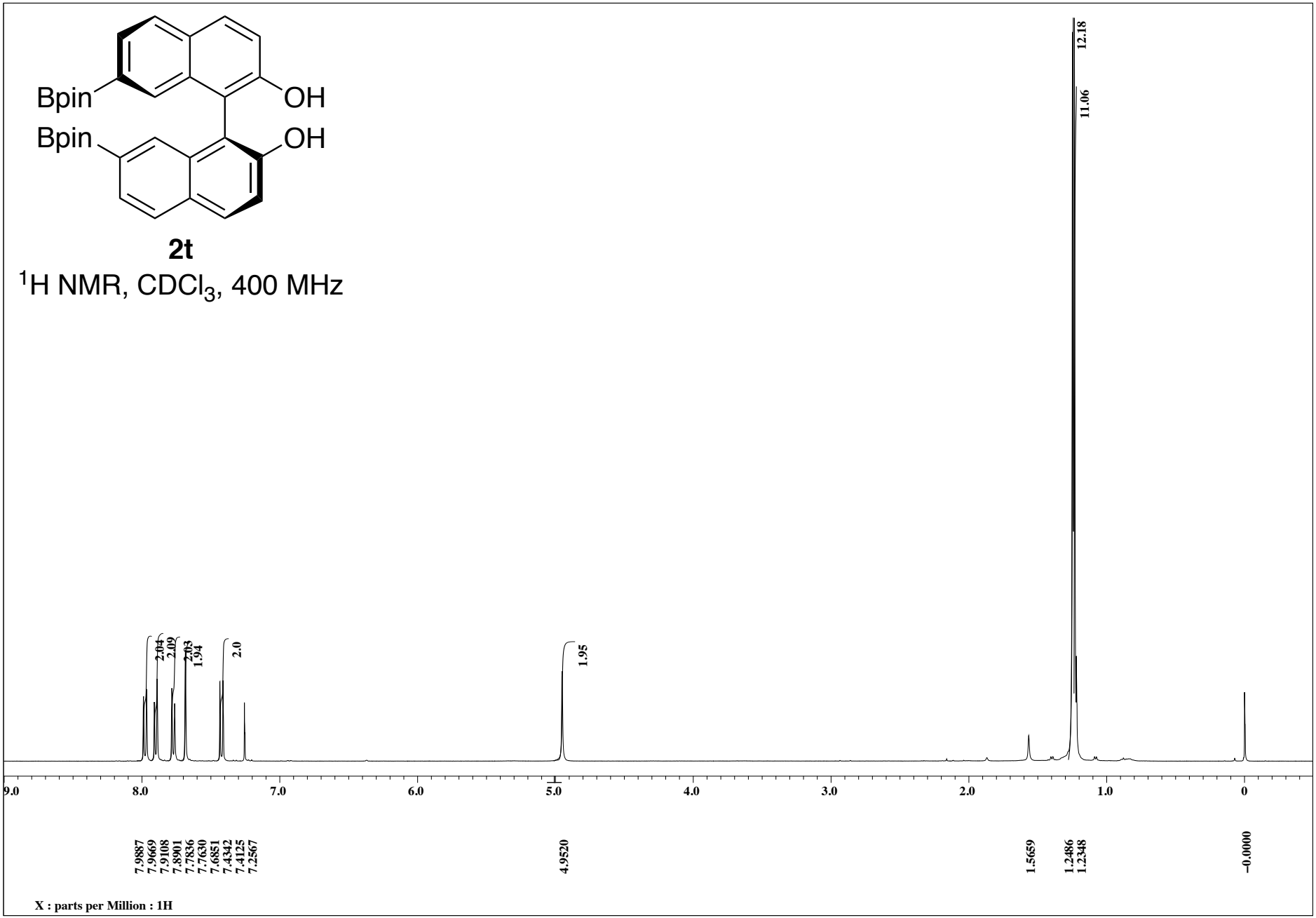
^{13}C NMR spectrum of **2r** ($CDCl_3$, 100 MHz)



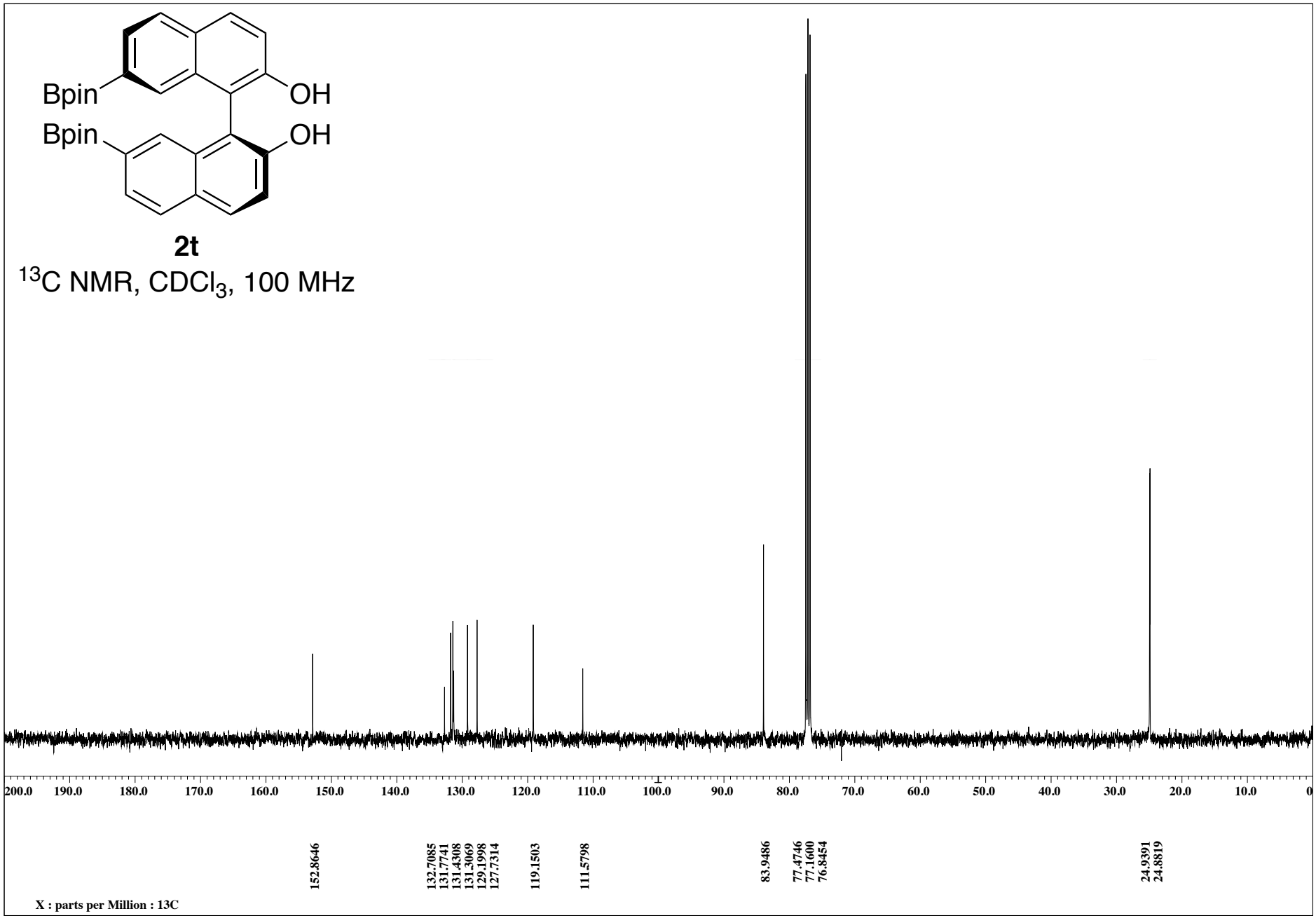
^{1}H NMR spectrum of **2s** ($CDCl_3$, 400 MHz)



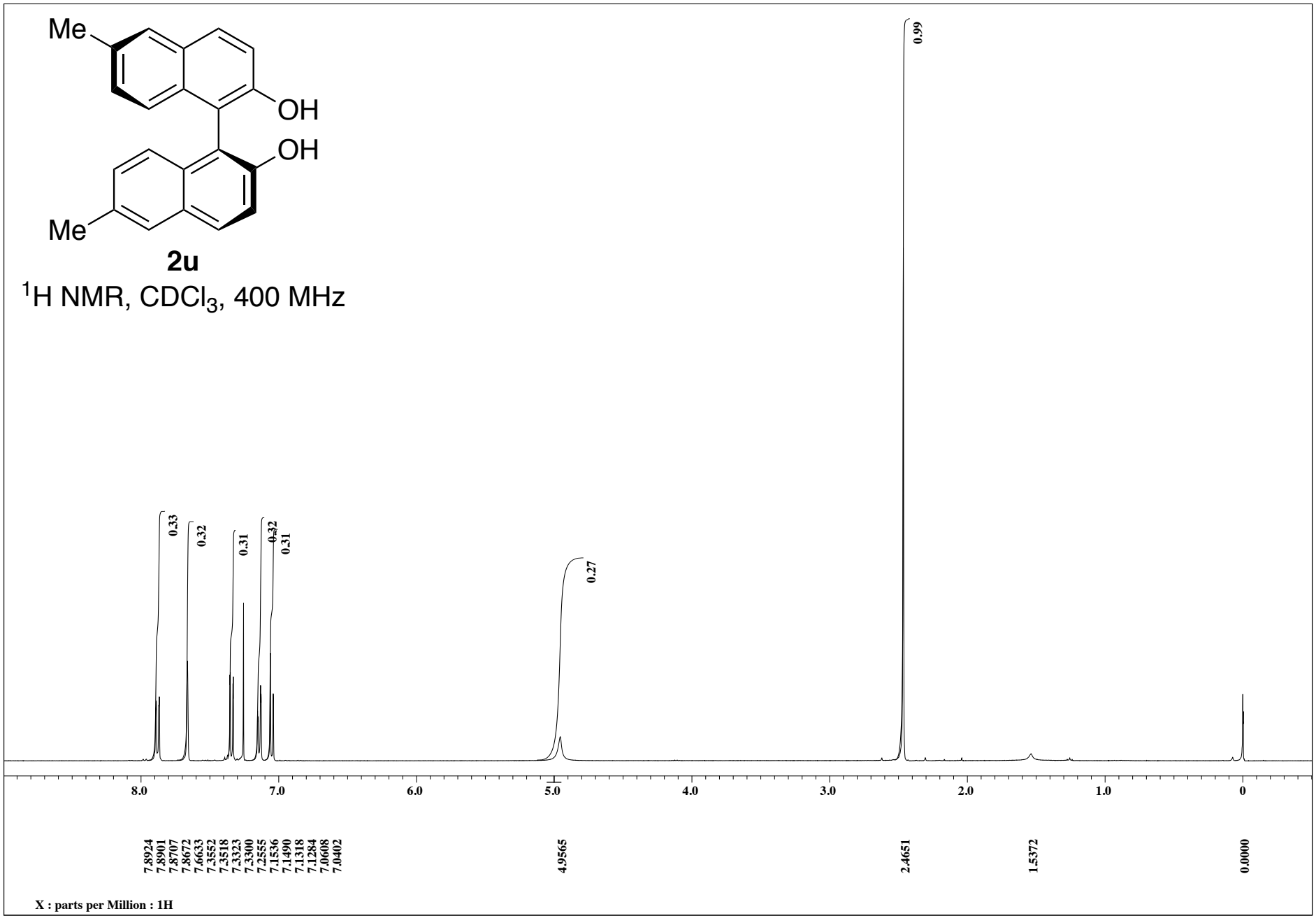
^{13}C NMR spectrum of **2s** ($CDCl_3$, 100 MHz)



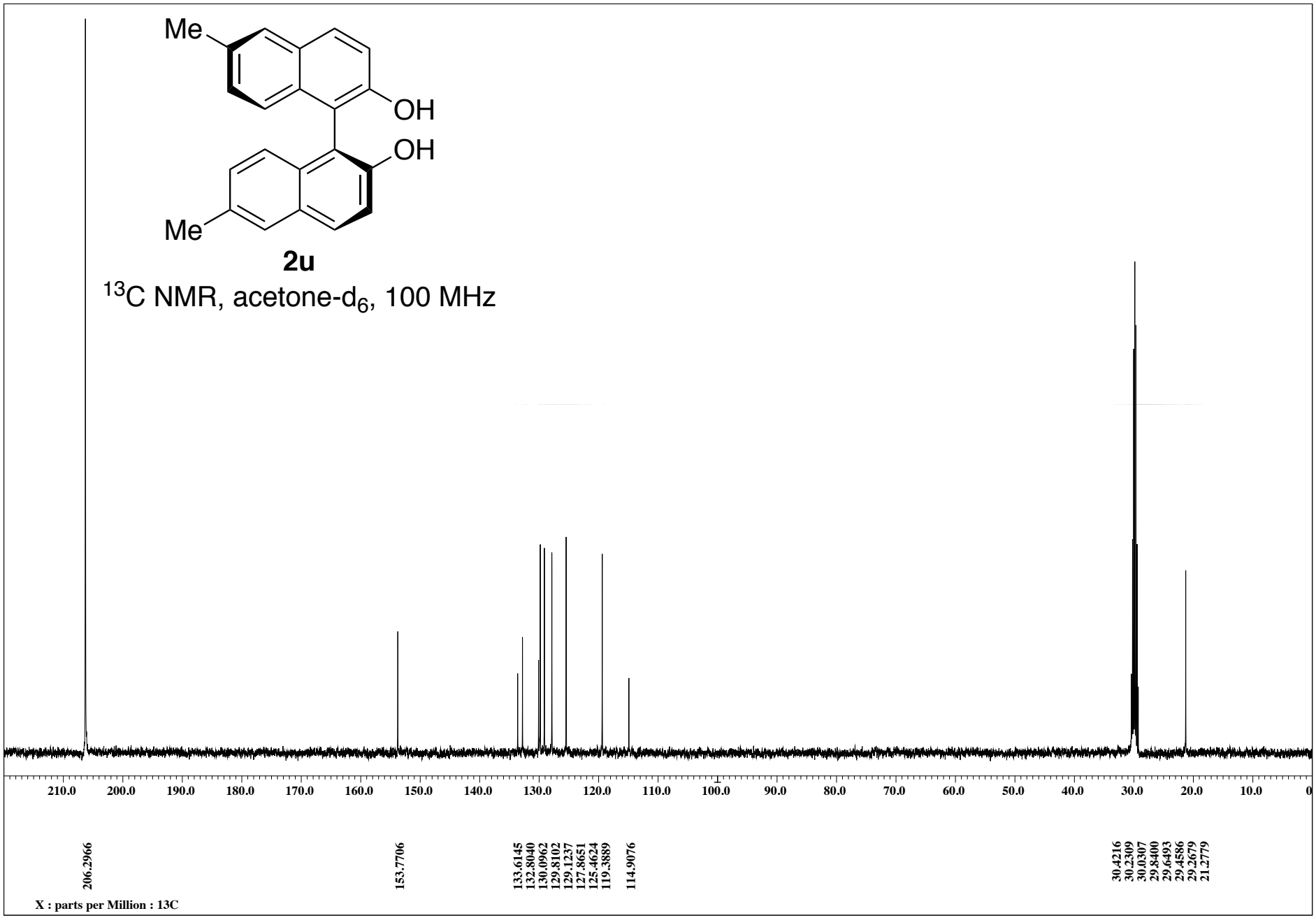
^{1}H NMR spectrum of **2t** ($CDCl_3$, 400 MHz)



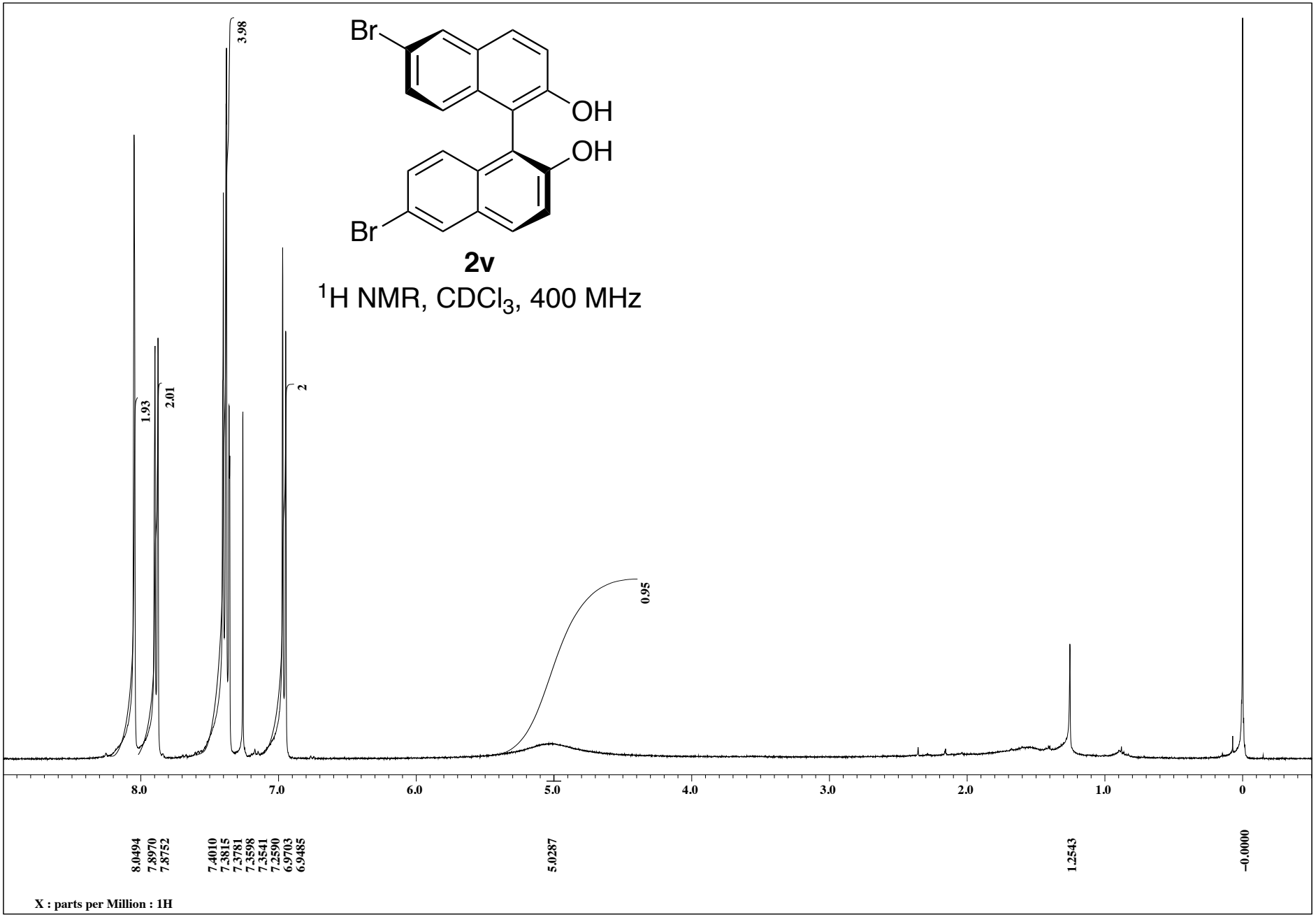
^{13}C NMR spectrum of **2t** ($CDCl_3$, 100 MHz)



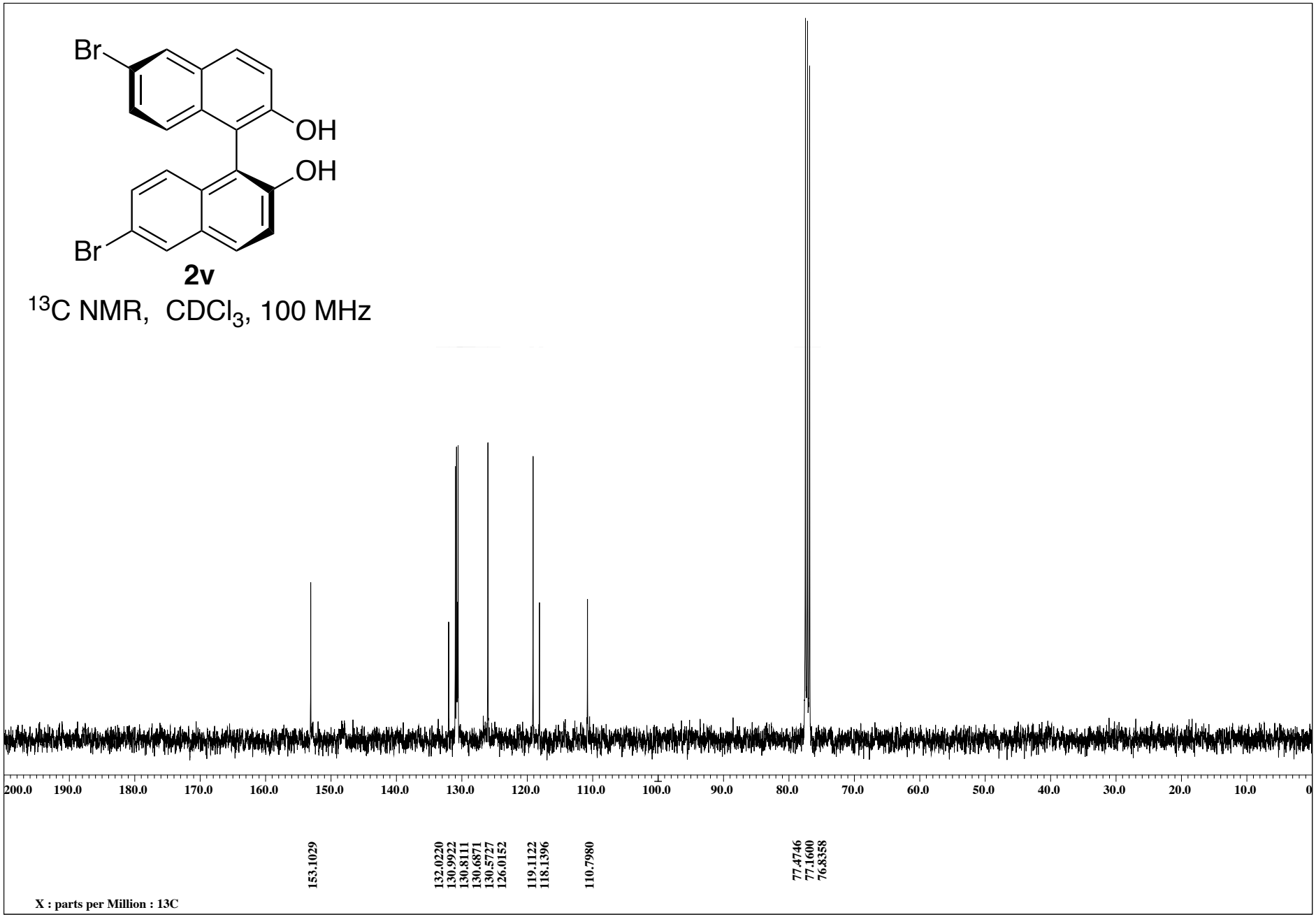
^{1}H NMR spectrum of **2u** ($CDCl_3$, 400 MHz)



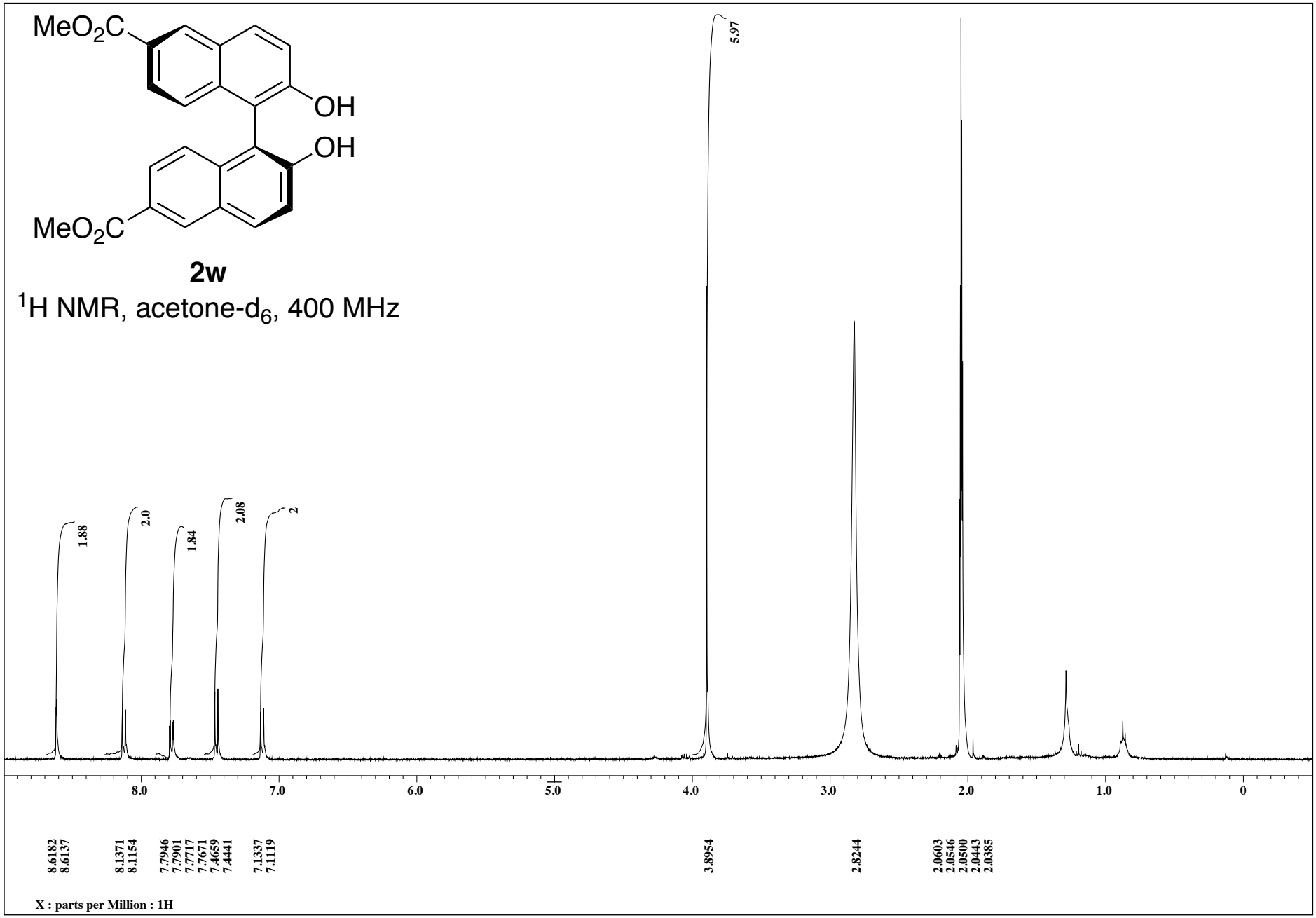
^{13}C NMR spectrum of **2u** (acetone-d_6, 100 MHz)



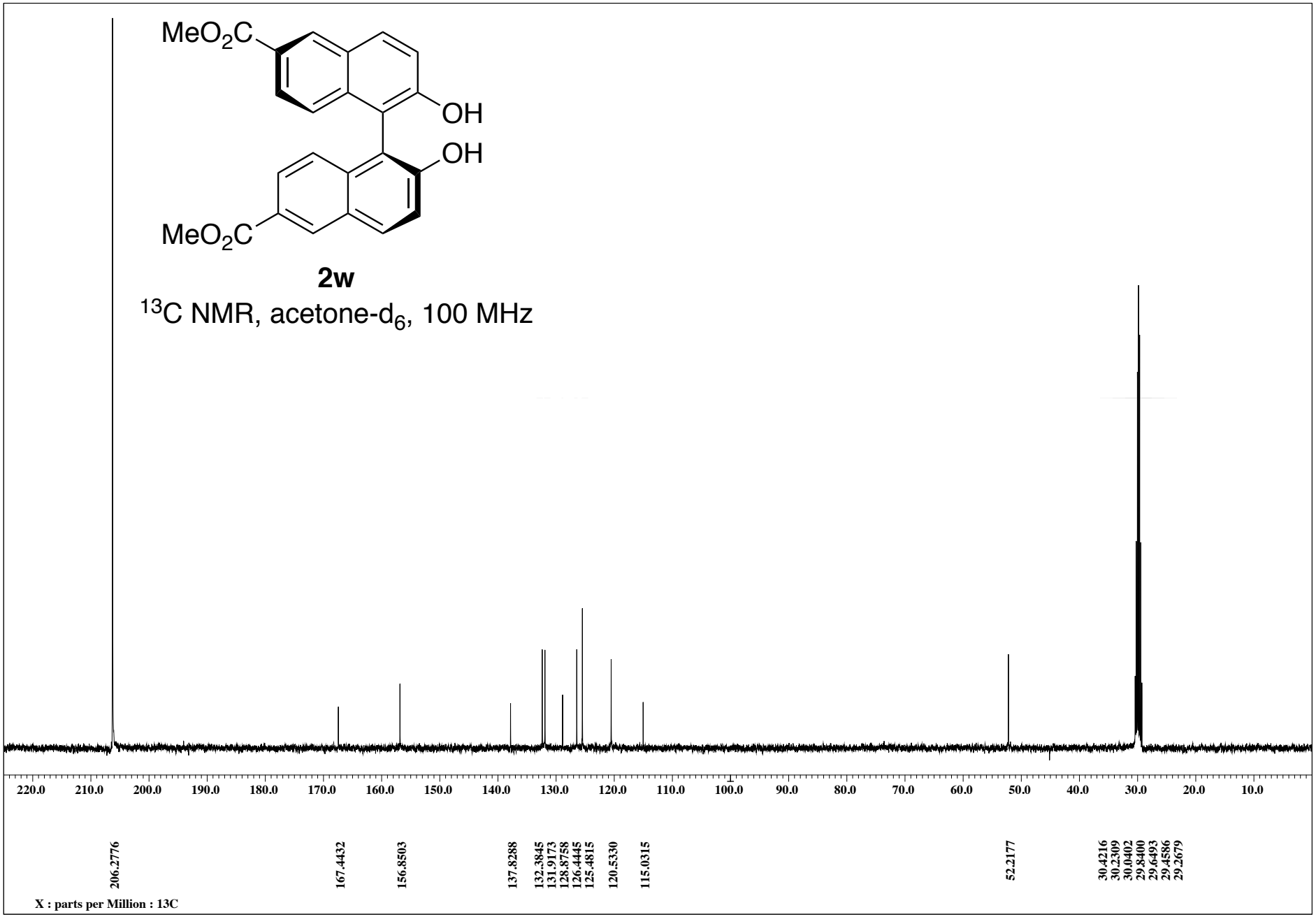
^{1}H NMR spectrum of **2v** ($CDCl_3$, 400 MHz)



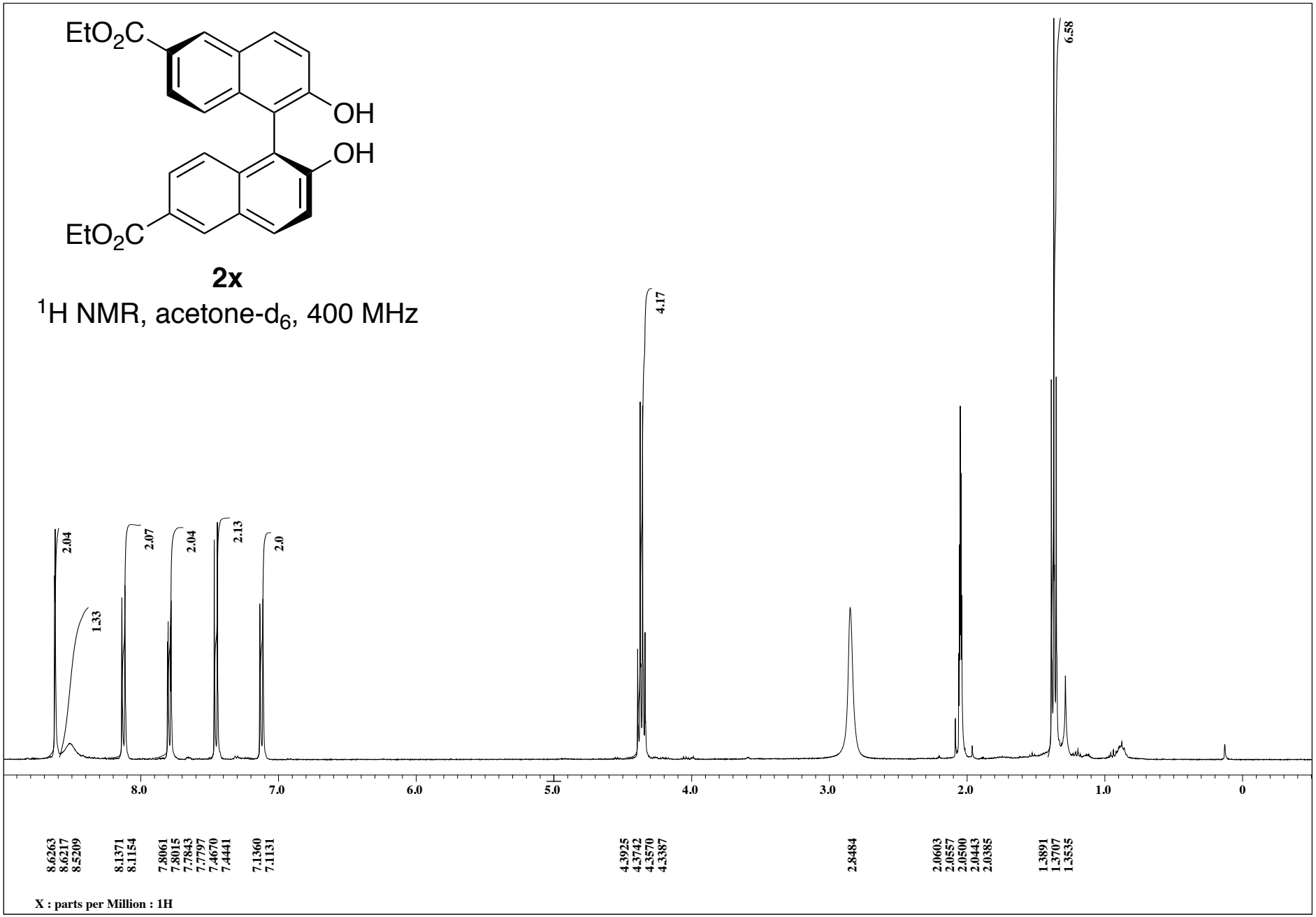
^{13}C NMR spectrum of **2v** ($CDCl_3$, 100 MHz)



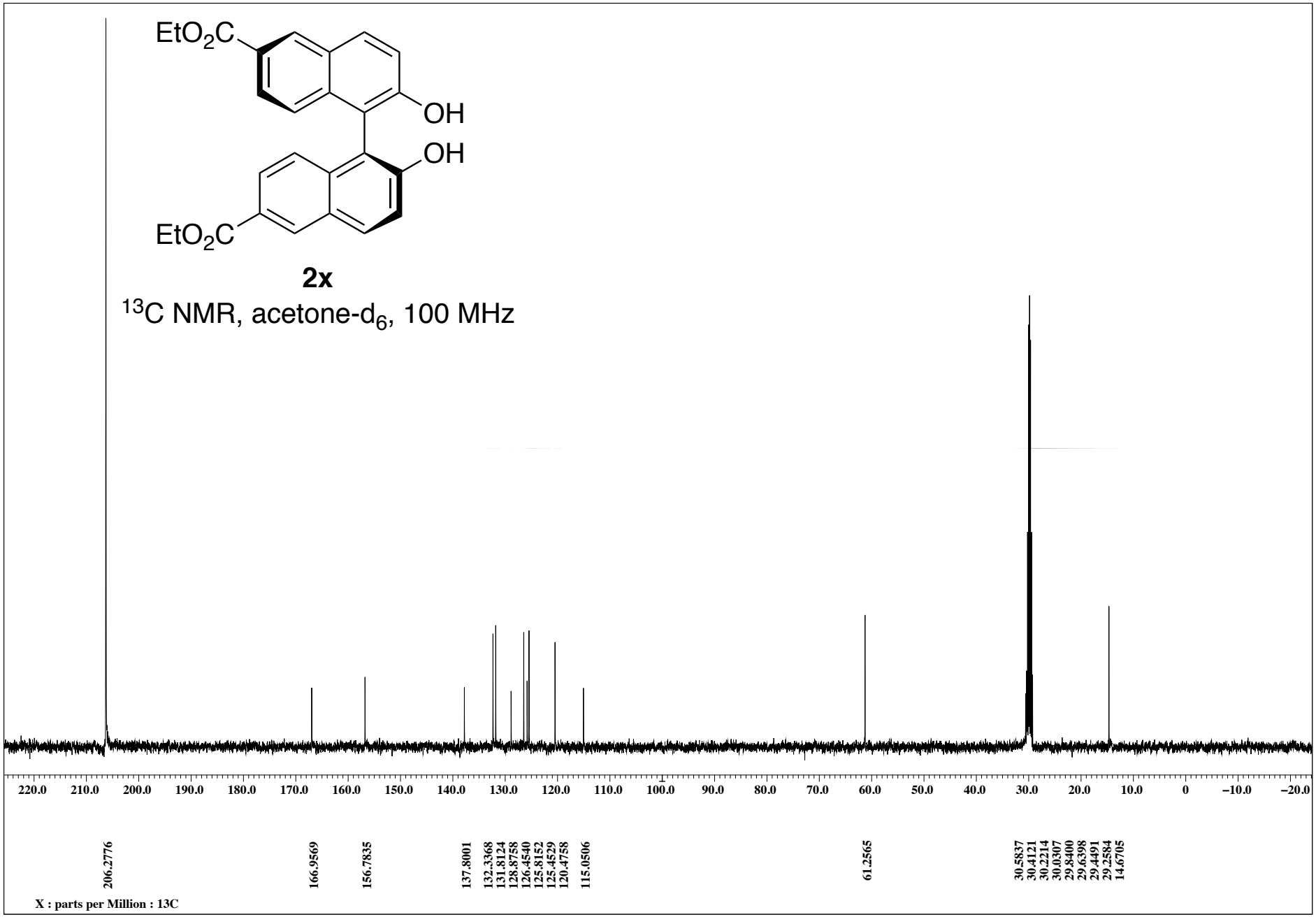
^{1}H NMR spectrum of **2w** (acetone-d_6, 400 MHz)



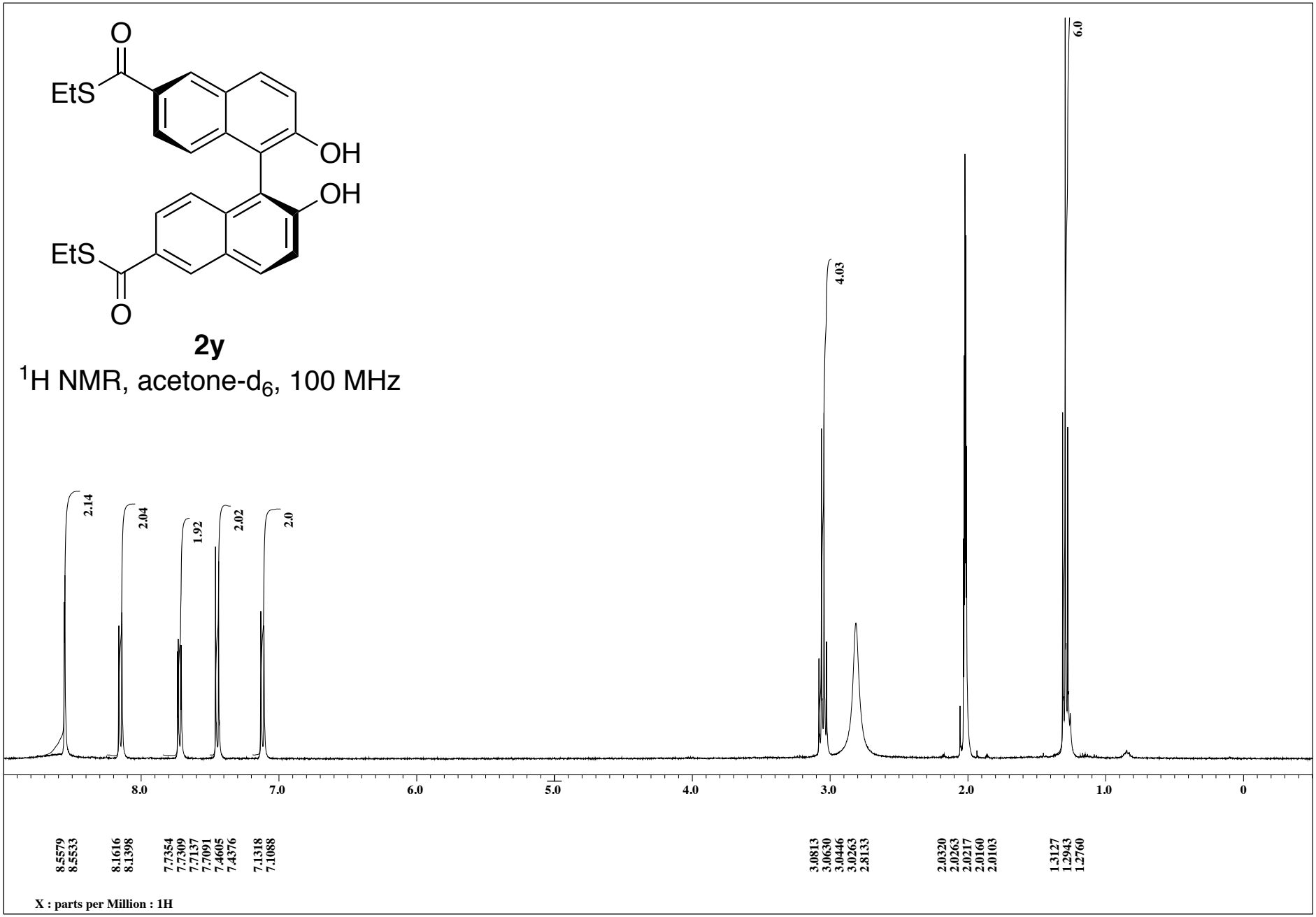
^{13}C NMR spectrum of **2w** (acetone-d_6, 100 MHz)



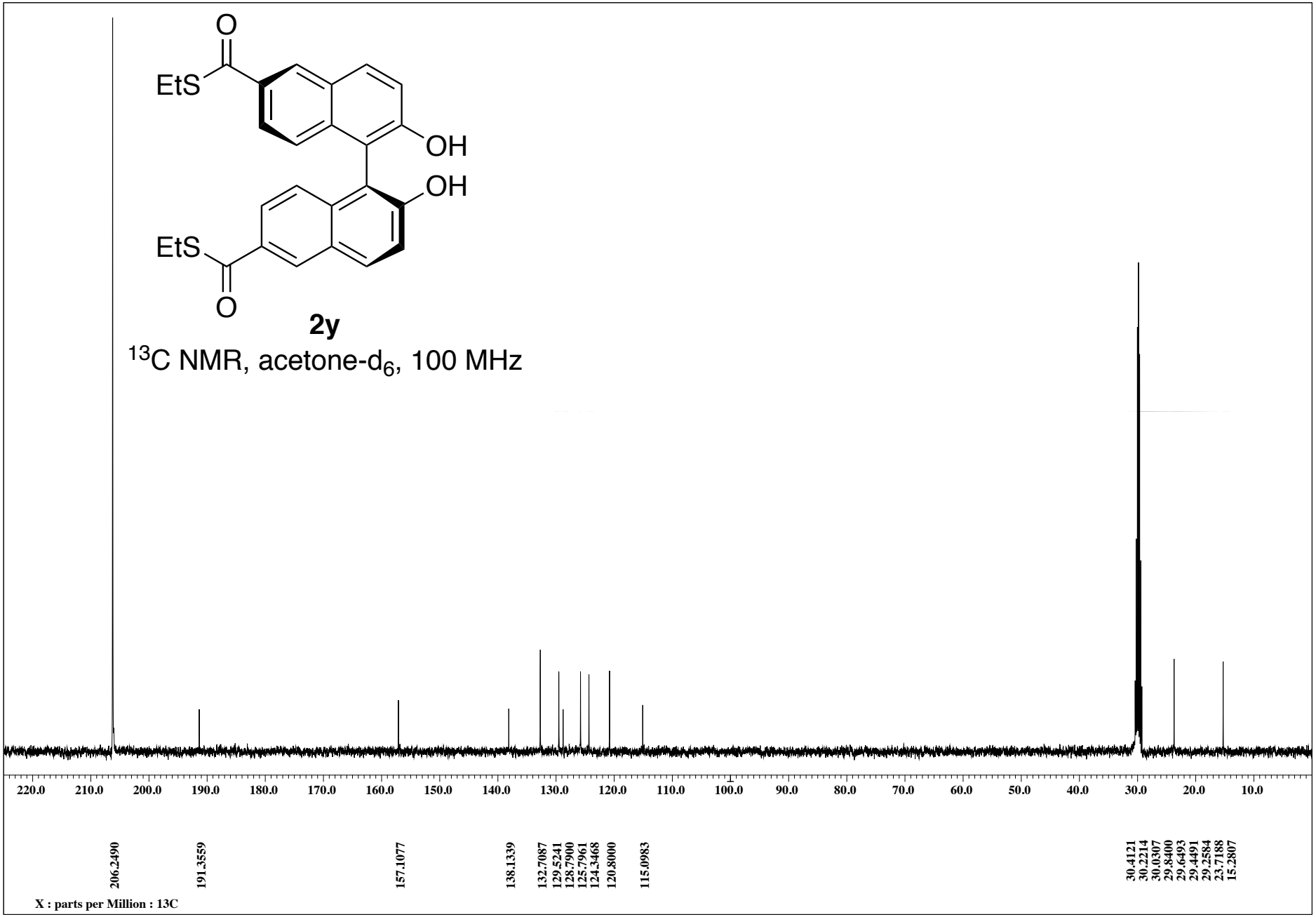
^{1}H NMR spectrum of **2x** (acetone-d_6, 400 MHz)



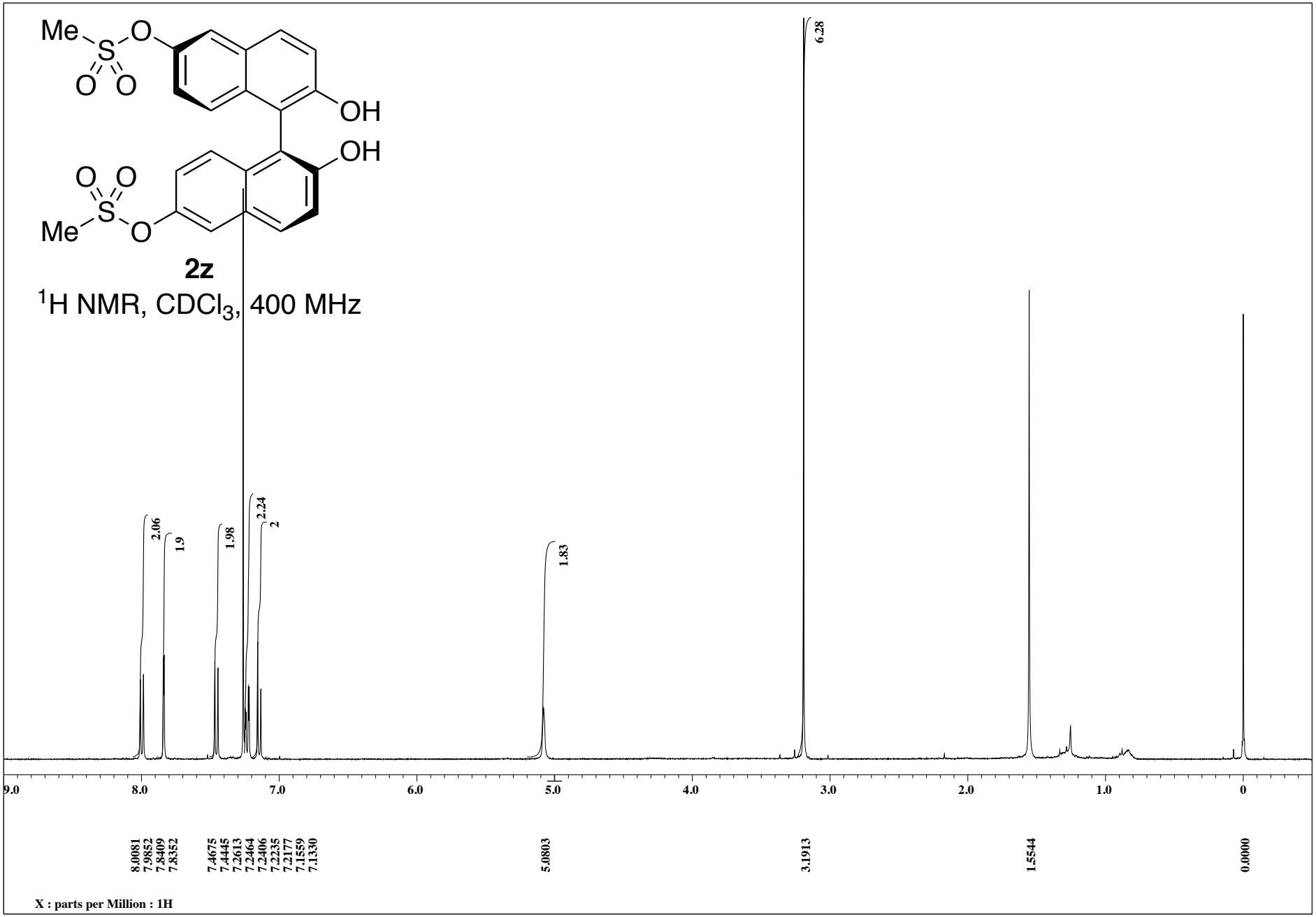
^{13}C NMR spectrum of **2x** (acetone-d_6, 100 MHz)



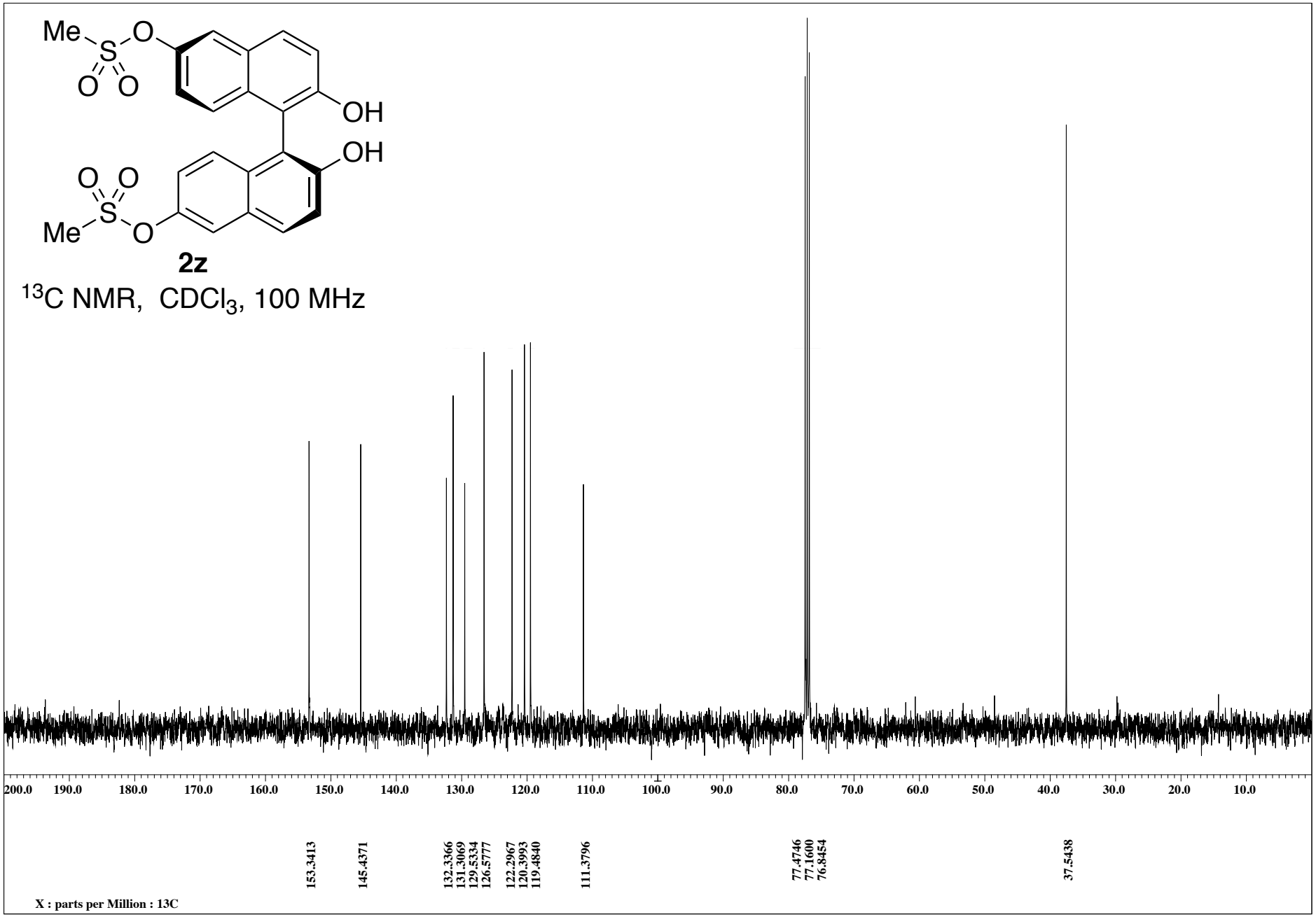
^{1}H NMR spectrum of **2y** (acetone-d$_6$, 400 MHz)



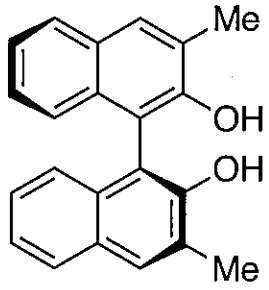
^{13}C NMR spectrum of **2y** (acetone-d_6, 100 MHz)



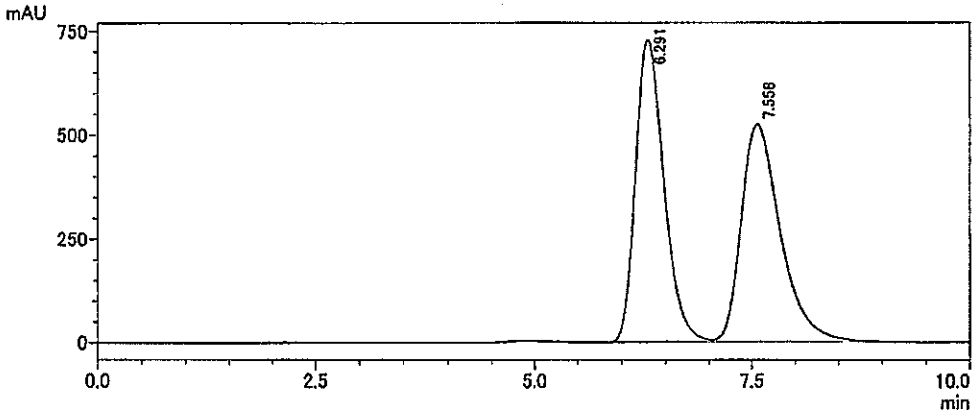
^{1}H NMR spectrum of **2z** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **2z** ($CDCl_3$, 100 MHz)

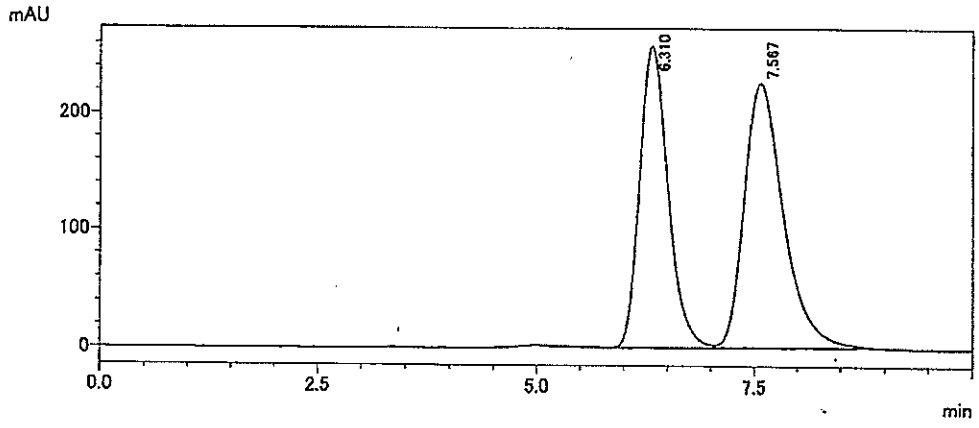


2b



PDA Ch1 229nm

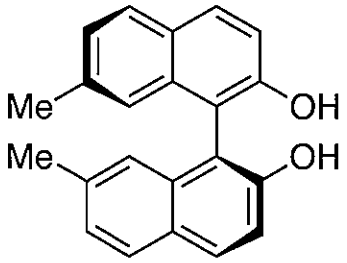
Peak No.	RT (min)	Area	Height	% Area
1	6.291	16594301	727363	49.968
2	7.558	16615530	523563	50.032
Total		33209832	1250925	100.000



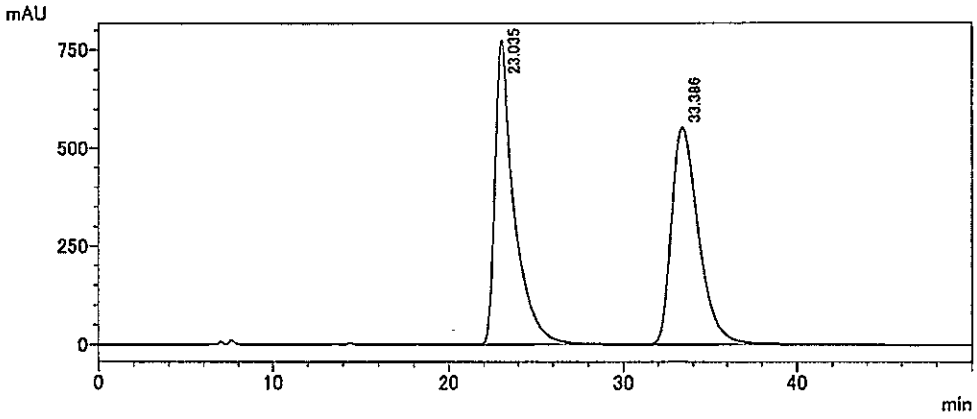
PDA Ch1 229nm

Peak No.	RT (min)	Area	Height	% Area
1	6.310	5874097	257073	45.193
2	7.567	7123655	225073	54.807
Total		12997752	482146	100.000

HPLC data of **2b**



2c



PDA Ch1 230nm

Peak No.	RT (min)	Area	Height	% Area
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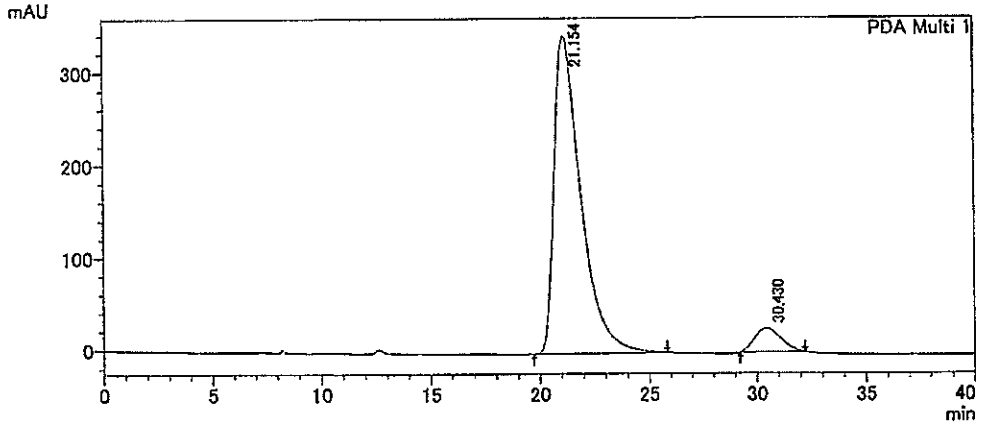
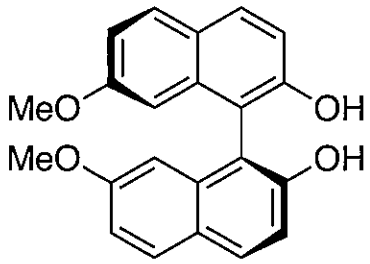


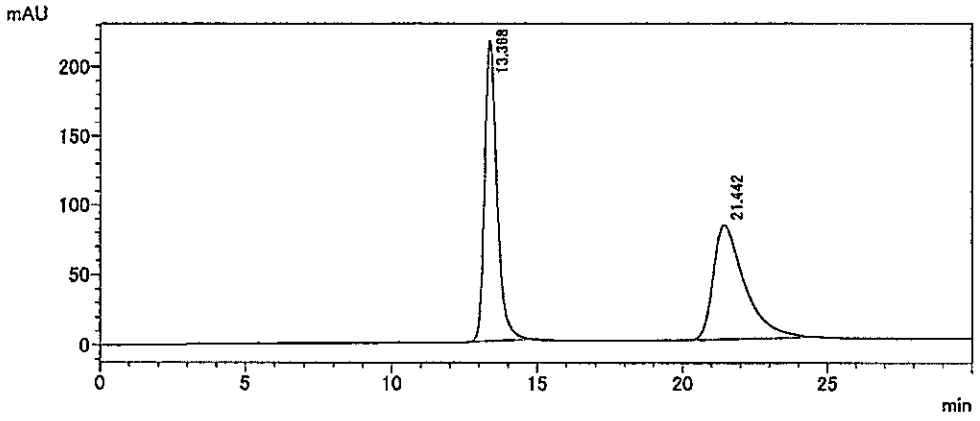
PDA Ch1 230nm 4nm

ピーク#	保持時間	高さ	面積%
1	21.154	343180	93.254
2	30.430	25398	6.746
Total		368578	100.000

HPLC data of **2c**

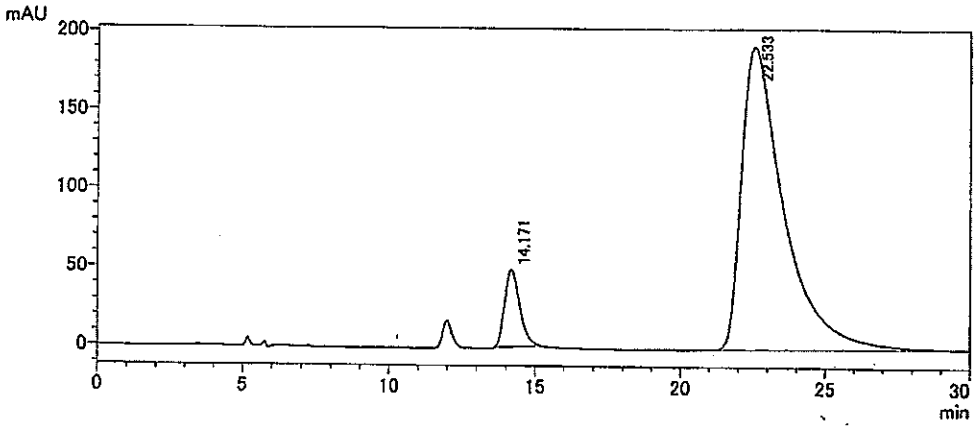


2d



PDA Ch1 234nm

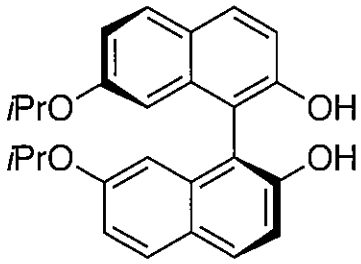
Peak No.	RT (min)	Area	Height	% Area
1	13.368	6305806	215457	50.681
2	21.442	6136337	80975	49.319
Total		12442143	296432	100.000



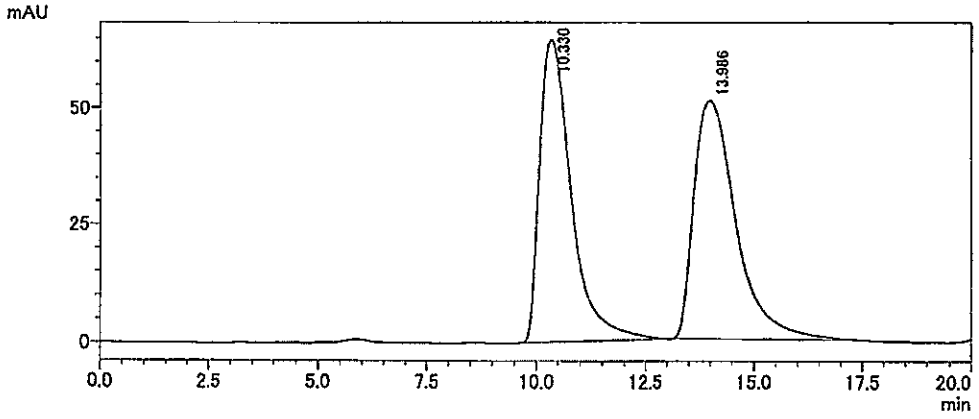
PDA Ch1 234nm

Peak No.	RT (min)	Area	Height	% Area
1	14.171	1753752	48655	8.239
2	22.533	19533072	192291	91.761
Total		21286824	240945	100.000

HPLC data of **2d**

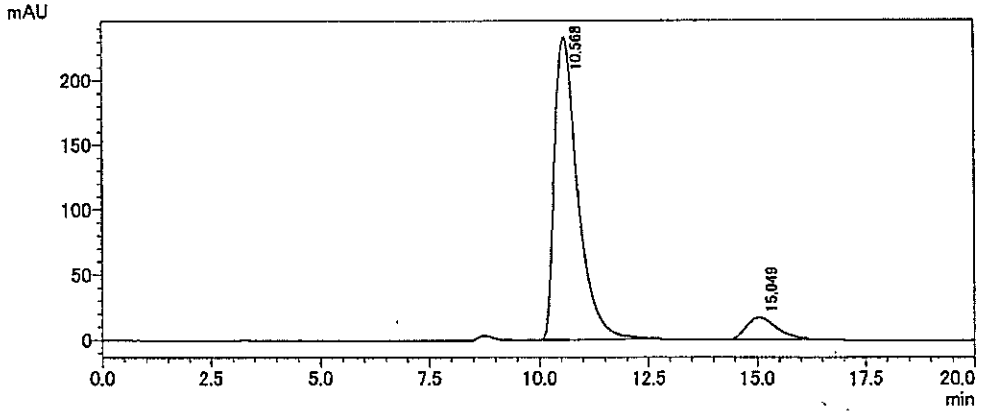


2e



PDA Ch1 237nm

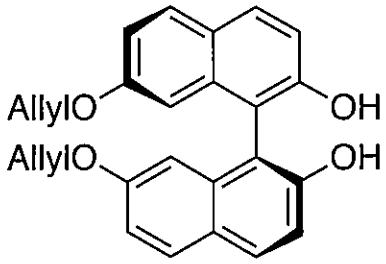
Peak No.	RT (min)	Area	Height	% Area
1	10.330	3240616	64507	48.674
2	13.986	3417240	50665	51.326
Total		6657856	115172	100.000



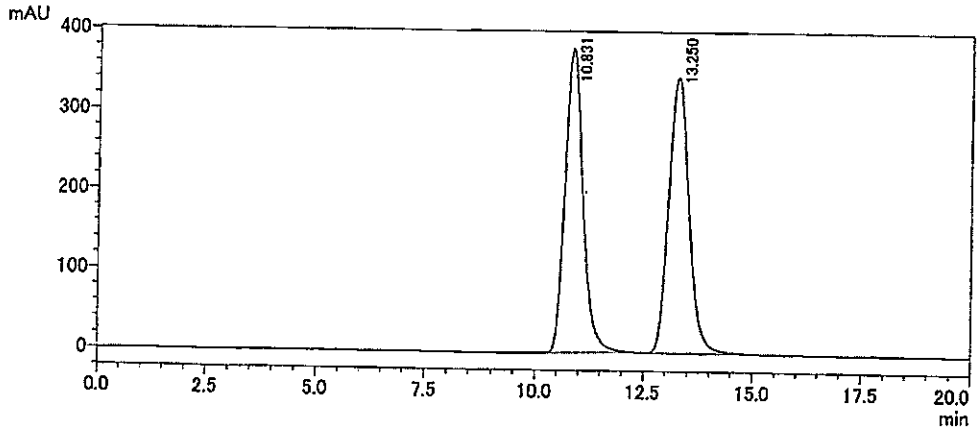
PDA Ch1 237nm

Peak No.	RT (min)	Area	Height	% Area
1	10.568	8535450	232823	91.035
2	15.049	840557	17057	8.965
Total		9376008	249880	100.000

HPLC data of **2e**

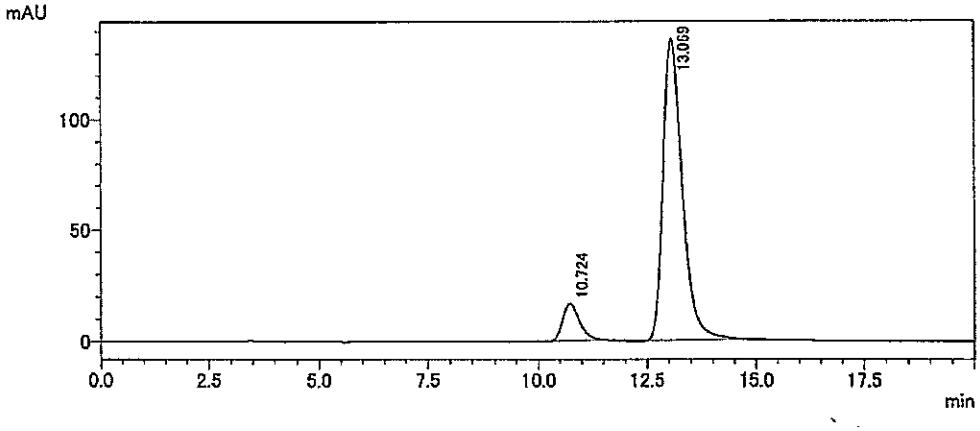


2f



PDA Ch1 235nm

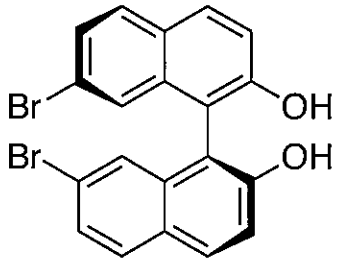
Peak No.	RT (min)	Area	Height	% Area
1	10.831	10975702	379224	49.853
2	13.250	11040373	343496	50.147
Total		22016075	722720	100.000



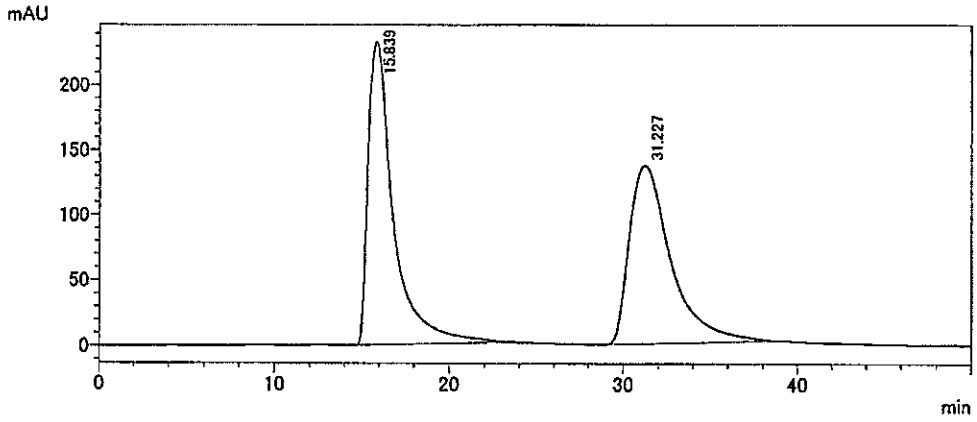
PDA Ch1 235nm

Peak No.	RT (min)	Area	Height	% Area
1	10.724	448391	16567	9.707
2	13.069	4170910	136454	90.293
Total		4619301	153021	100.000

HPLC data of **2f**

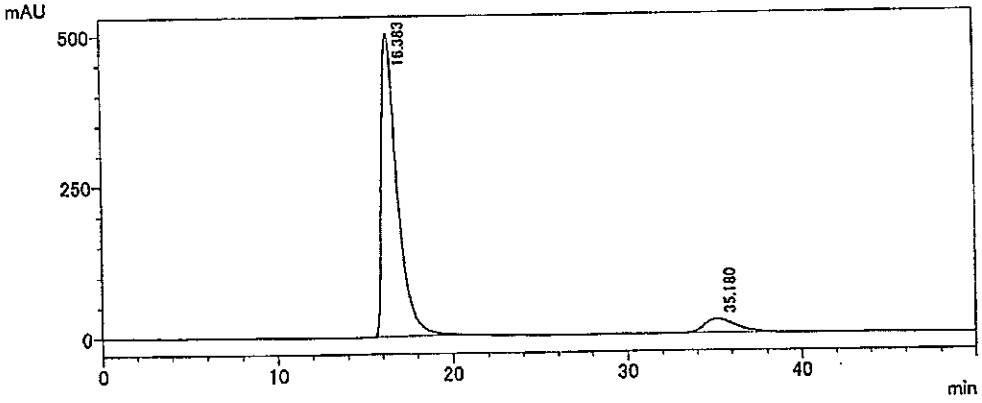


2g



PDA Ch1 235nm

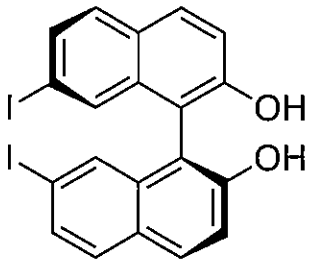
Peak No.	RT (min)	Area	Height	% Area
1	15.839	23359200	232889	50.756
2	31.227	22663257	136187	49.244
Total		46022457	369076	100.000



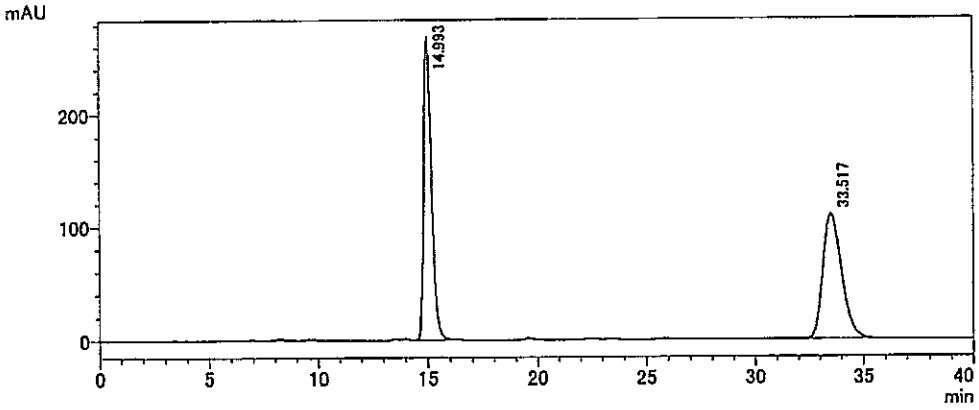
PDA Ch1 235nm

Peak No.	RT (min)	Area	Height	% Area
1	16.383	30942418	500696	91.484
2	35.180	2880325	23182	8.516
Total		33822743	523878	100.000

HPLC data of **2g**

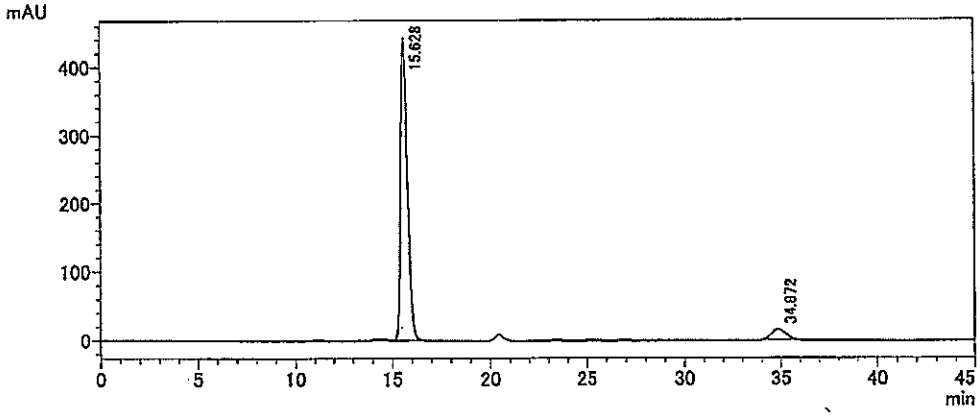


2h



PDA Ch1 243nm

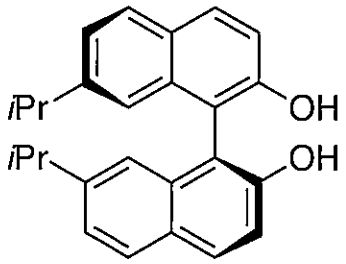
Peak No.	RT (min)	Area	Height	% Area
1	14.993	6522531	268733	49.989
2	33.517	6525320	109755	50.011
Total		13047852	378488	100.000



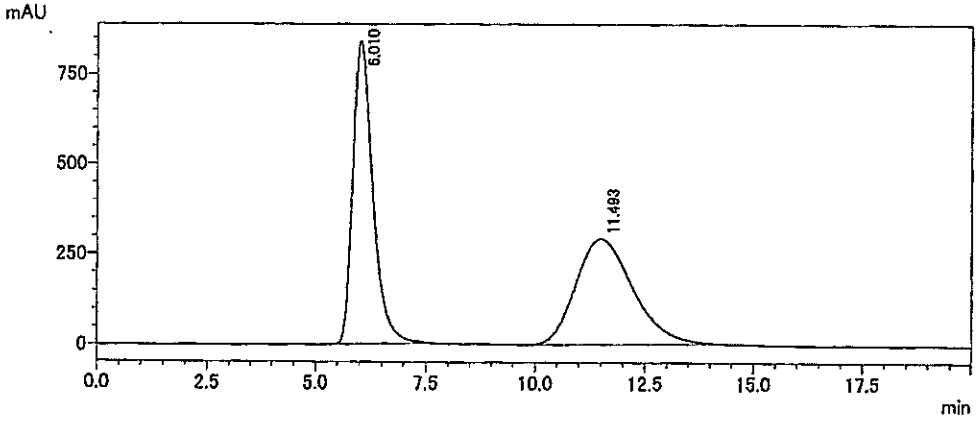
PDA Ch1 243nm

Peak No.	RT (min)	Area	Height	% Area
1	15.628	10677026	443802	93.415
2	34.872	752658	14707	6.585
Total		11429684	458509	100.000

HPLC data of **2h**

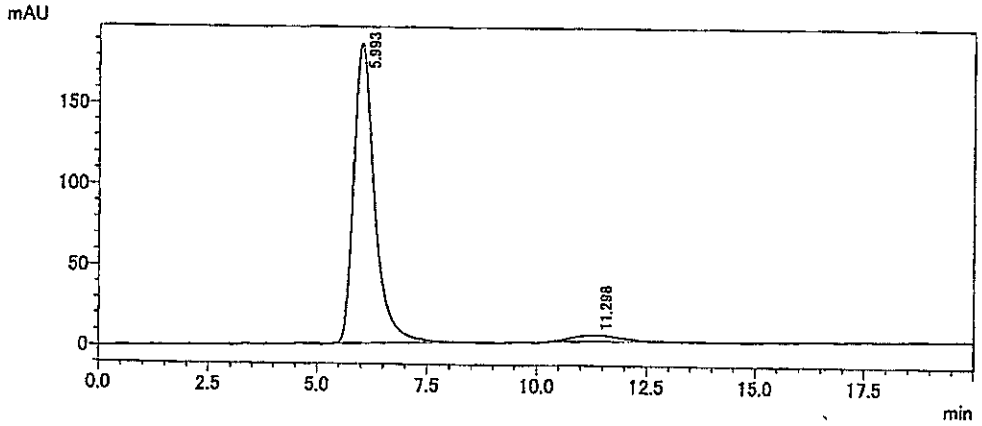


2i



PDA Ch1 230nm

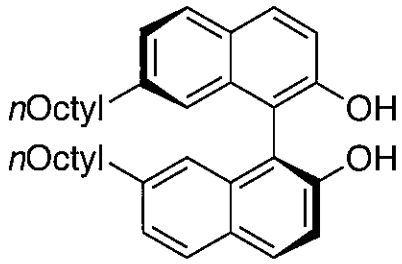
Peak No.	RT (min)	Area	Height	% Area
1	6.010	26693101	837984	50.353
2	11.493	26318350	290929	49.647
Total		53011451	1128913	100.000



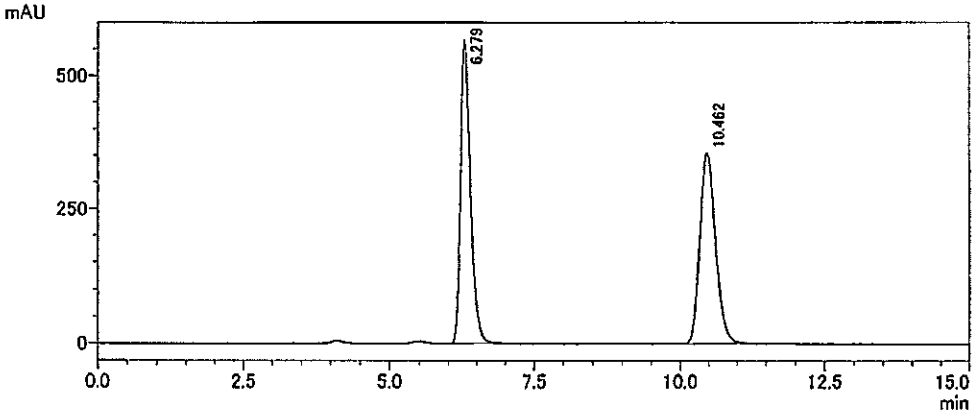
PDA Ch1 230nm

Peak No.	RT (min)	Area	Height	% Area
1	5.993	6128106	185157	95.245
2	11.298	305945	4000	4.755
Total		6434051	189157	100.000

HPLC data of **2i**

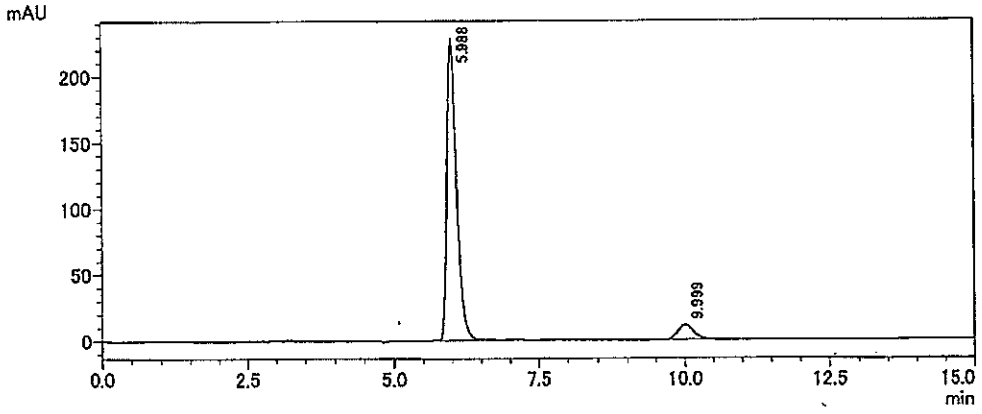


2j



PDA Ch1 232nm

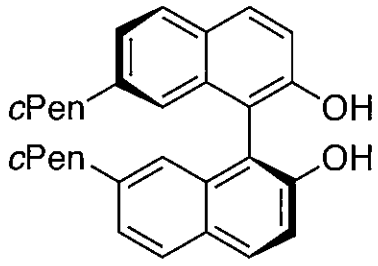
Peak No.	RT (min)	Area	Height	% Area
1	6.279	6786775	566353	49.853
2	10.462	6826670	354561	50.147
Total		13613445	920914	100.000



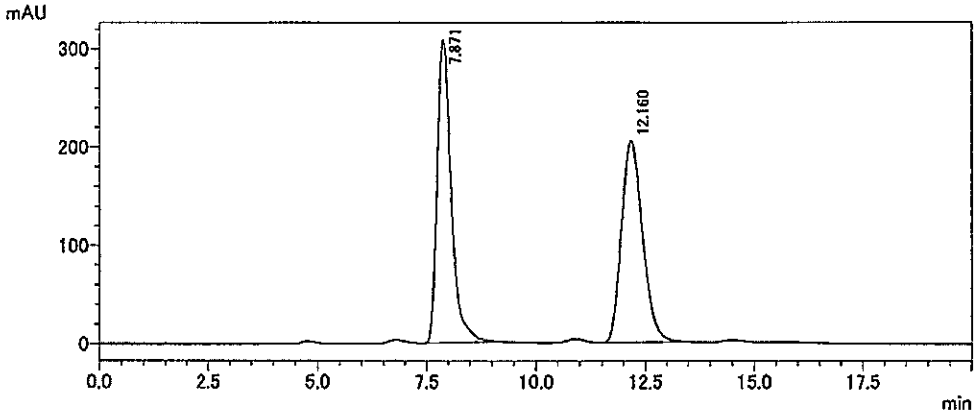
PDA Ch1 232nm

Peak No.	RT (min)	Area	Height	% Area
1	5.988	2636437	228637	92.633
2	9.999	209669	11092	7.367
Total		2846106	239730	100.000

HPLC data of **2j**

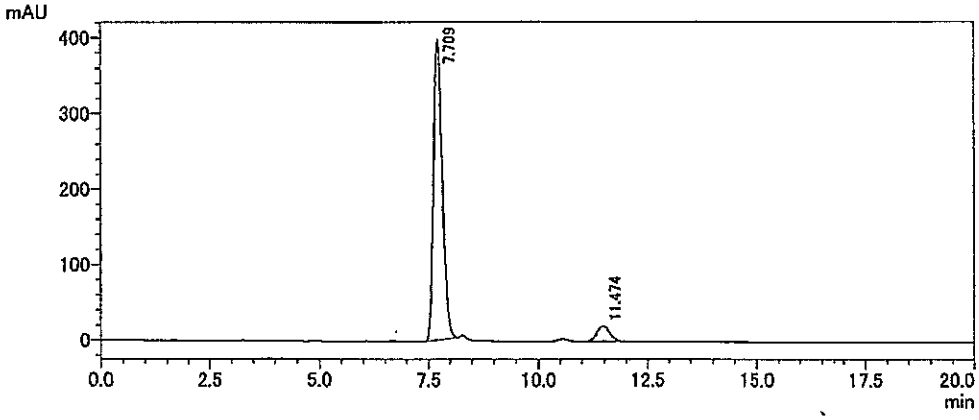


2k



PDA Ch1 232nm

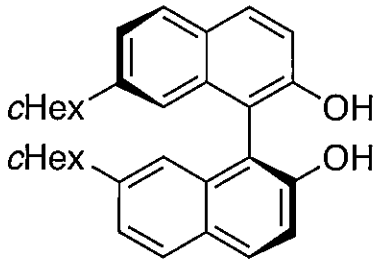
Peak No.	RT (min)	Area	Height	% Area
1	7.871	7095061	308358	50.561
2	12.160	6937582	204949	49.439
Total		14032643	513307	100.000



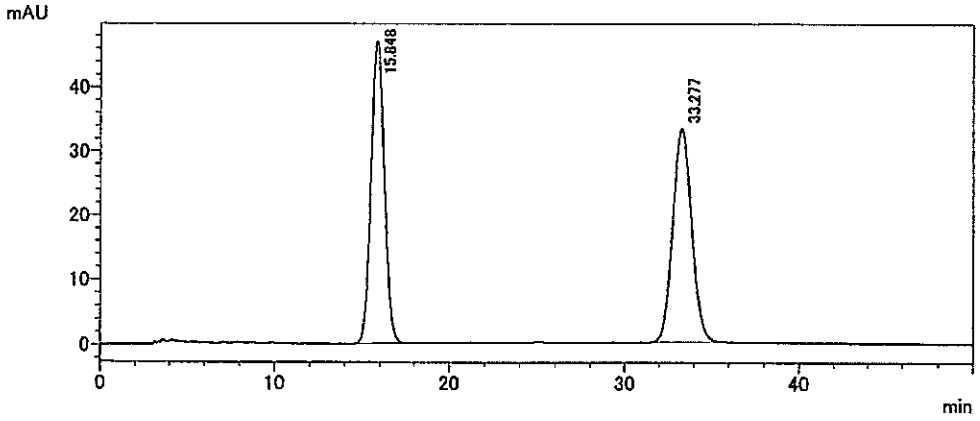
PDA Ch1 232nm

Peak No.	RT (min)	Area	Height	% Area
1	7.709	5605101	397887	92.903
2	11.474	428212	20491	7.097
Total		6033312	418377	100.000

HPLC data of **2k**

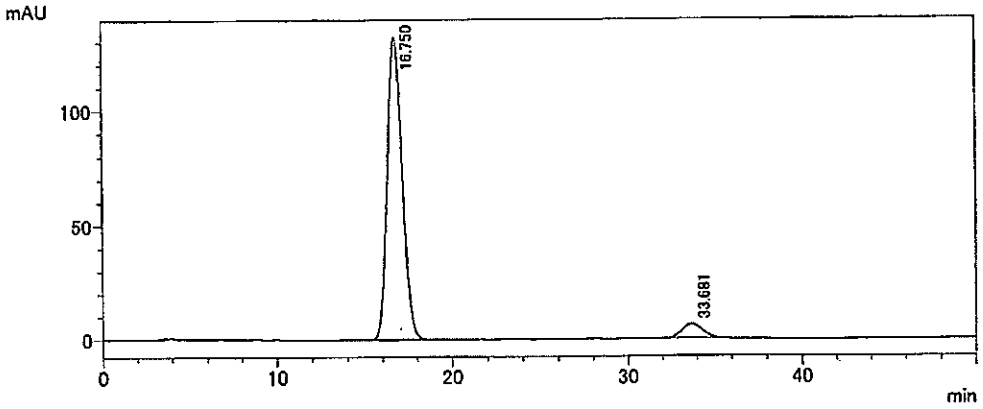


2l



PDA Ch1 232nm

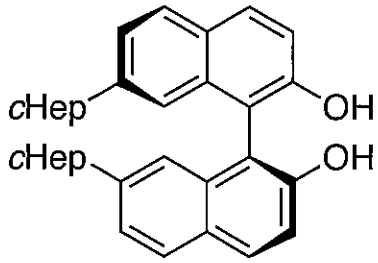
Peak No.	RT (min)	Area	Height	% Area
1	15.848	2489661	46940	50.021
2	33.277	2487560	33165	49.979
Total		4977221	80105	100.000



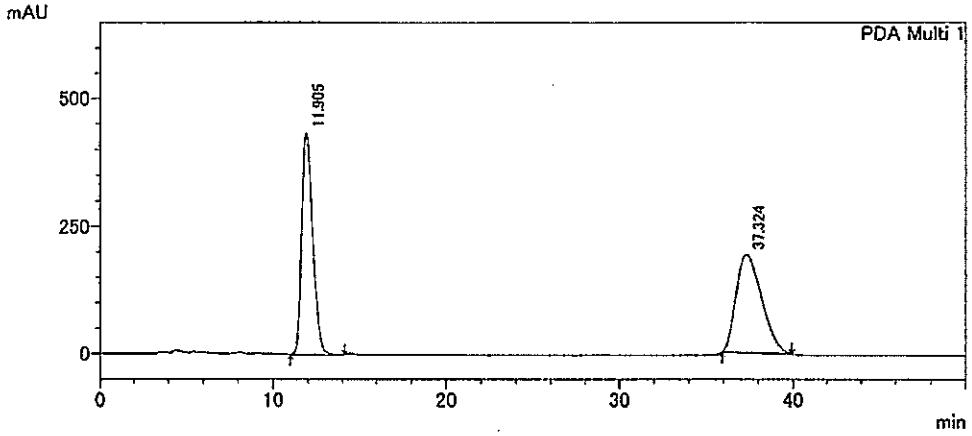
PDA Ch1 232nm

Peak No.	RT (min)	Area	Height	% Area
1	16.750	7940041	132180	94.117
2	33.681	496305	6204	5.883
Total		8436346	138384	100.000

HPLC data of **2l**

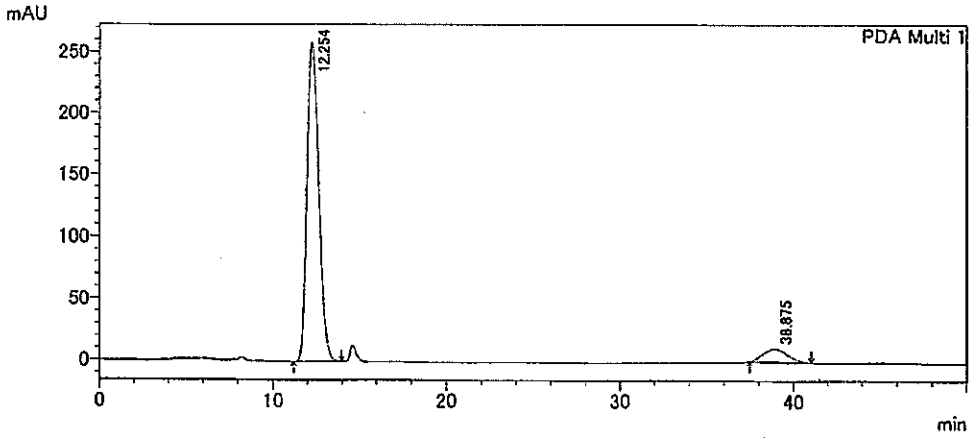


2m



PDA Ch1 260nm 4nm

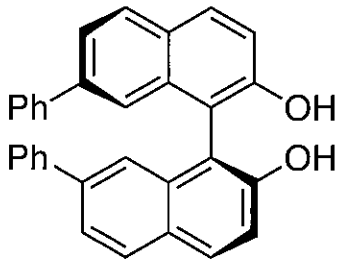
ピーク#	保持時間	高さ	面積%
1	11.905	434743	49.115
2	37.324	193196	50.885
Total		627939	100.000



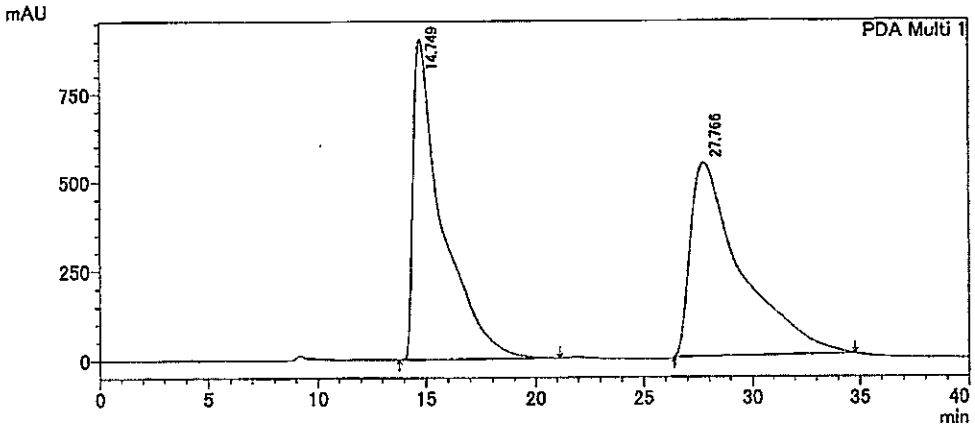
PDA Ch1 260nm 4nm

ピーク#	保持時間	高さ	面積%
1	12.254	259279	91.854
2	38.875	10719	8.146
Total		269998	100.000

HPLC data of **2m**

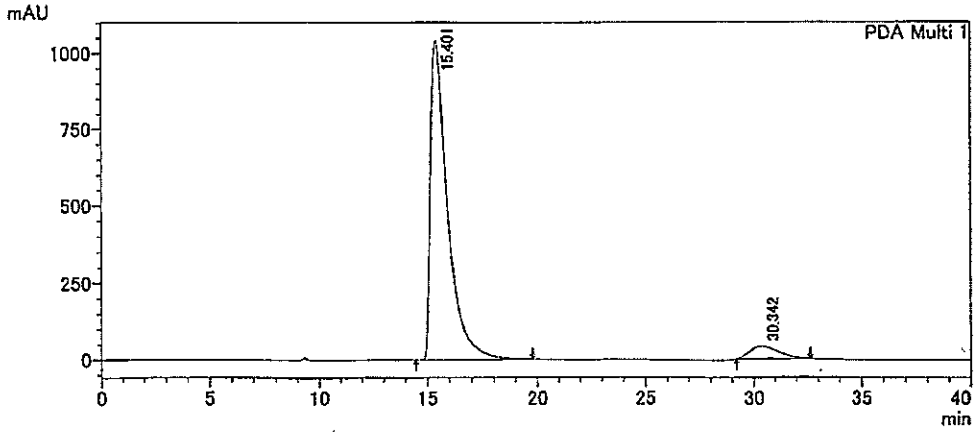


2n



PDA Ch1 254nm 4nm

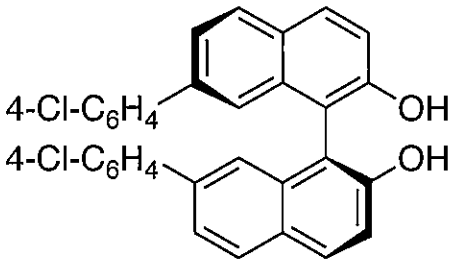
ピーク#	保持時間	高さ	面積%
1	14.749	902993	48.127
2	27.766	544663	51.873
Total		1447655	100.000



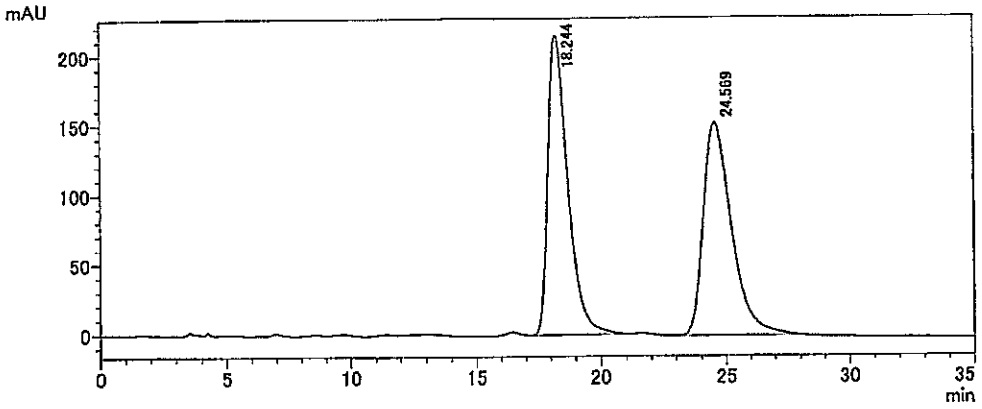
PDA Ch1 254nm 4nm

ピーク#	保持時間	高さ	面積%
1	15.401	1044788	93.589
2	30.342	41038	6.411
Total		1085825	100.000

HPLC data of **2n**

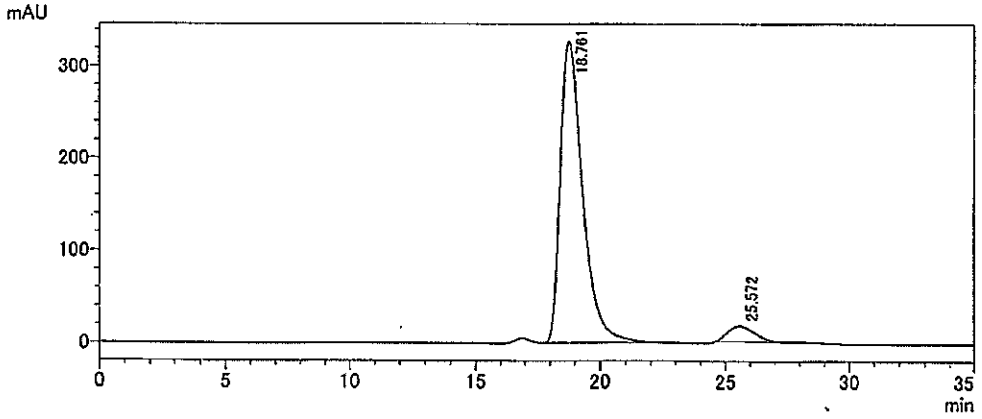


2o



PDA Ch1 259nm

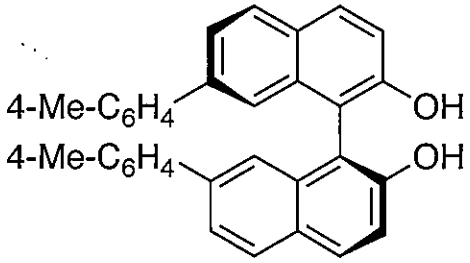
Peak No.	RT (min)	Area	Height	% Area
1	18.244	12034041	215085	49.819
2	24.569	12121285	152361	50.181
Total		24155326	367445	100.000



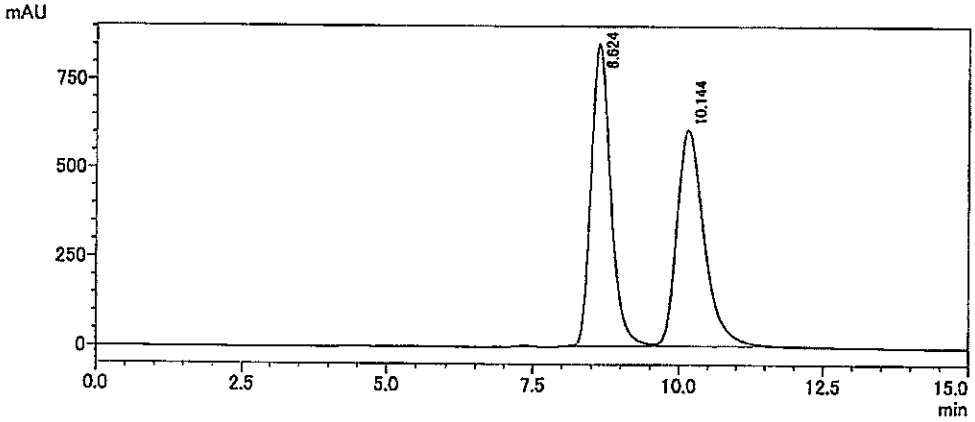
PDA Ch1 259nm

Peak No.	RT (min)	Area	Height	% Area
1	18.761	20162096	327304	94.128
2	25.572	1257786	16561	5.872
Total		21419882	343865	100.000

HPLC data of **2o**

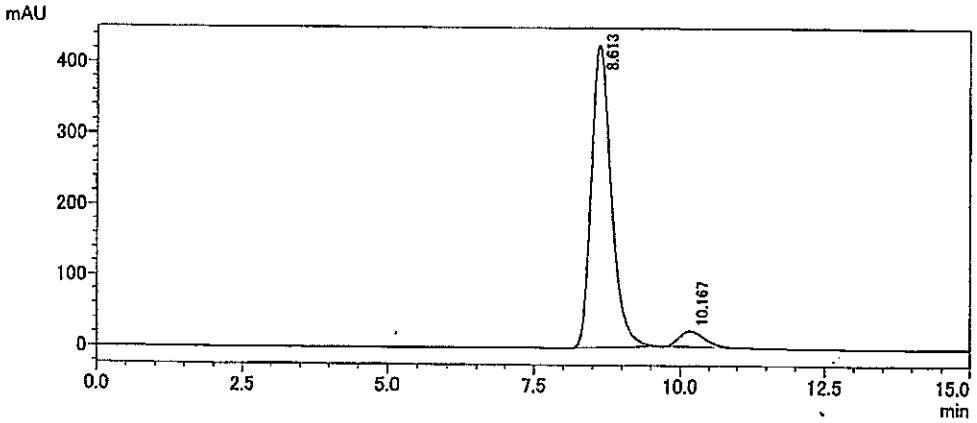


2p



PDA Ch1 258nm

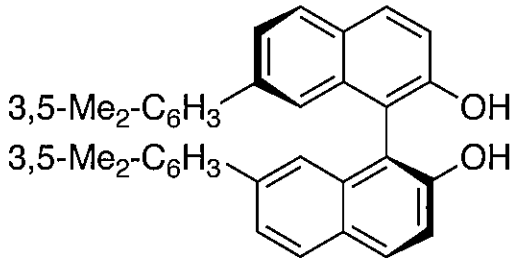
Peak No.	RT (min)	Area	Height	% Area
1	8.624	19774965	851281	49.796
2	10.144	19937146	605920	50.204
Total		39712111	1457201	100.000



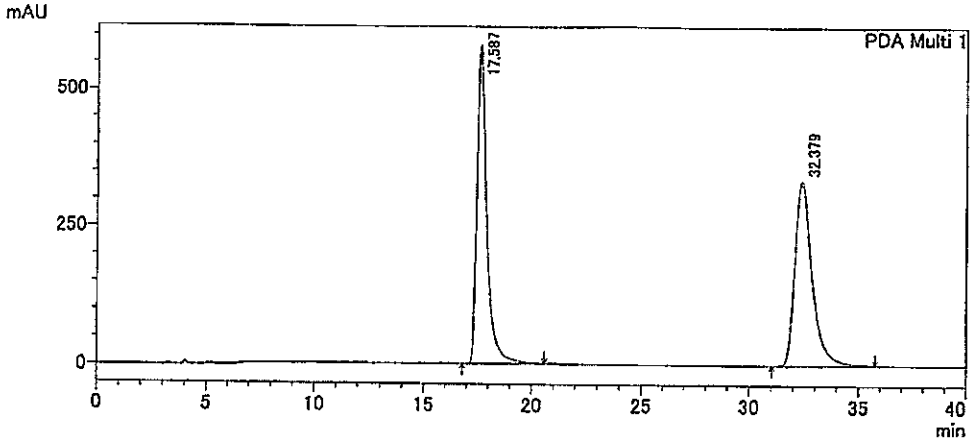
PDA Ch1 258nm

Peak No.	RT (min)	Area	Height	% Area
1	8.613	10098557	425784	93.803
2	10.167	667173	21824	6.197
Total		10765730	447608	100.000

HPLC data of **2p**

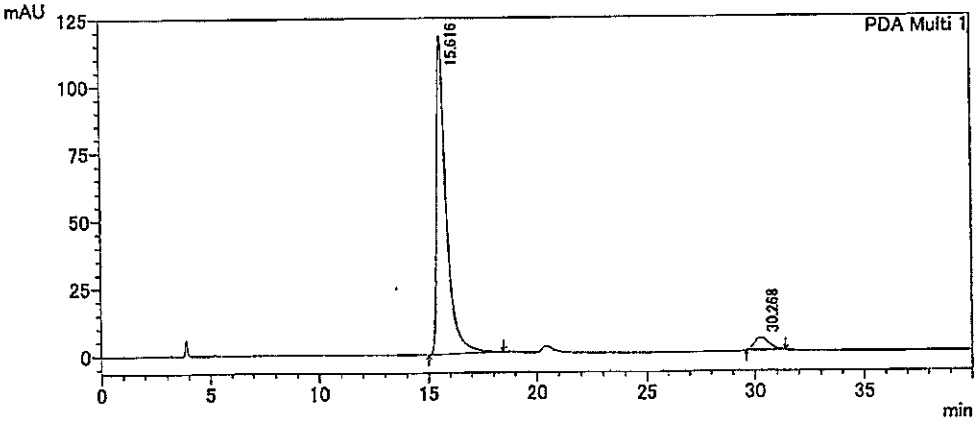


2q



PDA Ch1 257nm 4nm

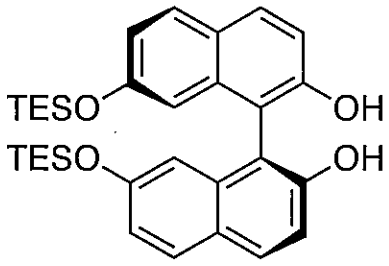
ピーク#	保持時間	高さ	面積%
1	17.587	579511	49.957
2	32.379	334310	50.043
Total		913821	100.000



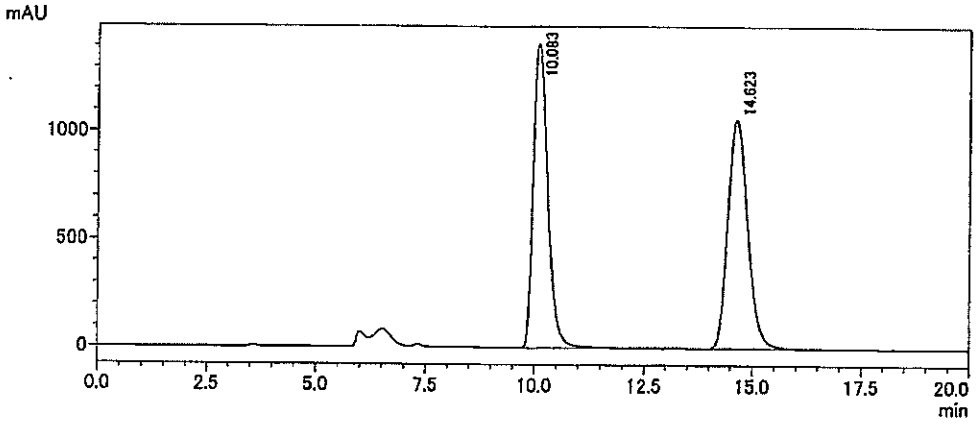
PDA Ch1 257nm 4nm

ピーク#	保持時間	高さ	面積%
1	15.616	118034	94.572
2	30.268	4500	5.428
Total		122535	100.000

HPLC data of **2q**

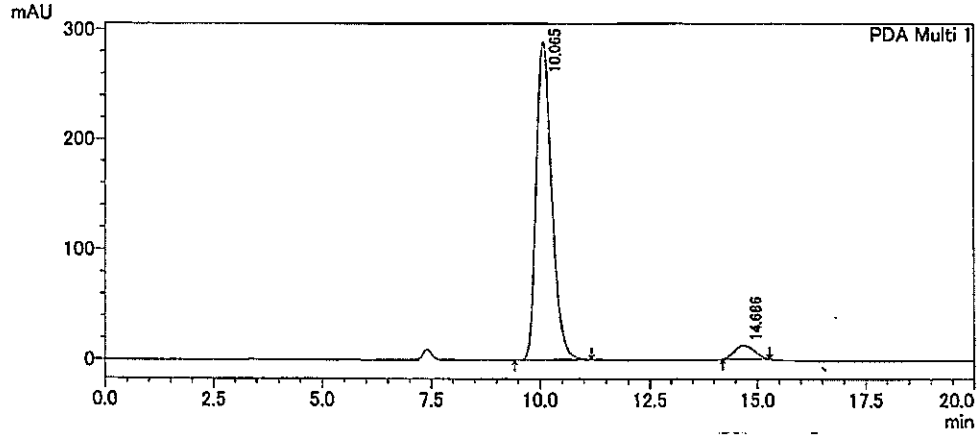


2r



PDA Ch1 235nm

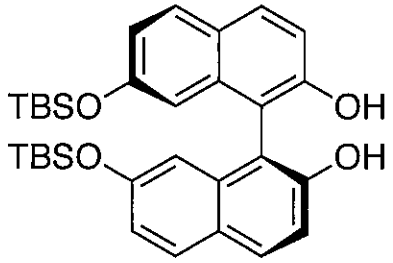
Peak No.	RT (min)	Area	Height	% Area
1	10.083	32443612	1412253	49.226
2	14.623	33463512	1057726	50.774
Total		65907124	2469979	100.000



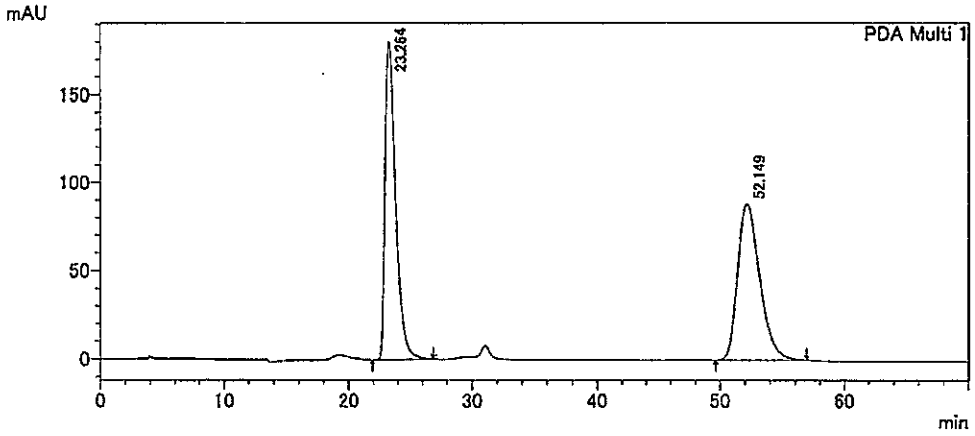
PDA Ch1 235nm 4nm

ピーク#	保持時間	高さ	面積%
1	10.065	289097	94.772
2	14.686	12046	5.228
Total		301143	100.000

HPLC data of **2r**

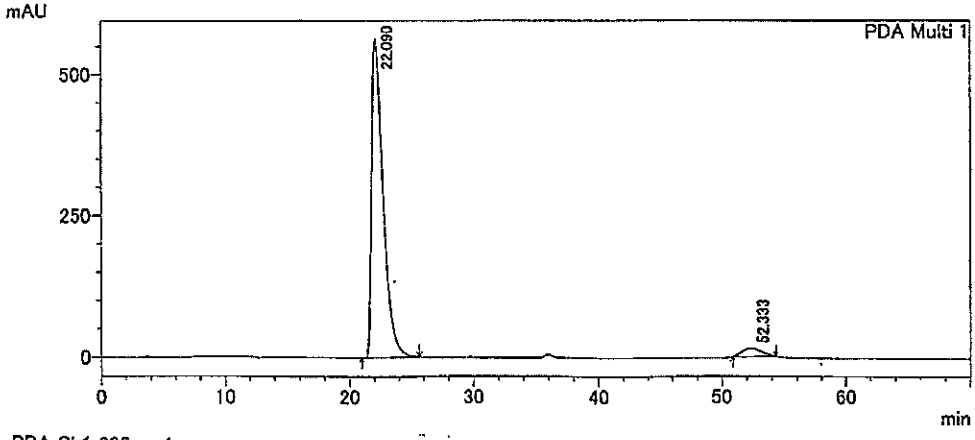


2s



PDA Ch1 235nm 4nm

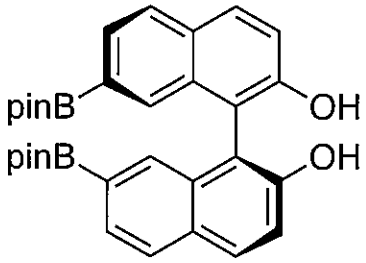
ピーク#	保持時間	高さ	面積%
1	23.264	180938	50.081
2	52.149	88310	49.919
Total		269247	100.000



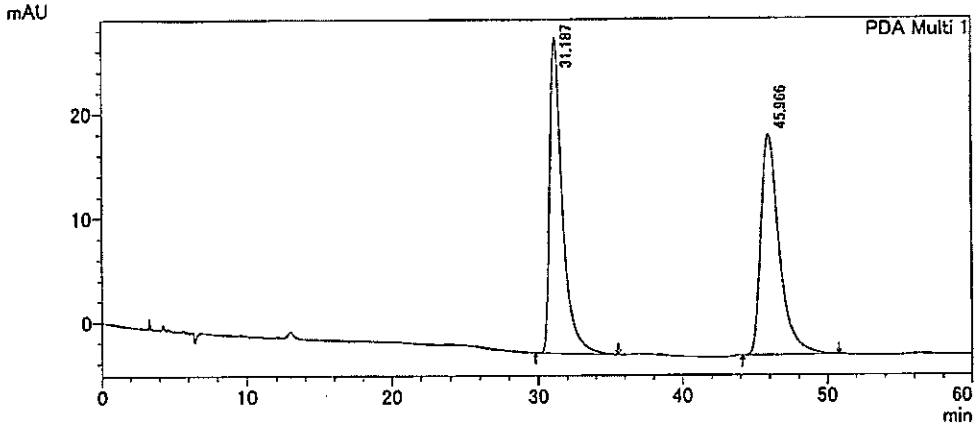
PDA Ch1 235nm 4nm

ピーク#	保持時間	高さ	面積%
1	22.090	564174	96.035
2	52.333	14034	3.965
Total		578209	100.000

HPLC data of **2s**

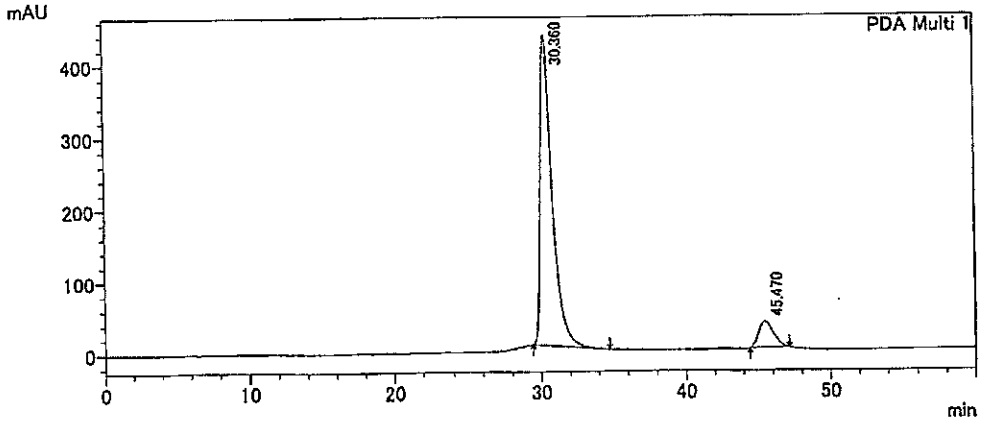


2t



PDA Ch1 234nm 4nm

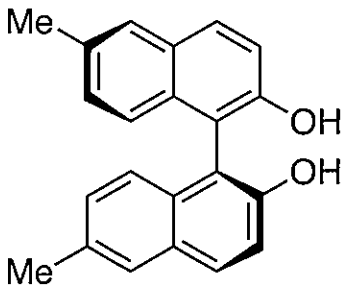
ピーク#	保持時間	高さ	面積%
1	31.187	30364	50.022
2	45.966	21117	49.978
Total		51480	100.000



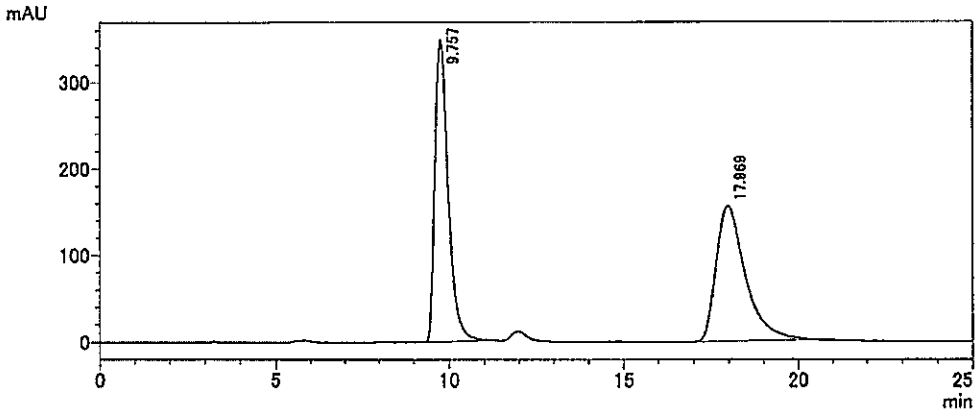
PDA Ch1 234nm 4nm

ピーク#	保持時間	高さ	面積%
1	30.360	431644	90.520
2	45.470	36347	9.480
Total		467991	100.000

HPLC data of **2t**

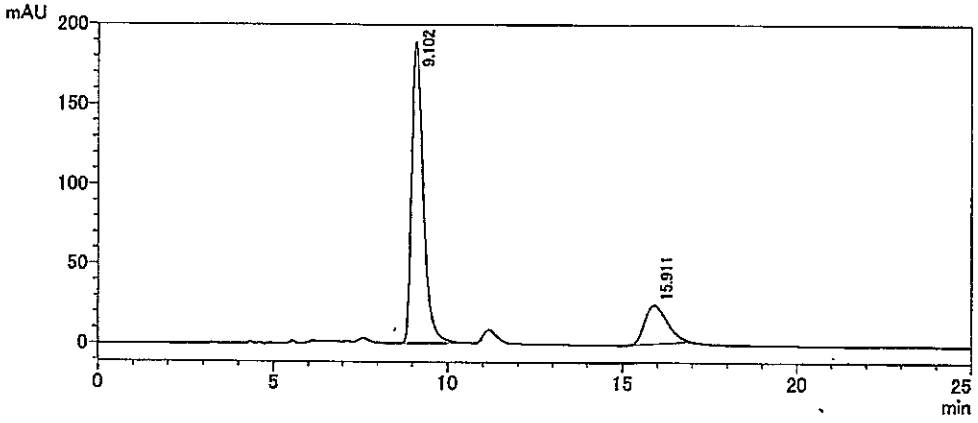


2u



PDA Ch1 228nm

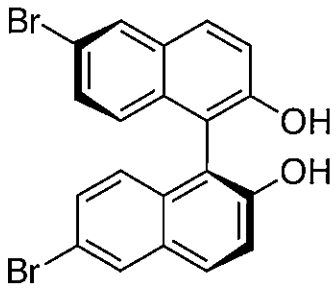
Peak No.	RT (min)	Area	Height	% Area
1	9.757	9057733	348982	49.848
2	17.969	9112846	155834	50.152
Total		18170578	504816	100.000



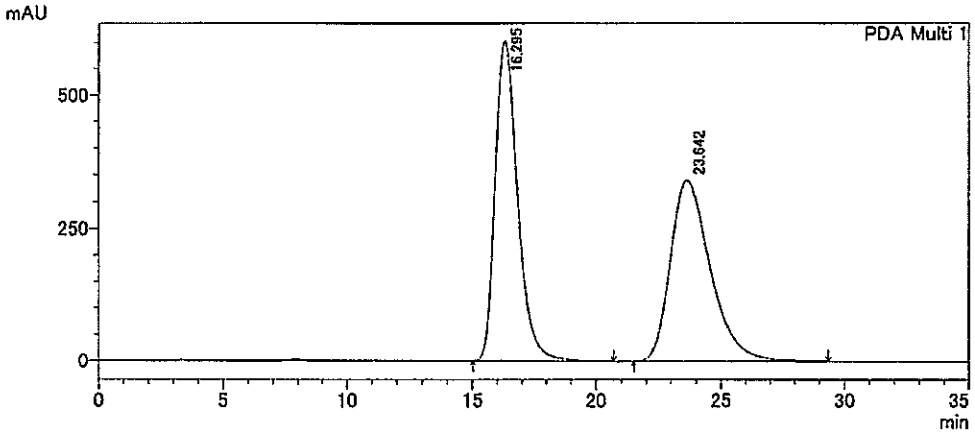
PDA Ch1 228nm

Peak No.	RT (min)	Area	Height	% Area
1	9.102	4379626	188994	80.104
2	15.911	1087793	23980	19.896
Total		5467420	212974	100.000

HPLC data of **2u**

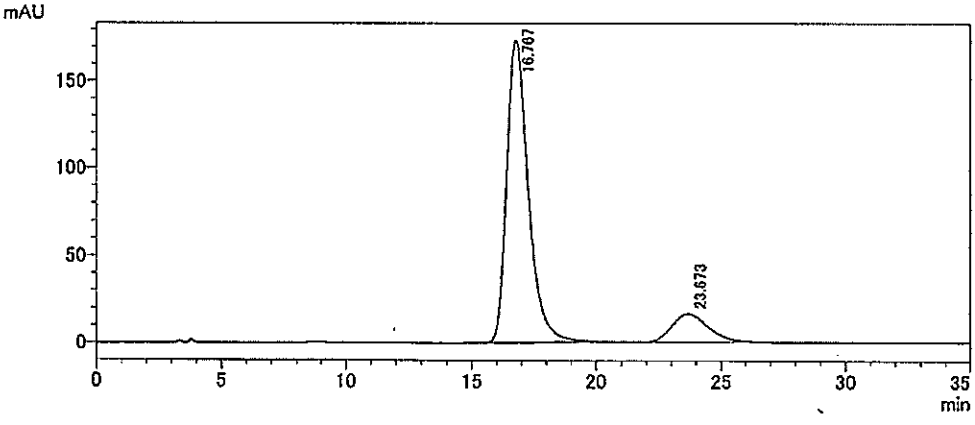


2v



PDA Ch1 231nm 4nm

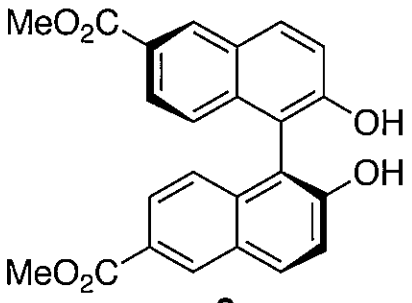
ピーク#	保持時間	高さ	面積%
1	16.295	603522	49.922
2	23.642	340885	50.078
Total		944407	100.000



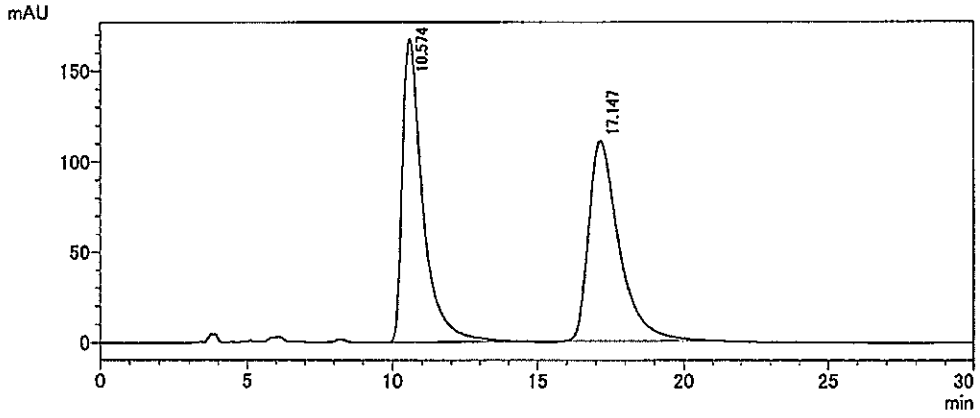
PDA Ch1 231nm

Peak No.	RT (min)	Area	Height	% Area
1	16.767	10579728	173481	86.774
2	23.673	1612524	16059	13.226
Total		12192252	189540	100.000

HPLC data of **2v**

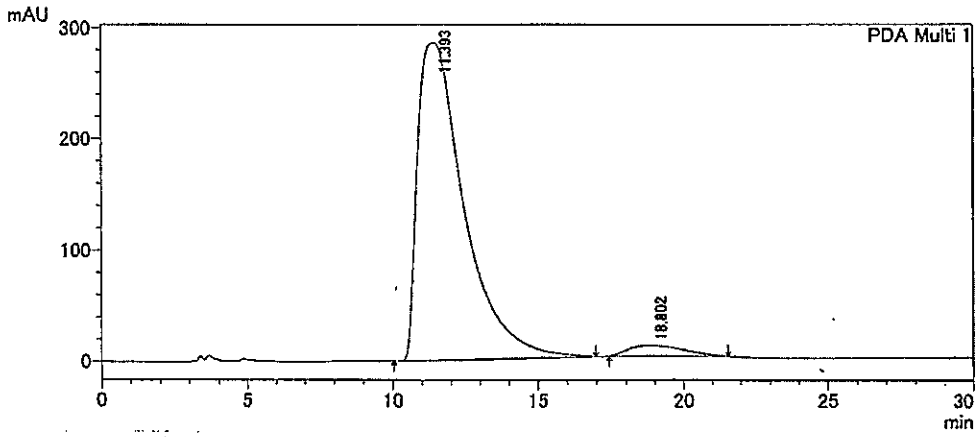


2w



PDA Ch1 239nm

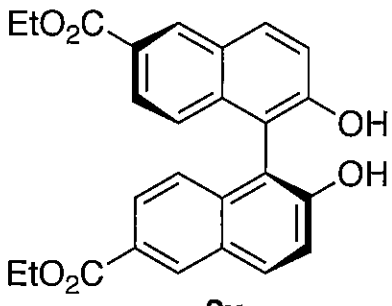
Peak No.	RT (min)	Area	Height	% Area
1	10.574	8067659	166900	50.250
2	17.147	7987230	110379	49.750
Total		16054888	277278	100.000



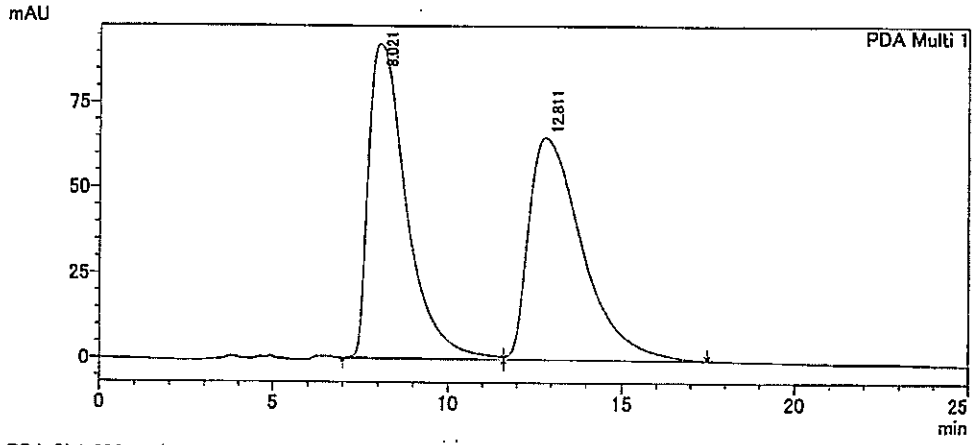
PDA Ch1 239nm 4nm

ピーク#	保持時間	高さ	面積%
1	11.393	285316	96.170
2	18.802	9609	3.830
Total		294925	100.000

HPLC data of **2w**

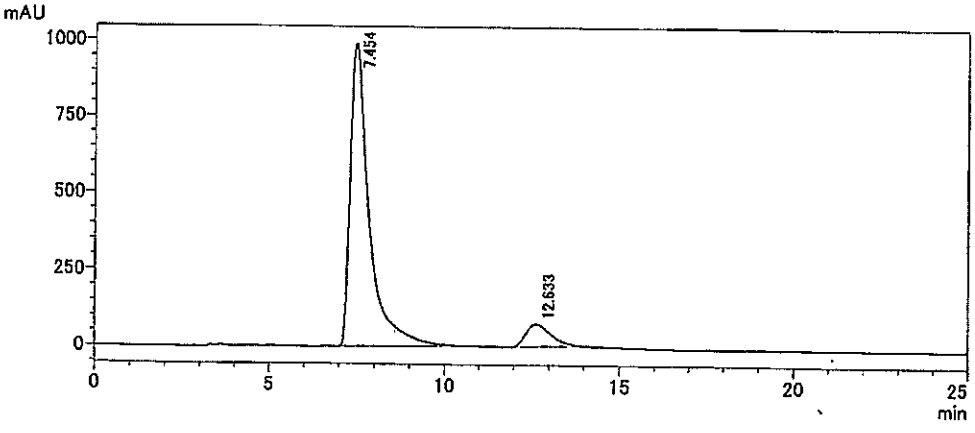


2x



PDA Ch1 239nm 4nm

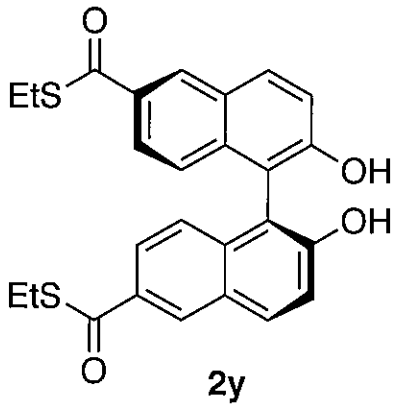
ピーク#	保持時間	高さ	面積%
1	8.021	92307	49.873
2	12.811	65083	50.127
Total		157370	100.000



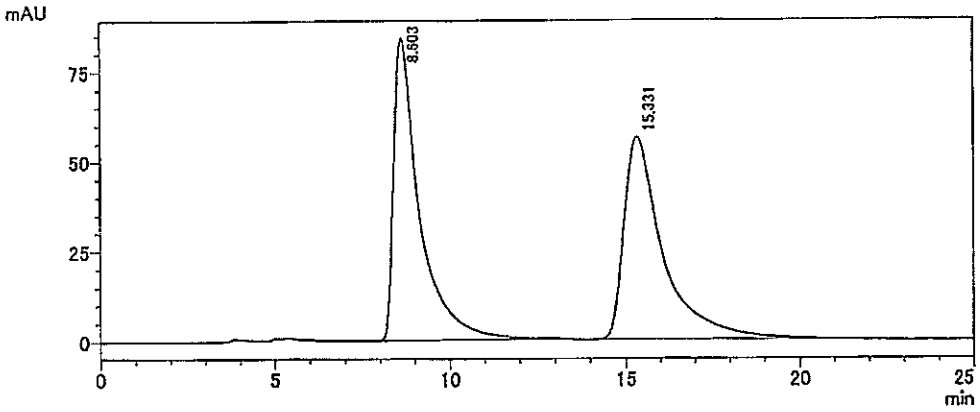
PDA Ch1 239nm

Peak No.	RT (min)	Area	Height	% Area
1	7.454	36562548	988996	90.686
2	12.633	3755042	73562	9.314
Total		40317590	1062559	100.000

HPLC data of **2x**

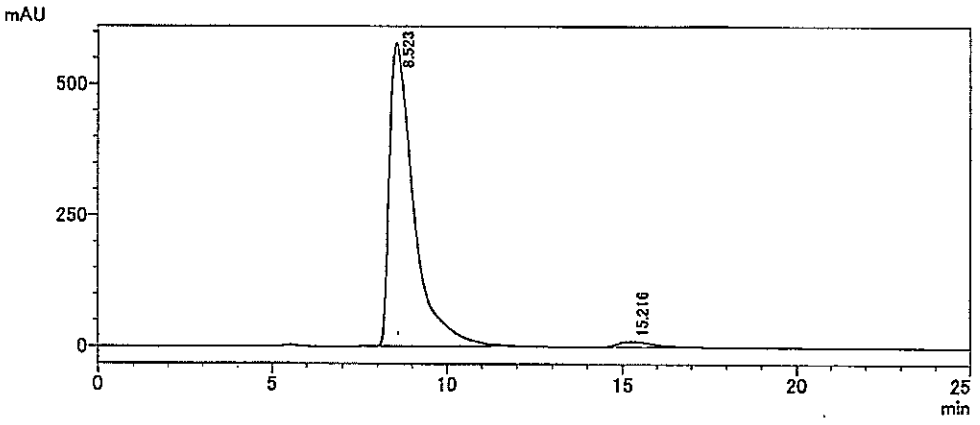


2y



PDA Ch1 244nm

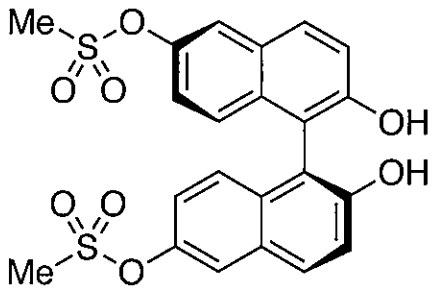
Peak No.	RT (min)	Area	Height	% Area
1	8.603	4396947	84154	50.005
2	15.331	4396073	56148	49.995
Total		8793021	140303	100.000



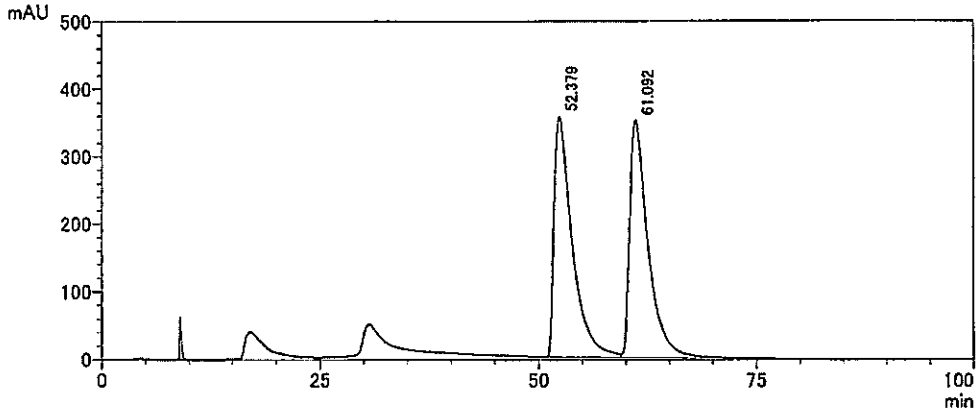
PDA Ch1 244nm

Peak No.	RT (min)	Area	Height	% Area
1	8.523	28507356	578107	97.431
2	15.216	751799	10706	2.569
Total		29259155	588813	100.000

HPLC data of **2y**

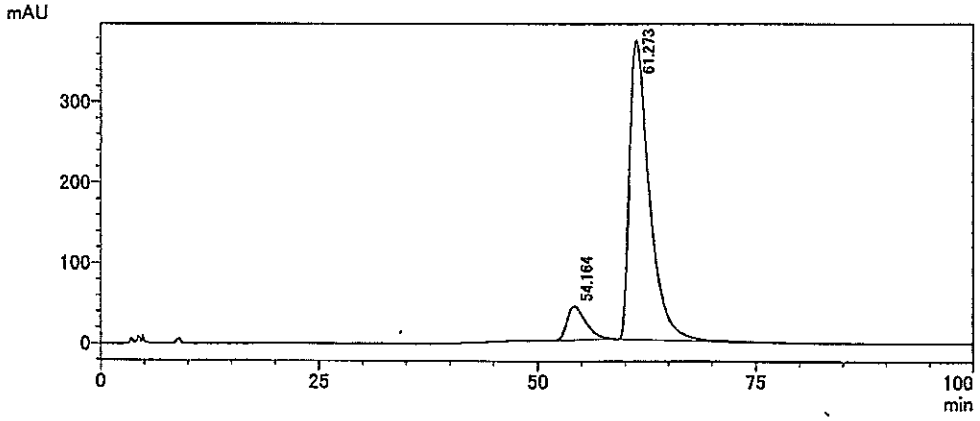


2z



PDA Ch1 230nm

Peak No.	RT (min)	Area	Height	% Area
1	52.379	51025285	354829	49.773
2	61.092	51490608	349674	50.227
Total		102515893	704503	100.000



PDA Ch1 230nm

Peak No.	RT (min)	Area	Height	% Area
1	54.164	6258426	41684	9.527
2	61.273	59431582	371293	90.473
Total		65690009	412978	100.000

HPLC data of **2z**