Electronic Supplementary Information

Design of novel chiral *N,N,O*-tridentate phenanthroline ligands and its application to enantioselective addition of organozinc reagents to aldehydes

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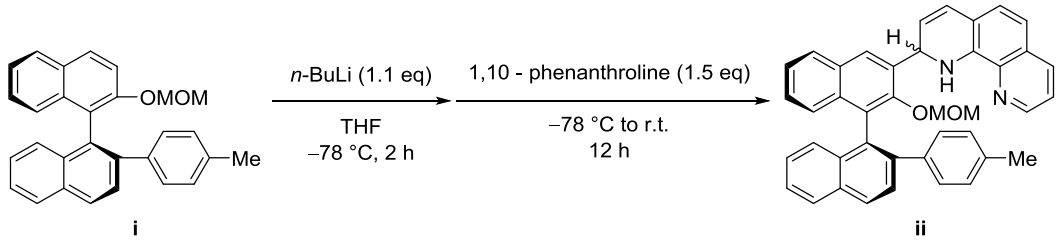
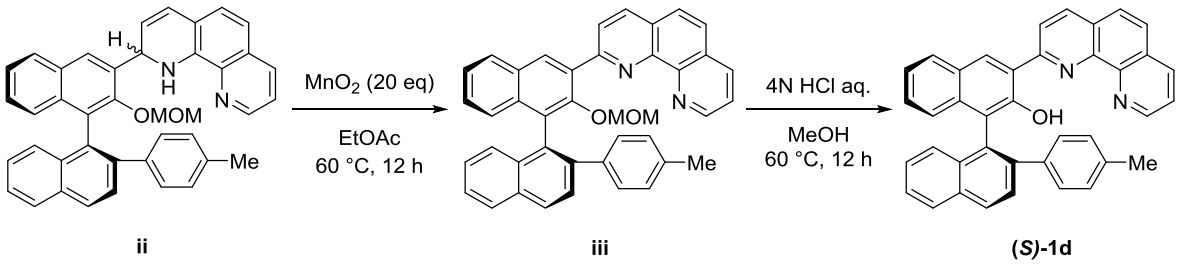
General Information. Infrared (IR) spectra were recorded on a JASCO FT/IR-230 spectrometer. ^{1}H NMR spectra were measured at 25 ˚C on a Varian Mercury 300 (300 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity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

In experiments requiring dry solvent, toluene and THF was purchased from Kanto Chemical Co. Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Other common dry solvents were purchased from Kanto Chemical Co. Inc. and used as received. 1,10-Phenanthroline monohydrate (Kanto) was dried and purified by passing through silica gel pad prior to use. Diethylzinc was purchased from Kanto Chemical Co. Inc. and used as received. Aldehydes were used after distillation or column chromatography on silica gel.

·General procedure for the synthesis of BinThro ligands (*S*)-1

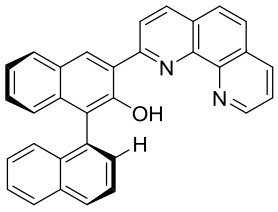


To a stirred solution of (*S*)-1,1'-binaphthyl-2,2'-diol derivative **i**[S1] (1.21 g, 3.0 mmol) in THF (15 mL), *n*-BuLi (1.6M solution in hexane, 2.06 mL, 3.3 mmol) was added dropwise at -78 °C under Ar atmosphere. After stirring for 2 h at the same temperature, 1,10-phenanthroline (810 mg, 4.1 mmol) in THF (20 mL) was added dropwise to the resulting mixture, and the dark purple solution was stirred at the same temperature for additional 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The filtrated organic layer was dried over $MgSO_4$ and evaporated. The residue was used for the next step without further purifications.



To a stirred solution of the crude product **ii** in ethyl acetate (20 mL), MnO_2 (5.20 g, 60 mmol) was added at room temperature. The black suspension was kept stirred at 60 °C for 12 h. The resulting mixture was cooled down to room temperature and filtered through a celite pad to remove MnO_2. The combined organic layers were evaporated and resolved in MeOH (10 mL). To the stirred MeOH solution, 4 M HCl (1 mL) was added, and the mixture was stirred at 60 °C for 12 h. After that, water was added to the reaction mixture which was extracted three times with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (eluting with hexane/ethyl acetate = 2 : 1) to afford (*S*)-**1d** as an orange solid in overall 44% yield (716 mg, 1.3 mmol).

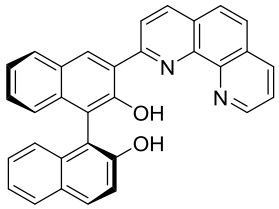
(*R*)-3-(1,10-Phenanthrolin-2-yl)-[1,1'-binaphthalen]-2-ol (1a)



IR (KBr): 3448, 3056, 1624, 1592, 1558, 1508 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.03 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.72 (s, 1H), 8.60 (d, *J* = 8.7 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 8.22 (dd, *J* = 4.8, 1.5 Hz, 1H) 8.01-7.95 (m, 3H) 7.85 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.72 -7.52 (m, 5H), 7.46 (m, 1H), 7.34-7.22 (m, 2H),

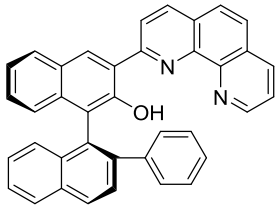
7.10 (m, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 157.1, 155.2, 150.4, 144.4, 142.8, 137.4, 135.7, 135.6, 134.8, 133.6, 132.9, 128.7, 128.5, 128.0, 127.6, 127.5, 127.3, 126.9, 126.7, 126.4, 125.6, 125.5, 125.4, 124.8, 123.2, 122.8, 122.2, 121.4, 119.6 (Three peaks were overlapped.); $[\alpha]_D^{24}$ = –274.2 (c = 0.5, $CHCl_3$); HRMS (ESI) Calcd for $C_{32}H_{21}N_2O$ ($[M+H]^+$) 449.1648. Found 449.1640.

(*S*)-3-(1,10-Phenanthrolin-2-yl)-[1,1'-binaphthalene]-2,2'-diol (1b)



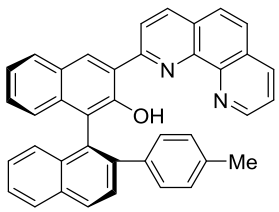
IR (KBr) 3419, 1622, 1596, 1558, 1508, 1467 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.06 (dd, *J* = 4.5, 2.1, 1H), 8.77 (s, 1H), 8.58 (d, *J* = 9.0 Hz,1H), 8.48 (d, *J* = 8.7 Hz, 1H), 8.24 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.98-7.83 (m, 5H), 7.59 (m, 1H), 7.44 (d, 1H), 7.35-7.13 (m, 7H) ; ^{13}C NMR (75 MHz, $CDCl_3$) : δ(ppm) = 156.6, 156.4, 151.4, 150.5, 144.3, 142.6, 137.6, 135.6, 135.5, 133.7, 129.5, 129.1, 128.7, 128.1, 127.9, 127.3, 126.9, 126.8, 126.1, 125.4, 125.2, 124.2, 123.4, 123.3, 122.9, 121.4, 119.2, 117.9, 115.7, 114.7. (one peak was overlaped); $[\alpha]_D^{20}$ = –174.0 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{32}H_{21}N_2O_2$ ($[M+H]^+$) 465.1598. Found 465.1595.

(*S*)-3-(1,10-Phenanthrolin-2-yl)-2'-phenyl-[1,1'-binaphthalen]-2-ol (1c)



IR (KBr): 3470, 3050, 1622, 1592, 1557, 1507 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.07 (d, *J* = 4.2, 1.5 Hz, 1H), 8.54 (s, 1H), 8.44 (d, *J* = 8.7, 1H), 8.34 (d, *J* = 8.7, 1H), 8.20 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H) 7.98 (d, *J* = 8.4 Hz, 1H), 7.77-7.70 (m, 4H), 7.58 (dd, *J* = 4.5, 4.2 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.48-7.43 (m, 3H), 7.24 (m, 1H), 7.17-7.14 (m, 2H), 7.04-6.95 (m, 4H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 157.1, 155.9, 150.3, 144.4, 142.6, 142.3, 140.0, 137.2, 135.5, 135.3, 133.0, 132.8, 132.3, 128.8, 128.6, 128.4, 128.2, 127.8, 127.7, 127.6, 127.2, 127.1, 126.9, 126.61, 126.55, 126.4, 126.1, 126.0, 125.4, 124.5, 123.1, 122.6, 121.0, 120.7, 119.3 (Three peaks were overlapped.); $[\alpha]_D^{21}$ = +19.3 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{32}H_{25}N_2O$ ($[M+H]^+$) 525.1961. Found 525.1962.

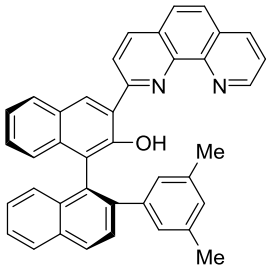
(*S*)-3-(1,10-Phenanthrolin-2-yl)-2'-(p-tolyl)-[1,1'-binaphthalen]-2-ol (1d)



IR (KBr): 3433, 3055, 1624, 1592, 1558, 1508, 1467 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.06 (dd, *J* = 4.5, 1.8 Hz, 1H), 8.52 (s, 1H), 8.39 (d, *J* = 8.7 Hz, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 8.18 (dd, *J* = 7.5, 1.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H) 7.97 (d, *J* = 7.8 Hz, 1H), 7.76 -7.69 (m, 4H), 7.57 (dd, *J* = 8.4, 4.5 Hz, 1H), 7.50-7.42 (m, 2H), 7.38-7.35 (m, 2H), 7.26 (m, 1H), 7.19-7.13 (m, 2H), 6.99 (m, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 2.09 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 157.0, 155.8, 150.2, 144.3,

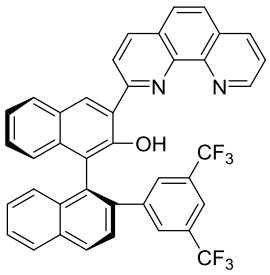
142.5, 140.0, 139.4, 137.2, 135.5, 135.4, 133.0, 132.7, 132.2, 128.7, 128.5, 128.4, 128.0, 127.71, 127.68, 127.59, 127.2, 126.9, 126.6, 126.5, 126.2, 126.0, 125.3, 125.3, 124.6, 123.0, 122.6, 121.1, 120.7, 119.2, 21.2. (Two peaks were overlapped.); $[\alpha]_D^{22}$ = + 100.6 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{39}H_{26}N_2ONa$ ($[M+Na]^+$) 561.1943. Found 561.1936.

(*S*)-2'-(3,5-Dimethylphenyl)-3-(1,10-phenanthrolin-2-yl)-[1,1'-binaphthalen]-2-ol (1e)



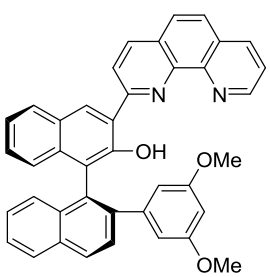
IR (KBr): 3436, 2924, 1623, 1598, 1557, 1508, 1467 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.06 (dd, *J* = 3.9, 1.5 Hz, 1H), 8.48 (s, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.30 (d, *J* = 8.7 Hz, 1H), 8.16 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.78-7.68 (m, 4H), 7.56 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.51 (d, *J* = 9.3 Hz, 1H) 7.45 (m, 1H), 7.28 (m, 1H), 7.20-7.15 (m, 2H), 7.08 (s, 2H), 7.00 (m, 2H), 6.58 (s, 1H), 1.99 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 156.7, 155.6, 150.1, 144.2, 142.28, 142.25, 140.1, 137.2, 136.2, 135.8, 135.3, 133.1, 132.7, 132.2, 128.5, 128.42, 128.39, 127.75, 127.66, 127.56, 127.45, 127.1, 127.0, 126.8, 126.5, 126.3, 126.1, 126.0, 125.3, 124.8, 122.9, 122.5, 121.1, 120.8, 119.0, 21.4. (Two peaks were overlapped.); $[\alpha]_D^{21}$ = +99.4 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{40}H_{28}N_2ONa$ ($[M+Na]^+$) 575.2094. Found 575.2097.

(*S*)-2'-(3,5-Bis(trifluoromethyl)phenyl)-3-(1,10-phenanthrolin-2-yl)-[1,1'-binaphthalen]-2-ol (1f)



IR (KBr) 3447, 1623, 1598, 1558, 1508, 1467 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.07 (dd, *J* = 2.1, 1.8 Hz, 1H), 8.60 (s, 1H), 8.49 (d, *J* = 8.7 Hz, 1H), 8.43 (d, *J* = 8.7 Hz, 1H), 8.22 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.11 (d, *J* = 8.1, 1H) 8.01 (d, *J* = 8.4 Hz, 1H), 7.88-7.82 (m, 5H) 7.70 (d, *J* = 8.4 Hz, 1H) 7.63-7.50 (m, 3H), 7.40-7.32 (m, 2H), 7.26-7.16 (m, 2H), 6.89 (m, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 156.6, 155.9, 150.4, 144.4, 143.9, 142.7, 137.4, 136.8, 135.5, 135.0, 133.5, 133.3, 133.0, 129.9 (q, *J* = 33 Hz), 129.1(m), 128.7, 128.6, 128.3, 127.9, 127.8, 127.7, 127.2, 126.7, 126.6, 126.2, 125.4, 123.8, 123.2, 123.0 (q, *J* = 270 Hz) 122.9, 120.9, 119.7 (m), 119.1. (Two peaks were overlapped.); $[\alpha]_D^{20}$ = +148.4 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{40}H_{23}N_2OF_6$ ($[M+H]^+$) 661.1709. Found 661.1706.

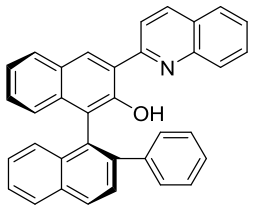
(*S*)-2'-(3,5-Bistrimethoxyphenyl)-3-(1,10-phenanthrolin-2-yl)-[1,1'-binaphthalen]-2-ol (1g)



IR (KBr) 3974, 3931, 3819, 1593, 1505, 1465, 1203, 1153, 847 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.00 (m, 1H), 8.41 (s, 1H), 8.21 (s, 2H), 8.11 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J*

= 8.7 Hz, 1H), 7.74 (m, 1H), 7.60 (s, 2H), 7.52-7.68 (m, 3H), 7.15-7.36 (m, 3H), 7.04 (m, 1H), 6.78 (m, 2H), 6.10 (t, *J* = 2.4 Hz, 1H), 3.41 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 159.2, 156.8, 155.4, 150.2, 144.3, 142.5, 140.0, 137.3, 135.7, 135.4, 133.1, 132.9, 132.3, 128.5, 128.0, 127.7, 127.6, 127.4, 126.8, 126.7, 126.5, 126.4, 126.2, 125.5, 125.3, 124.6, 123.1, 122.6, 121.2, 120.9, 119.2, 106.7, 99.4, 55.1 (Two peaks were overlapped.); $[\alpha]_D^{27}$ = +235.0 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{40}H_{28}N_2O_3$ ($[M+H]^+$) 585.2178. Found 585.2173.

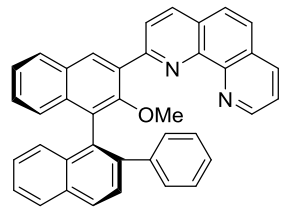
(*S*)-2'-Phenyl-3-(quinolin-2-yl)-[1,1'-binaphthalen]-2-ol (4a)



This ligand was synthesized according to general procedure using quinolone instead of 1,10-phenanthroline.

IR (KBr) 3462, 3050, 1602, 1508 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.53 (s, 1H), 8.35 (d, *J* = 9.0, 1H), 8.30 (d, *J* = 9.3, 1H), 8.06 (d, *J* = 8.4 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 6.6 Hz, 1H), 7.85 (d, *J* = 8.1, 1H), 7.80 (m, 1H), 7.74-7.68 (m, 2H), 7.56 (m, 1H), 7.49-7.44 (m, 2H), 7.38-7.35 (m, 2H), 7.29 (m, 1H), 7.23-7.15 (m, 2H), 7.04-6.94 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.5, 155.3, 144.3, 142.1, 140.0, 137.5, 135.2, 132.8, 132.7, 131.7, 130.3, 128.6, 128.5, 128.2, 127.93, 127.91, 127.88, 127.5, 127.4, 127.3, 127.1, 126.8, 126.7, 126.4, 126.3, 126.2, 126.1, 125.5, 124.5, 122.8, 120.8, 120.4, 117.7.; $[\alpha]_D^{20}$ = +75.8 (c = 1.0, $CHCl_3$); HRMS (ESI) Calcd for $C_{35}H_{23}NO$ ($[M+H]^+$) 474.1858. Found 474.1853.

(*S*)-2-(2-Methoxy-2'-phenyl-[1,1'-binaphthalen]-3-yl)-1,10-phenanthroline (4b)

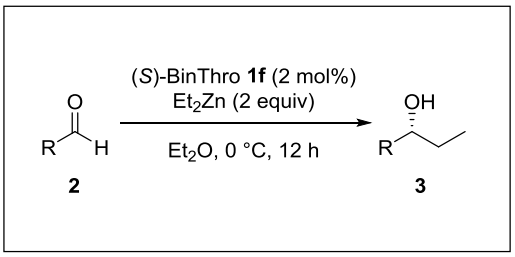


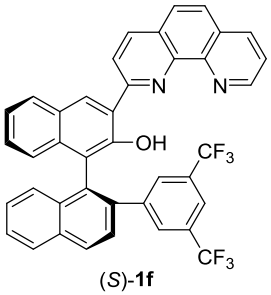
This ligand was synthesized with simple protection of hydroxy group of ligand (*S*)-**1c** using NaH and MeI in THF solvent at room temperature.

IR (KBr) 3418, 1588, 1505, 1454, 1410, 1018, 851, 826, 752, 701 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm) = 9.25 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.59 (s, 1H), 8.25 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.98-8.01 (m, 2H), 7.70-7.90 (m, 4H), 7.62 (m, 1H), 7.38-7.50 (m, 2H), 7.22-7.35 (m, 6H), 7.09-7.16 (m, 3H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) = 157.4, 153.7, 150.6, 146.5, 146.4, 142.3, 140.4, 136.3, 135.8, 135.1, 133.9, 133.5, 133.0, 132.9, 131.9, 130.7, 129.24, 129.19, 129.0, 128.5, 128.3, 128.2, 128.1, 127.7, 127.6, 127.2, 127.1, 126.7, 126.63, 126.60, 126.5, 126.2, 125.9, 125.14, 125.06, 123.1, 61.5;

$[\alpha]_D^{27}$ = –33.8 (c = 0.5, $CHCl_3$); HRMS (ESI) Calcd for $C_{39}H_{26}N_2O$ ($[M+H]^+$) 539.2123. Found 539.2117.

·General procedure for the enantioselective addition of diethylzinc to aldehydes 2.

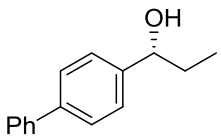




(*S*)-**1f**

To a solution of (*S*)-**1f** (2.64 mg, 0.004 mmol) in dry ether (1 mL) was added dropwise 1.0 M hexane solution of diethylzinc (400 μL, 0.4 mmol) at 0 °C under Ar and stirred for 30 min. Aldehydes **5** (0.20 mmol) was then added to the resulting orange solution at the same temperature, and the stirring was maintained for 12 h. The mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate and dried over $MgSO_4$. After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate) to give the desired product **3**.

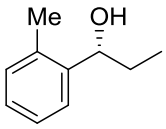
(*R*)-1-(Biphenyl-4-yl)propanol (3a).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.26-7.62 (m, 9H), 4.66 (t, *J* = 6.9 Hz, 1H), 2.03 (br, 1H), 1.70-2.00 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OJ-H, hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, retention time; 36.8 min (*S*) and 40.0 min(*R*)). [e.r. = 95.1/4.9][e.e. = 90.2%]

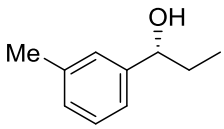
(*R*)-1-(*o*-Tolyl)propan-1-ol (3b).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.15-7.26 (m, 3H), 4.87 (t, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.72-1.85 (m, 3H), 1.00 (t, *J* =7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OB-H, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min, retention time; 11.7 min (*S*) and 15.3 min(*R*)). [e.r. = 95.4/4.6][e.e. = 90.8%]

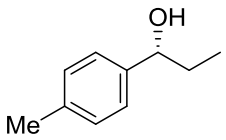
(*R*)-1-(*m*-Tolyl)propan-1-ol (3c).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.07–7.27 (m, 4H), 4.57 (t, *J* = 6.4 Hz, 1H), 2.37 (s, 3H), 1.81(s, 1H), 1.72–1.86 (m, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S3]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OB-H, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min, retention time; 12.4 min (*S*) and 14.2 min(*R*)). [e.r. = 95.5/4.5][e.e. = 91.0%]

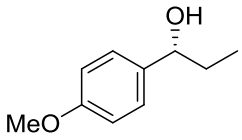
(*R*)-1-(*p*-Tolyl)propan-1-ol (3d).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.26 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.57 (t, *J* = 6.6 Hz, 1H), 2.36 (s, 3H), 1.65-1.95 (d, *J* =6.6 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OJ-H, hexane/isopropanol = 97/3, flow rate = 0.5 mL/min, retention time; 26.8 min (*R*) and 30.2 min(*S*)). [e.r. = 94.1/5.9][e.e. = 88.2%]

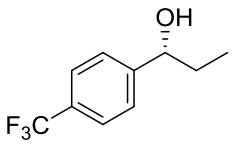
(*R*)-1-(4-Methoxyphenyl)propan-1-ol (3e).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.26 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.54 (t, *J* = 6.9 Hz, 1H), 3.81 (s, 3H), 1.62-1.84 (m, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S4]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD, hexane/isopropanol = 97/3, flow rate = 0.7 mL/min, retention time; 24.7 min (*R*) and 31.3 min(*S*)). [e.r. = 94.1/5.9][e.e. = 88.2%]

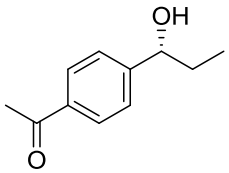
(*R*)-1-(4-Trifluoromethylphenyl)propan-1-ol (3f).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.60 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 4.69 (t, *J*= 6.9 Hz, 1H), 1.99 (br, 1H), 1.70-1.85 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OJ-H, hexane/isopropanol = 98/2, flow rate = 1.0 mL/min, retention time; 18.8 min (*S*) and 20.0 min(*R*)). [e.r. = 96.7/3.3][e.e. = 93.4%]

(*R*)-1-(4-(1-Hydroxypropyl)phenyl)ethan-1-one (3g).

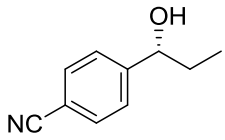


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.92-7.96 (m, 2H), 7.42-7.45 (m, 2H), 4.69 (t, *J* = 6.6 Hz, 1H), 2.61 (s, 3H), 1.98 (br, 1H), 1.72-1.84 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); $[\alpha]_D^{25}$ = +31.6 (c = 1.0, $CHCl_3$). The detailed spectral data has been reported in the literature.[S5]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 97/3, flow rate = 1.0 mL/min,

retention time; 21.6 min (*R*) and 23.4 min(*S*)). [e.r. = 96.3/3.7][e.e. = 92.6%]

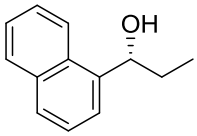
(*R*)-4-(1-Hydroxypropyl)benzonitrile (3h).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.61-7.65 (m, 2H), 7.44-7.47 (m, 2H), 4.69 (t, *J* = 6.3 Hz, 1H), 2.09 (br, 1H), 1.72-1.82 (m, 2H), 0.93 (t, *J* = 7.8 Hz, 3H). The detailed spectral data has been reported in the literature.[S3]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALPAK AD-H, hexane/isopropanol = 97/3, flow rate = 0.8 mL/min, retention time; 49.1 min (*R*) and 53.0 min(*S*)). [e.r. = 95.5/4.5][e.e. = 91.0%]

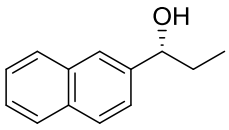
(*R*)-1-(Naphthalen-1-yl)propan-1-ol (3i).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.12 (m, 1H), 7.76-7.91 (m, 2H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.45-7.53 (m, 3H), 5.39 (t, *J* = 6.9 Hz, 1H), 1.86-2.07 (m, 3H), 1.05 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 90/10, flow rate = 1.0 mL/min, retention time; 9.0 min (*S*) and 16.0 min(*R*)). [e.r. = 97.3/2.7][e.e. = 94.6%]

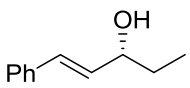
(*R*)-1-(Naphthalen-2-yl)propan-1-ol (3j).



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.82-7.86 (m, 3H), 7.77 (s, 1H), 7.45-7.52 (m, 3H), 4.76 (t, *J* =6.9 Hz, 1H), 2.13 (br, 1H), 1.80-2.03 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, retention time; 20.8 min (*S*) and 22.2 min(*R*)). [e.r. = 94.9/5.1][e.e. = 89.8%]

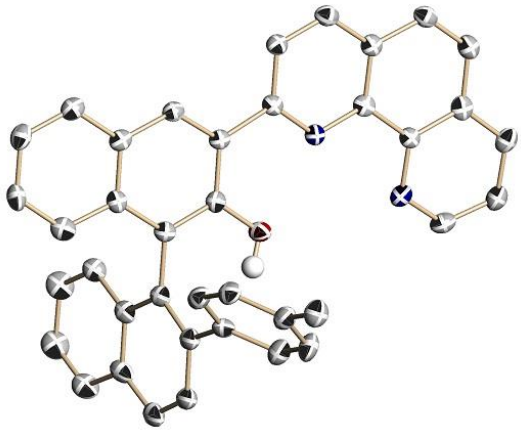
(*R*)-*trans*-1-Phenylpent-1-en-3-ol (3k).

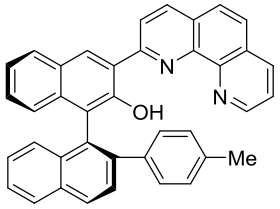


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.21-7.41 (m, 5H), 6.58 (d, *J* = 16.2 Hz, 1H), 6.22 (dd, *J* = 16.2 Hz, 6.9 Hz) 4.22 (q, *J* = 6.9 Hz), 1.50-1.88 (m, 3H), 0.99 (t, *J* = 7.5 Hz, 3H). The detailed spectral data has been reported in the literature.[S2]

The enantiomeric purity of the product was determined by HPLC analysis (Daicel CHIRALCEL OD-H, hexane/isopropanol = 90/10, flow rate = 0.5 mL/min, retention time; 18.4 min (*R*) and 28.2 min(*S*)). [e.r. = 79.8/20.4][e.e. = 59.4%]

X-ray crystallographic analysis of (*S*)-3-(1,10-Phenanthrolin-2-yl)-2'-(p-tolyl)-[1,1'-binaphthalen]-2-ol (1d).





The product was recrystallized from toluene/diethyl ether/hexanes.

A specimen of $C_{39}H_{22}N_2O$, approximate dimensions 0.200 mm x 0.200 mm x 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 17382 reflections to a maximum θ angle of 25.12° (0.84 Å resolution), of which 8726 were independent (average redundancy 1.992, completeness = 98.8%, R_{int} = 3.76%) and 7057 (80.87%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.8103(7) Å, b = 17.0401(15) Å, c = 20.5041(16) Å, β = 97.144(2)°, volume = 2707.7(4) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9690 and 0.9840.

The final anisotropic full-matrix least-squares refinement on F^2 with 761 variables converged at R1 = 4.41%, for the observed data and wR2 = 9.88% for all data. The goodness-of-fit was 1.149. The largest peak in the final difference electron density synthesis was 0.268 $e^-/Å^3$ and the largest hole was -0.198 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.311 g/cm^3 and F(000), 1112 e^-.

Table 1. Sample and crystal data

Chemical formula	$C_{39}H_{22}N_2O$	
Formula weight	534.58	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.200 x 0.400 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.8103(7) Å	α = 90°
	b = 17.0401(15) Å	β = 97.144(2)°
	c = 20.5041(16) Å	γ = 90°
Volume	2707.7(4) $Å^3$	
Z	4	
Density (calculated)	1.311 g/cm^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1112	

Table 2. Data collection and structure refinement

Theta range for data collection	2.33 to 25.12°	
Index ranges	−9<=h<=7, −19<=k<=20, −20<=l<=24	
Reflections collected	17382	
Independent reflections	8726 [R(int) = 0.0376]	
Absorption correction	multi-scan	
Max. and min. transmission	0.9840 and 0.9690	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8726 / 1 / 761	
Goodness-of-fit on F^2	1.149	
Δ/σ_{max}	0.018	
Final R indices	7057 data; $I>2\sigma(I)$	R1 = 0.0441, wR2 = 0.0911
	all data	R1 = 0.0659, wR2 = 0.0988
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0409P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.1(8)	
Largest diff. peak and hole	0.268 and −0.198 eÅ^{-3}	
R.M.S. deviation from mean	0.044 eÅ^{-3}	

·References.

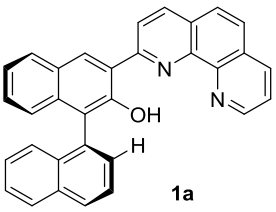
(S1) M. Ichinose, H. Suematsu, Y. Yasutomi, Y. Nishioka, T. Uchida and T. Katsuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 9884.

(S2) M. Hatano, T. Miyamoto and K. Ishihara, *J. Org. Chem.* **2006** , *71*, 6474.

(S3) S. Yi-Shan, R. Boobalan, C. Chen and G.-H. Lee, *Tetrahedron: Asymmetry* **2014**, *25*, 327.

(S4) Y.-J. Chen, R.-X. Lin and C. Chen, *Tetrahedon: Asymmetry* **2004**, *15*, 3561.

(S5) T. Werner, A. M. Riahi and H. Schramm, *Synthesis* **2011**, 3482.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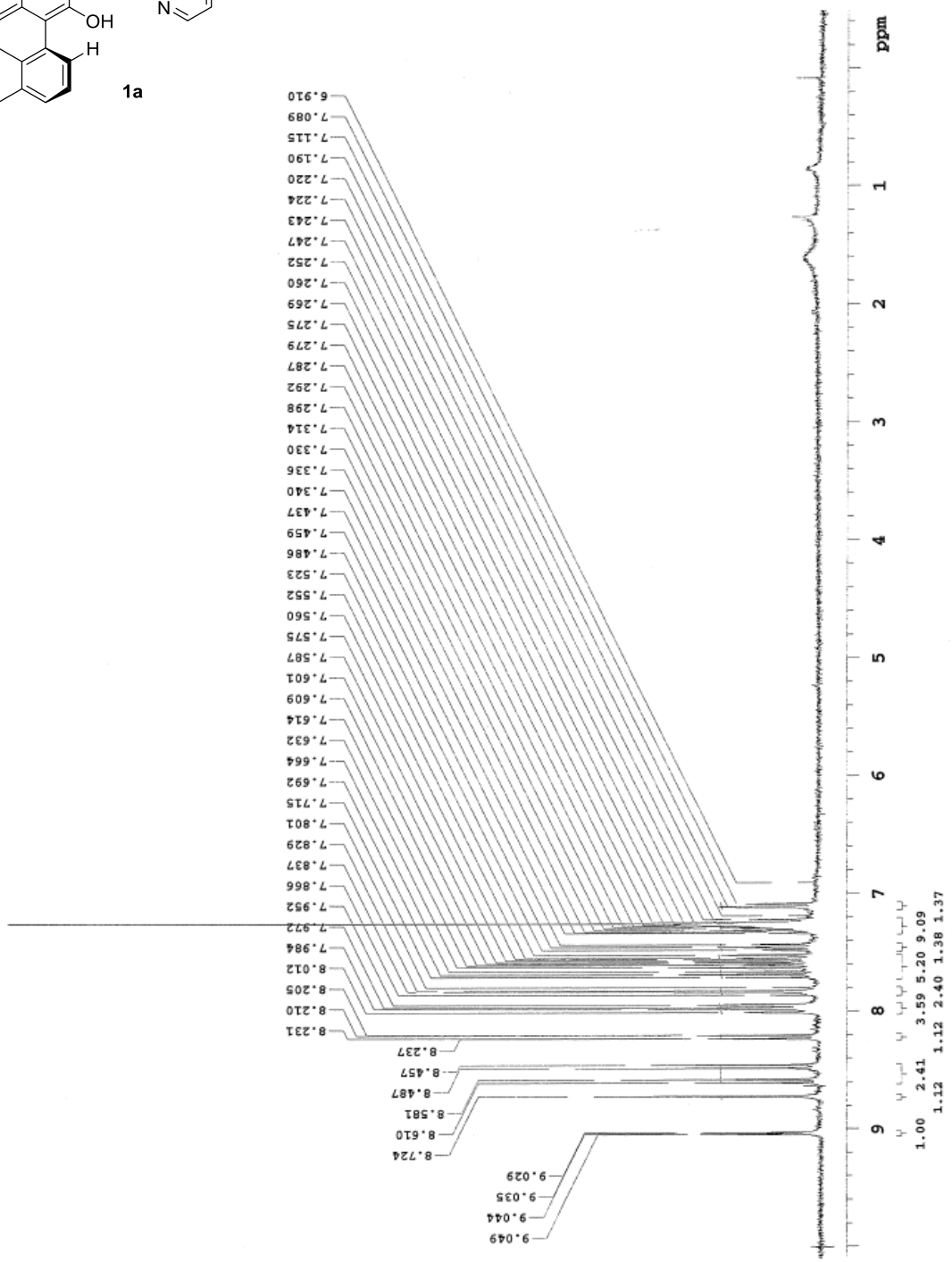
1a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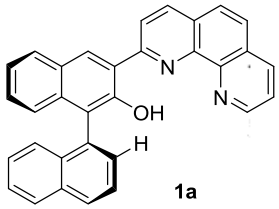
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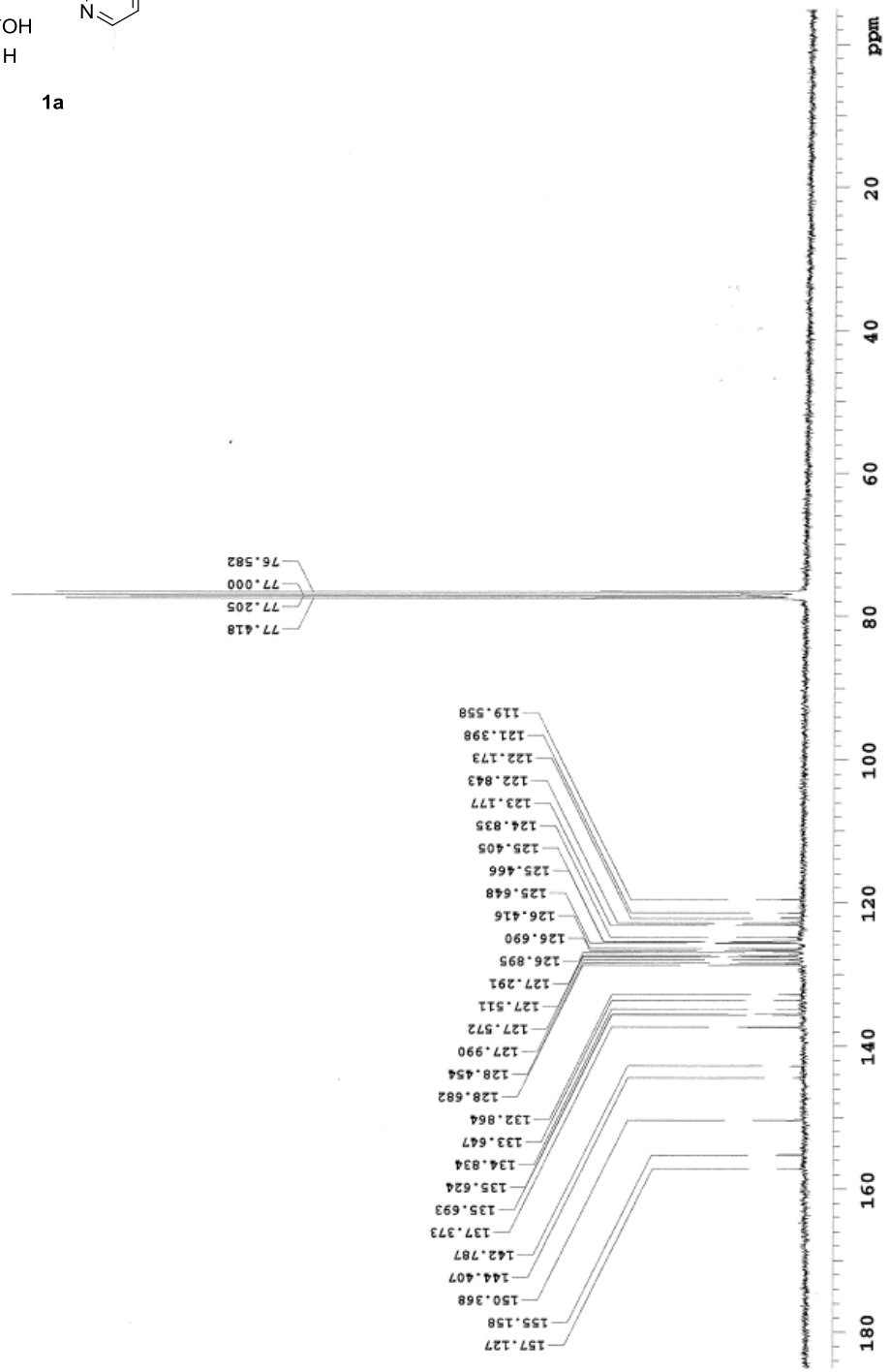
1a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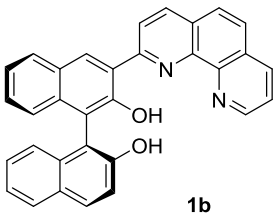
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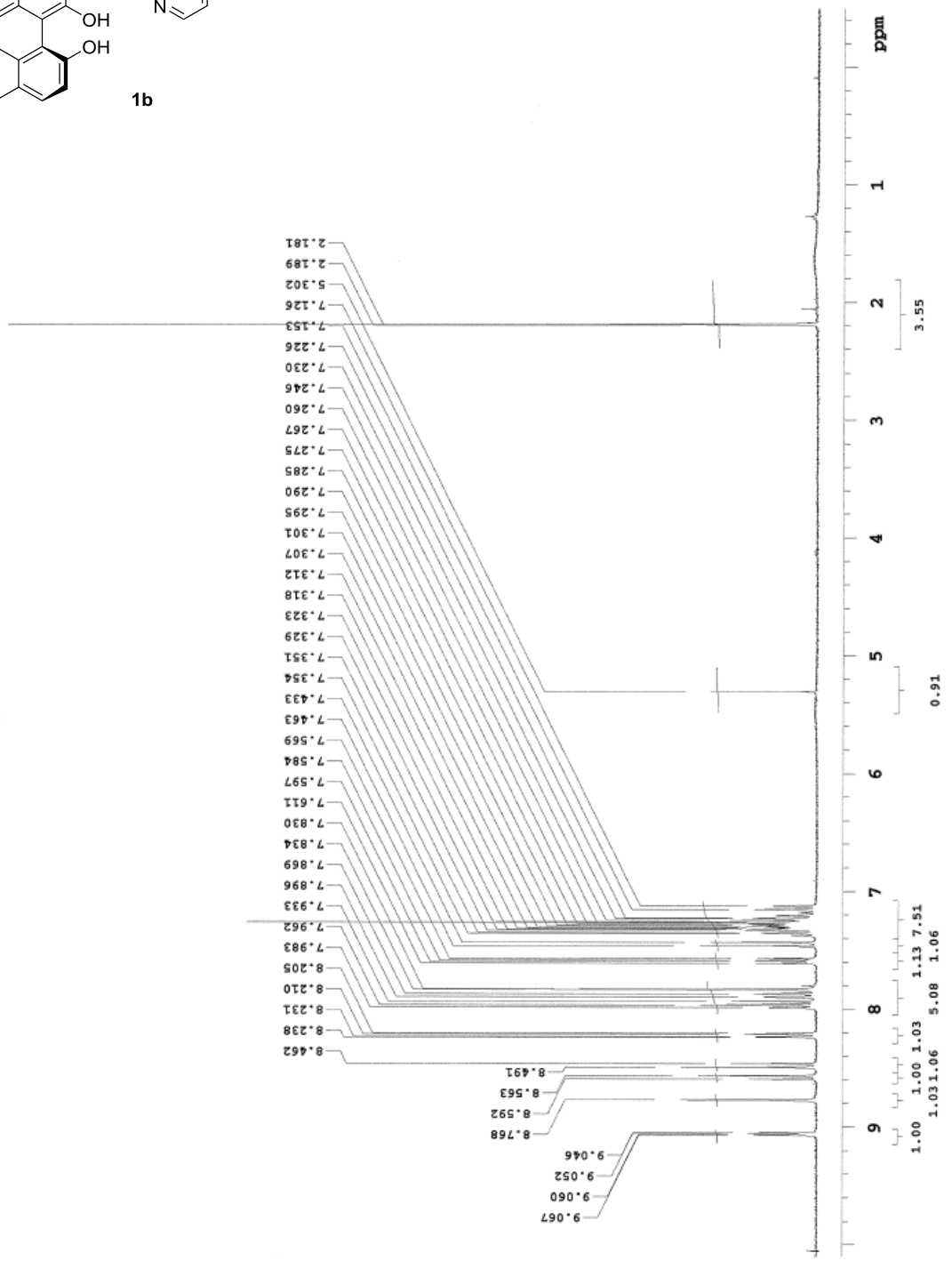
OH
OH

1b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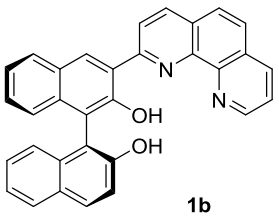
N
N
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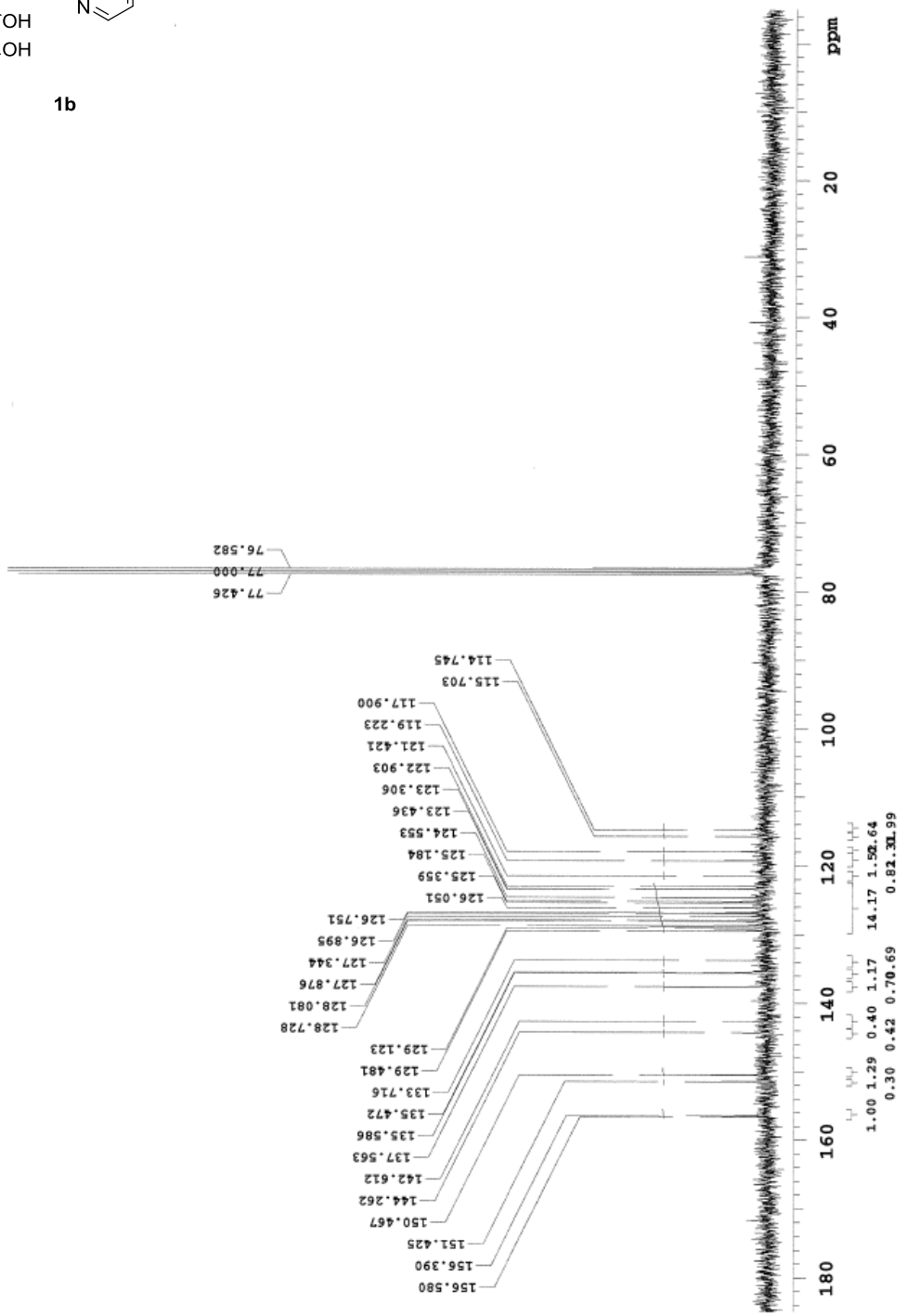
OH

1b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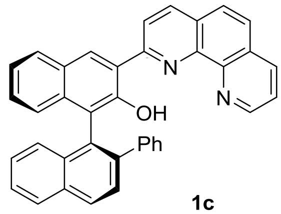
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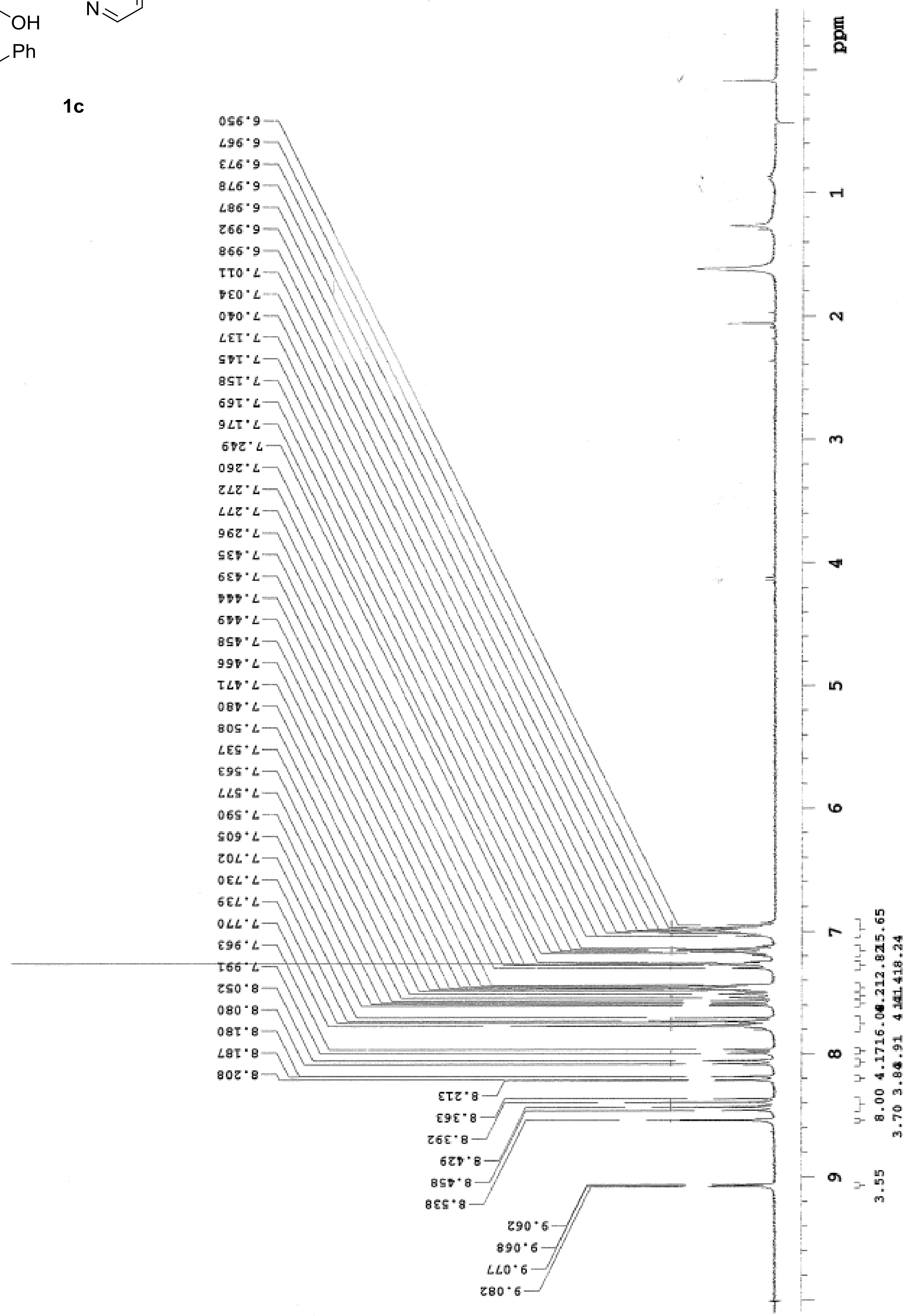
N
OH
Ph

1c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7.145
7.158
7.169
7.176
7.249
7.260
7.272
7.277
7.296
7.435
7.439
7.444
7.449
7.458
7.466
7.471
7.480
7.508
7.537
7.563
7.577
7.590
7.605
7.702
7.730
7.739
7.770
7.963
7.991
8.052
8.080
8.180
8.187
8.208
8.213
8.363
8.392
8.429
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9.068
9.077
9.082
ppm
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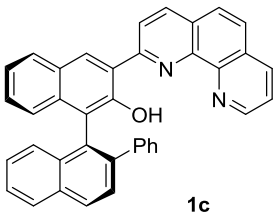
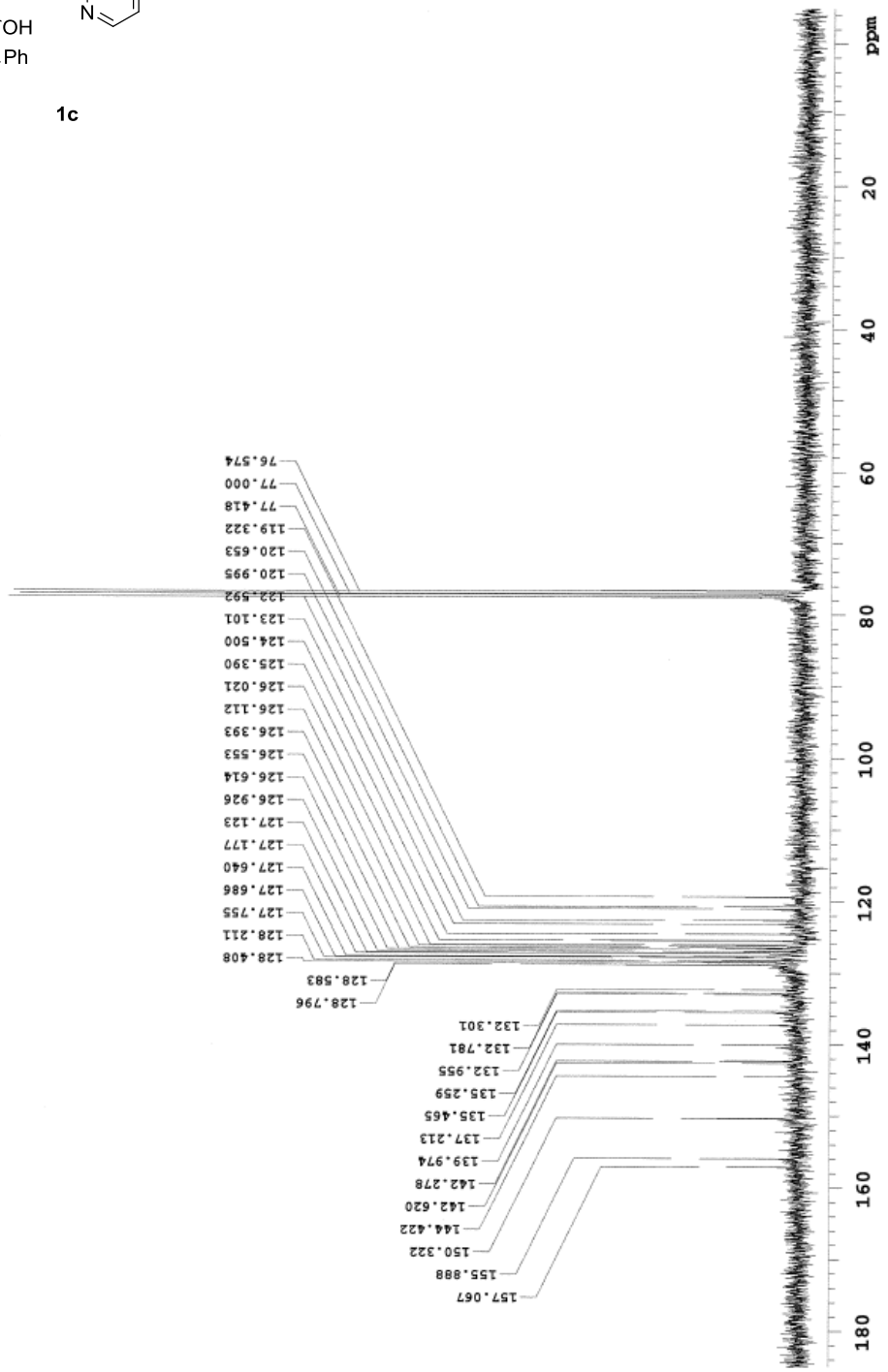
2
3
4
5
6
7
8
9


N
N
OH
Ph

1c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80
100
120
140
160
180
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77.000
77.418
119.322
120.653
120.995
122.592
123.101
124.500
125.390
126.021
126.112
126.393
126.553
126.614
126.926
127.123
127.177
127.640
127.686
127.755
128.211
128.408
128.583
128.796
132.301
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142.620
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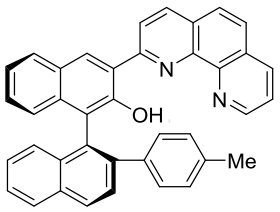
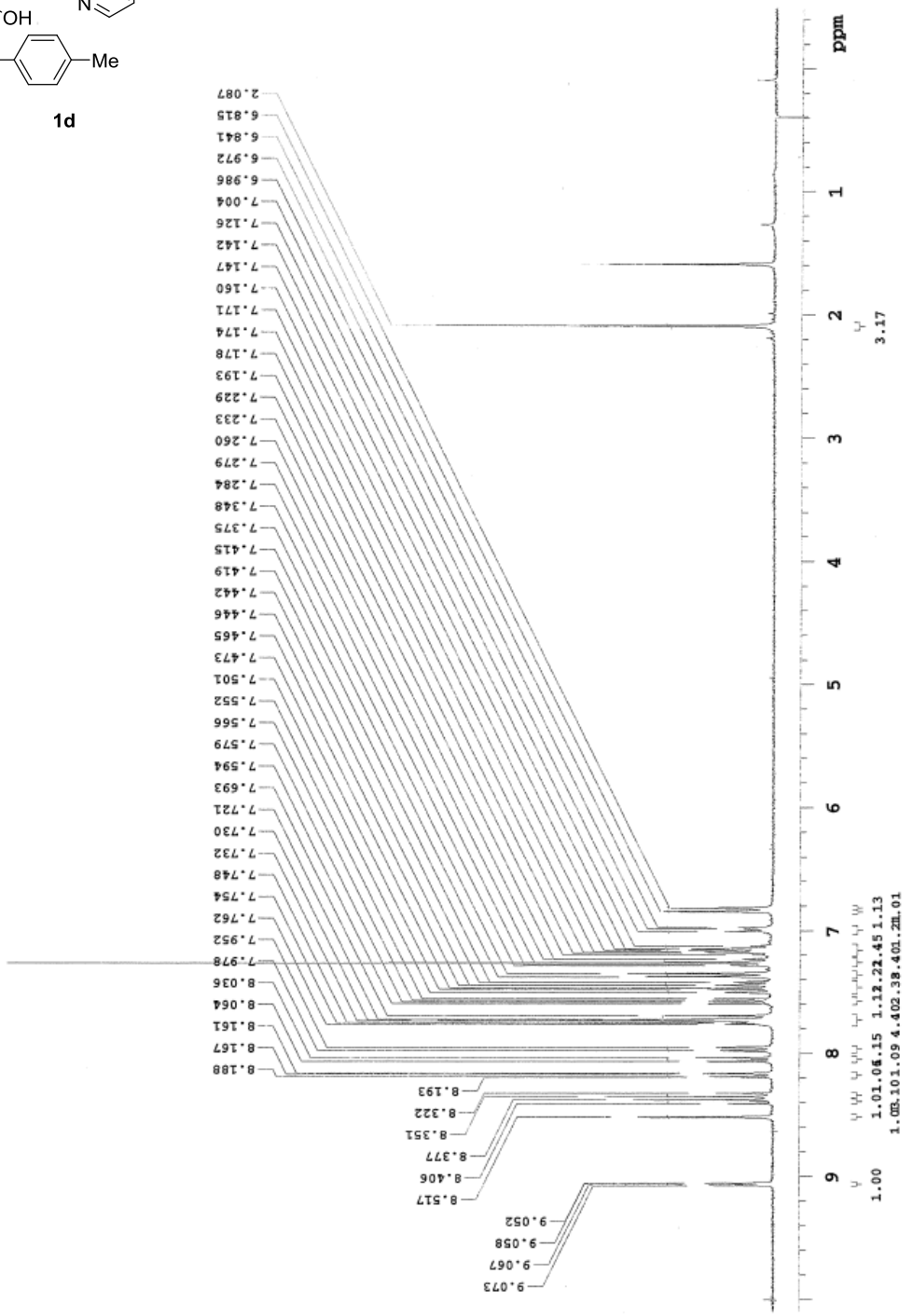
157.067


N
N
OH
Me

1d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6.841
6.972
6.986
7.004
7.126
7.142
7.147
7.160
7.171
7.174
7.178
7.193
7.229
7.233
7.260
7.279
7.284
7.348
7.375
7.415
7.419
7.442
7.446
7.465
7.473
7.501
7.552
7.566
7.579
7.594
7.693
7.721
7.730
7.732
7.748
7.754
7.762
7.952
7.978
8.036
8.064
8.161
8.167
8.188
8.193
8.322
8.351
8.377
8.406
8.517
9.052
9.058
9.067
9.073
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1.00
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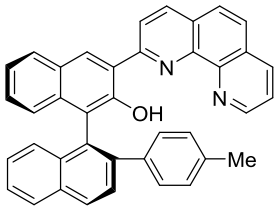
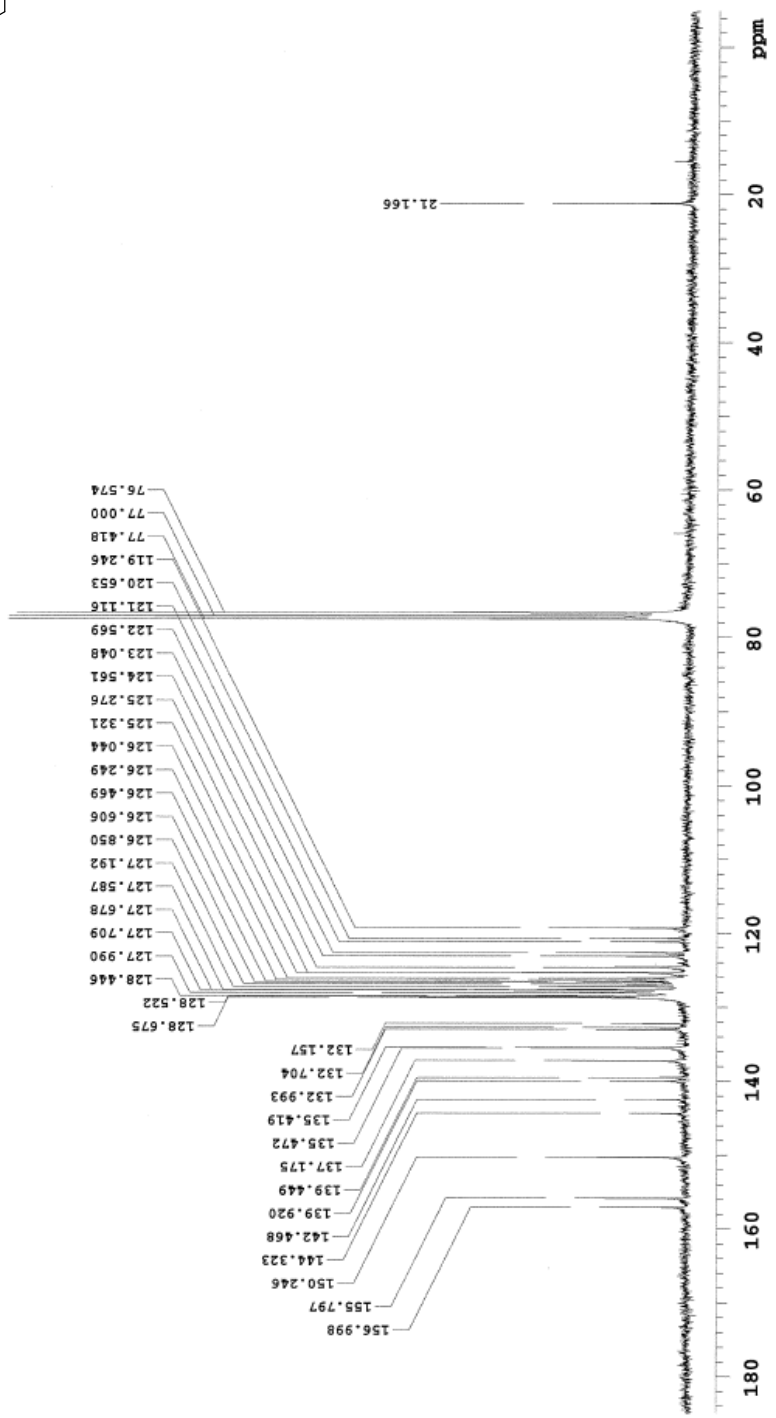
1.03.10 1.09 4.402.38.401.21.01


N
N
OH
Me

1d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77.418
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122.569
123.048
124.561
125.276
125.321
126.044
126.249
126.469
126.606
126.850
127.192
127.587
127.678
127.709
127.990
128.446
128.522
128.675
132.157
132.704
132.993
135.419
135.472
137.175
139.449
139.920
142.468
144.323
150.246
155.797
156.998
ppm
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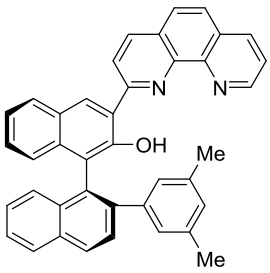
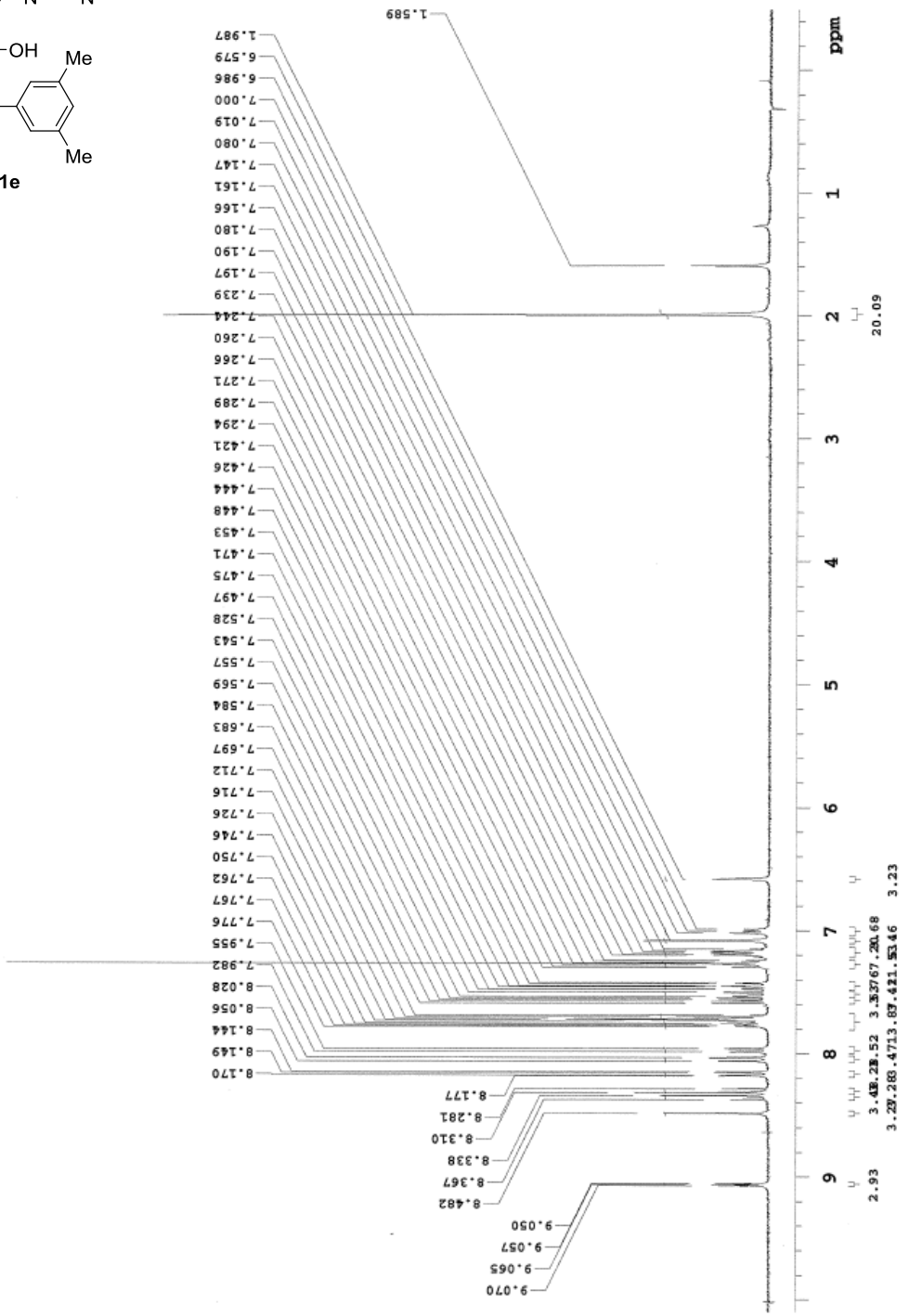
40
60
80
100
120
140
160
180


N
N
OH
Me
Me

1e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1.987
6.579
6.986
7.000
7.019
7.080
7.147
7.161
7.166
7.180
7.190
7.197
7.239
7.244
7.260
7.266
7.271
7.289
7.294
7.421
7.426
7.444
7.448
7.453
7.471
7.475
7.497
7.528
7.543
7.557
7.569
7.584
7.683
7.697
7.712
7.716
7.726
7.746
7.750
7.762
7.767
7.776
7.955
7.982
8.028
8.056
8.144
8.149
8.170
8.177
8.281
8.310
8.338
8.367
8.482
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9.057
9.065
9.070
ppm
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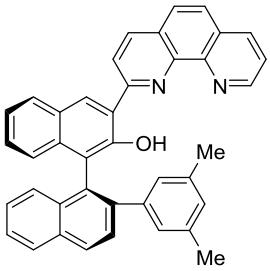
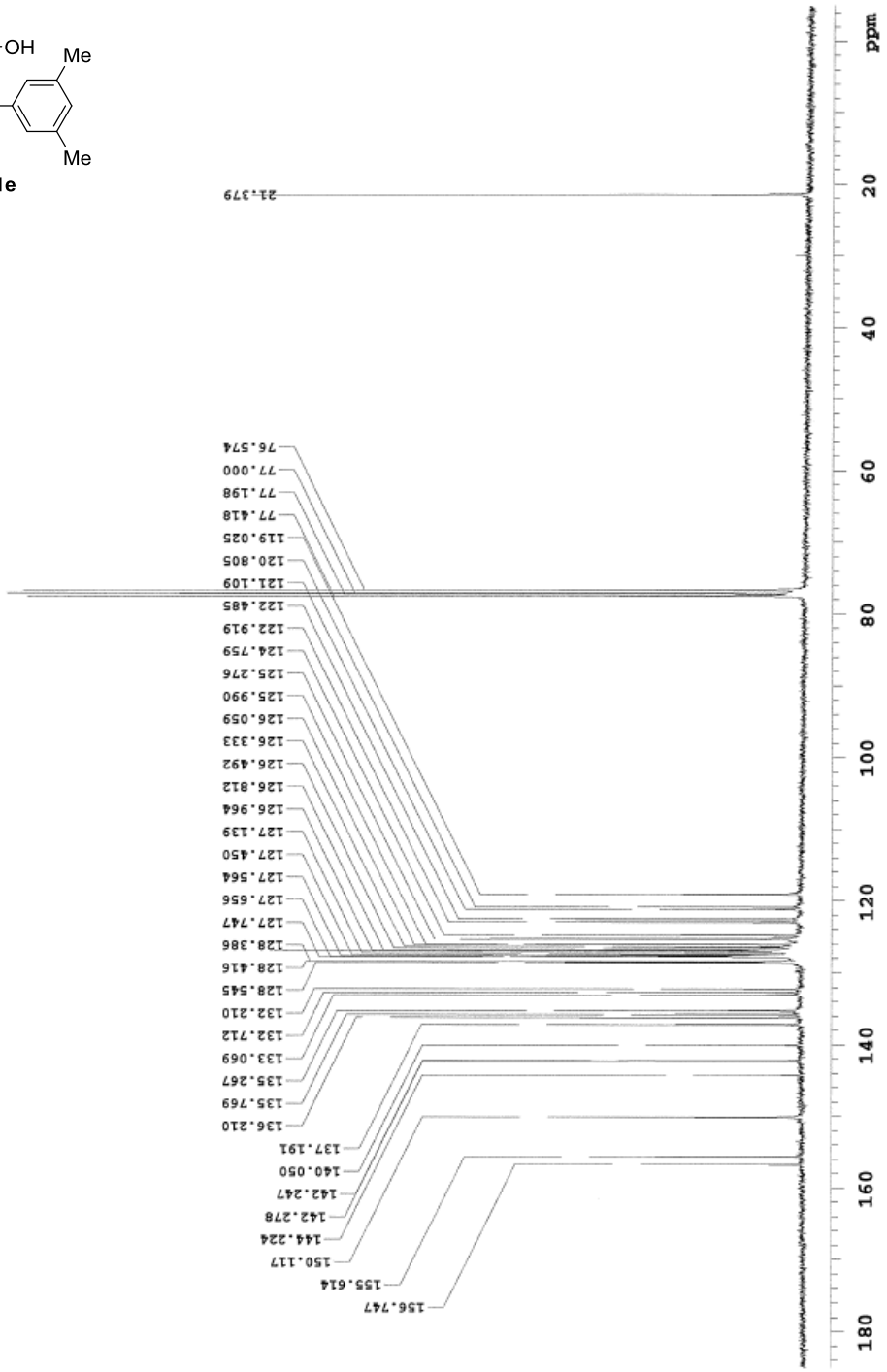
3.23
2.93


N
N
OH
Me
Me

1e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77.418
119.025
120.805
121.109
122.485
122.919
124.759
125.276
125.990
126.059
126.333
126.492
126.812
126.964
127.139
127.450
127.564
127.656
127.747
128.386
128.416
128.545
132.210
132.712
133.069
135.267
135.769
136.210
137.191
140.050
142.247
142.278
144.224
150.117
155.614
156.747
ppm
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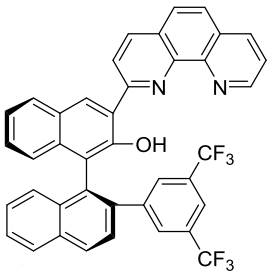
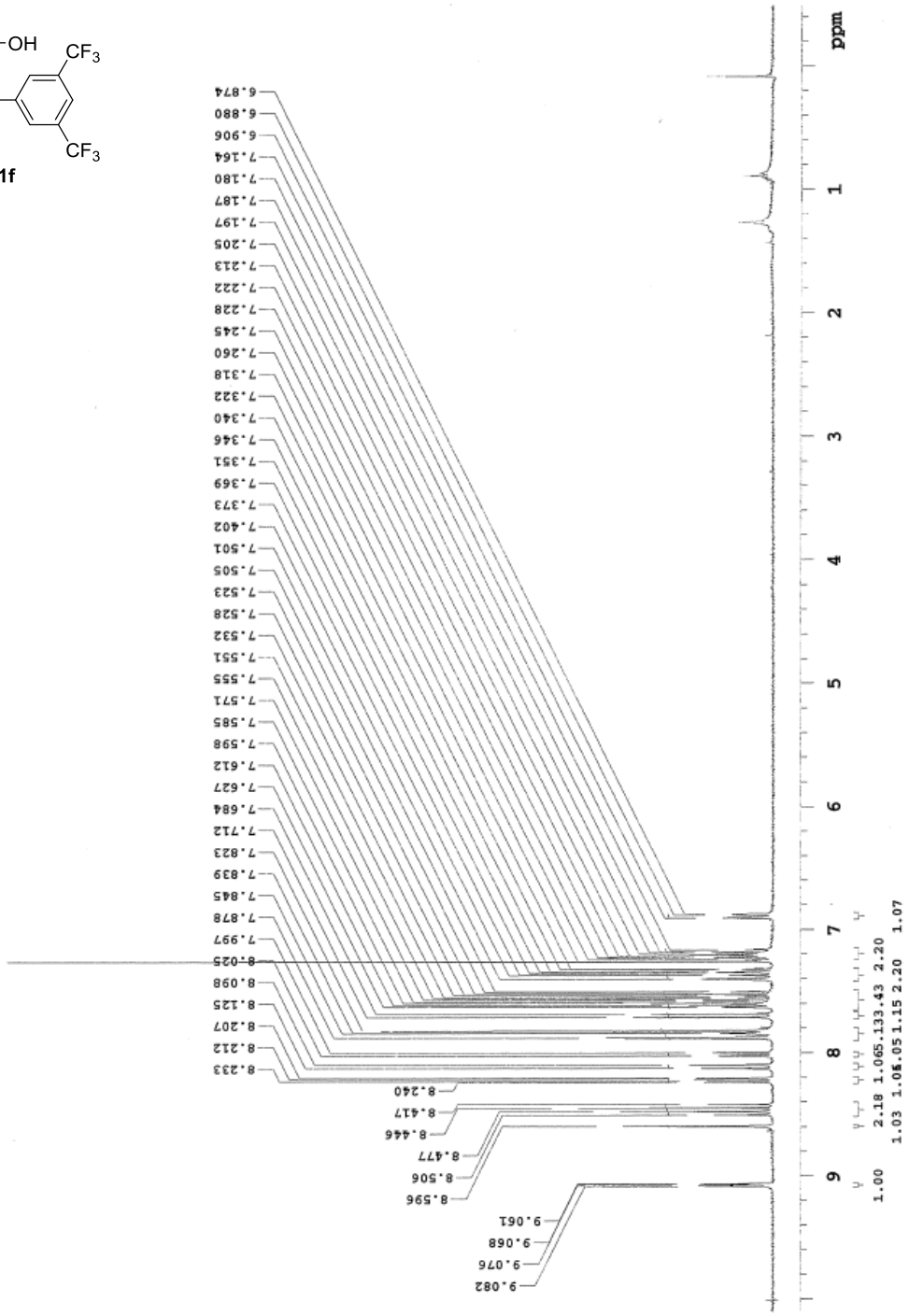
40
60
80
100
120
140
160
180


N
N
OH
CF3
CF3

1f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6.906
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7.180
7.187
7.197
7.205
7.213
7.222
7.228
7.245
7.260
7.318
7.322
7.340
7.346
7.351
7.369
7.373
7.402
7.501
7.505
7.523
7.528
7.532
7.551
7.555
7.571
7.585
7.598
7.612
7.627
7.684
7.712
7.823
7.839
7.845
7.878
7.997
8.025
8.098
8.125
8.207
8.212
8.233
8.240
8.417
8.446
8.477
8.506
8.596
9.061
9.068
9.076
9.082
ppm
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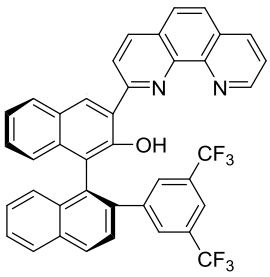
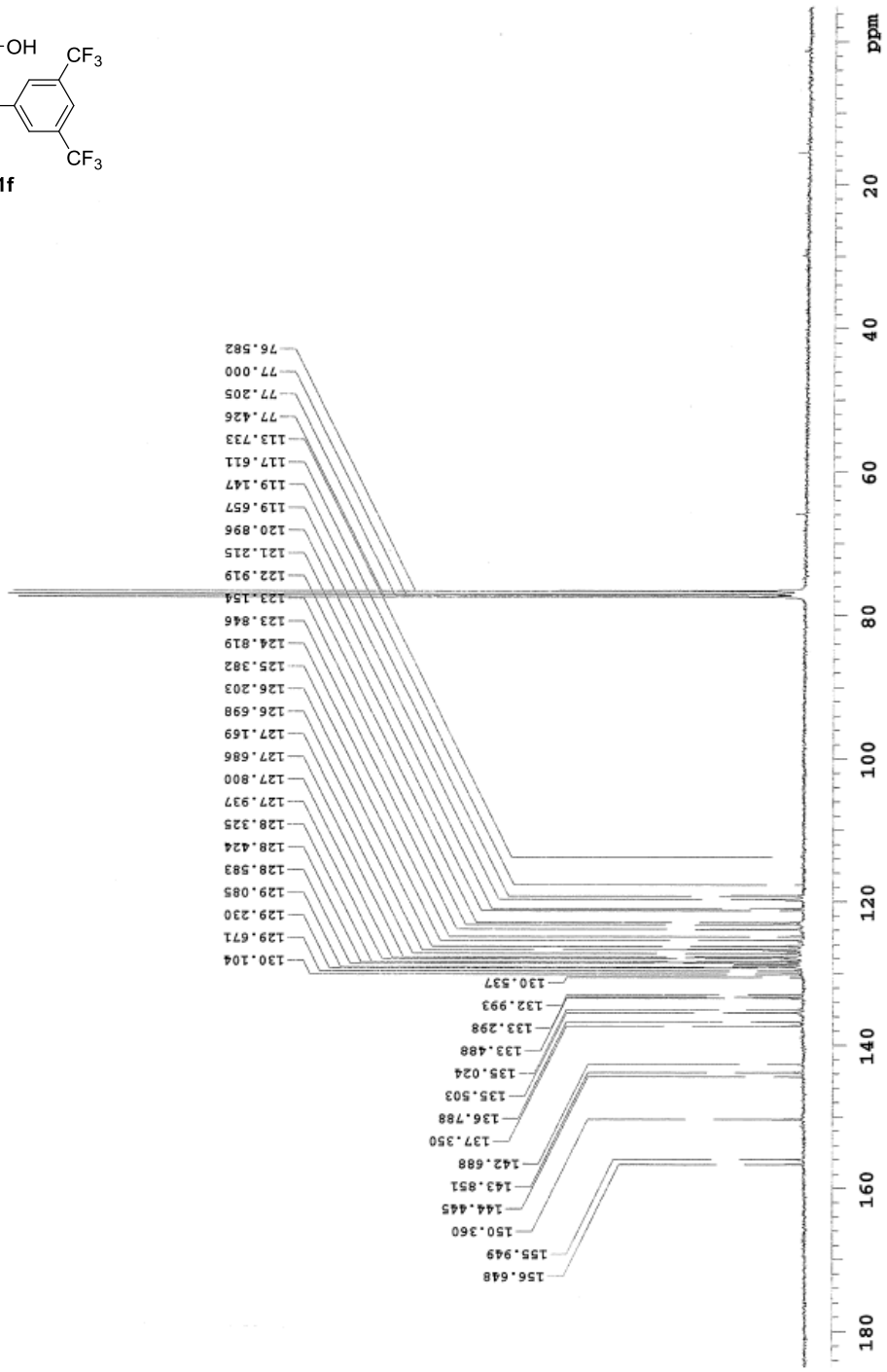
1.06
5.13
3.43
2.20
1.03
1.06
5.05
1.15
2.20
1.07


N
N
OH
CF3
CF3

1f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77.426
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119.147
119.657
120.896
121.215
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123.154
123.846
124.819
125.382
126.203
126.698
127.169
127.686
127.800
127.937
128.325
128.424
128.583
129.085
129.230
129.671
130.104
130.537
132.993
133.298
133.488
135.024
135.503
136.788
137.350
142.688
143.851
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150.360
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156.648
ppm
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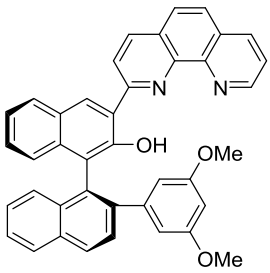
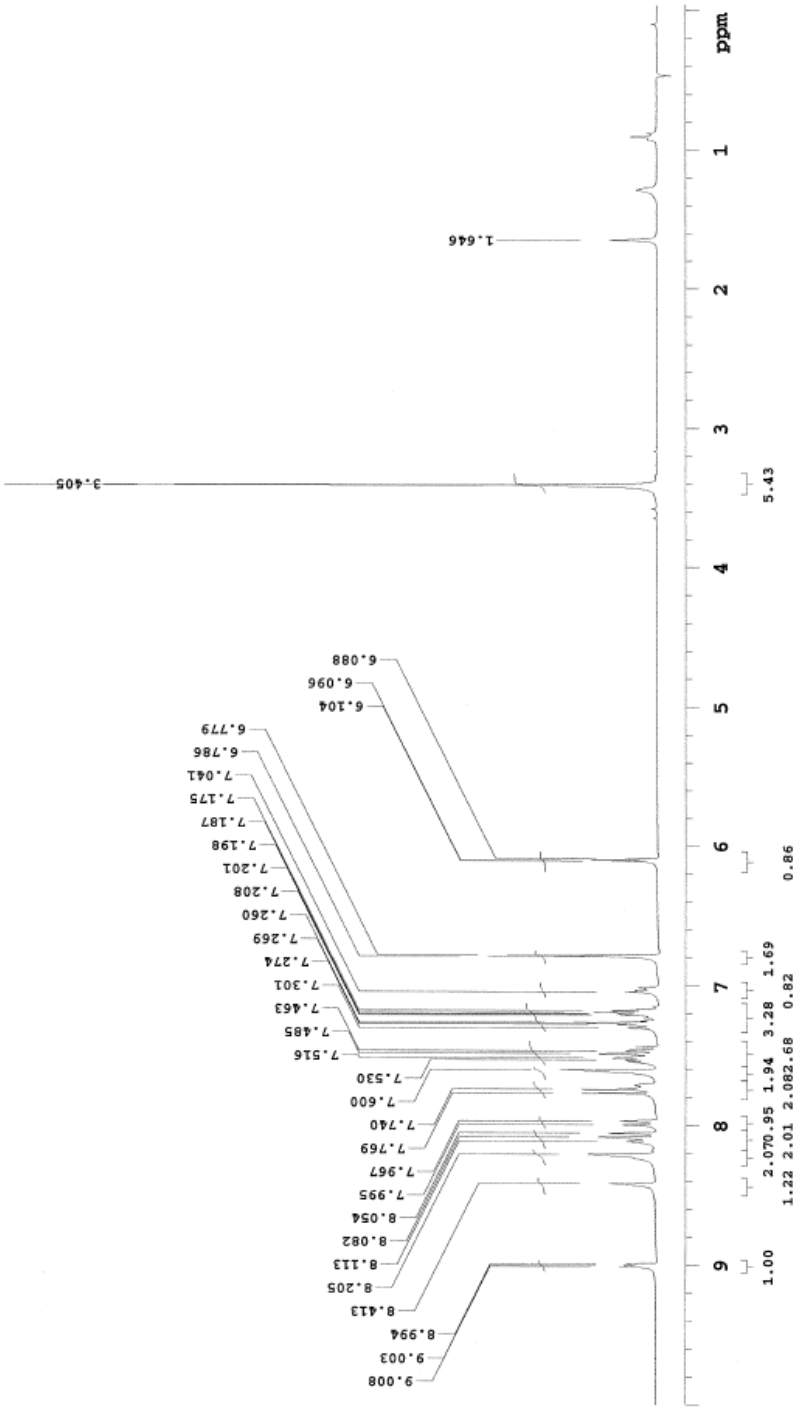
40
60
80
100
120
140
160
180


N
N
OH
OMe
OMe

1g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6.096
6.104
6.779
6.786
7.041
7.175
7.187
7.198
7.201
7.208
7.260
7.269
7.274
7.301
7.463
7.485
7.516
7.530
7.600
7.740
7.769
7.967
7.995
8.054
8.082
8.113
8.205
8.413
8.994
9.003
9.008
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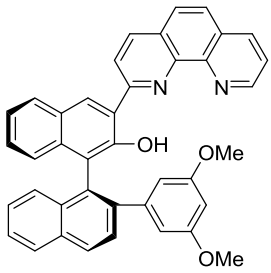
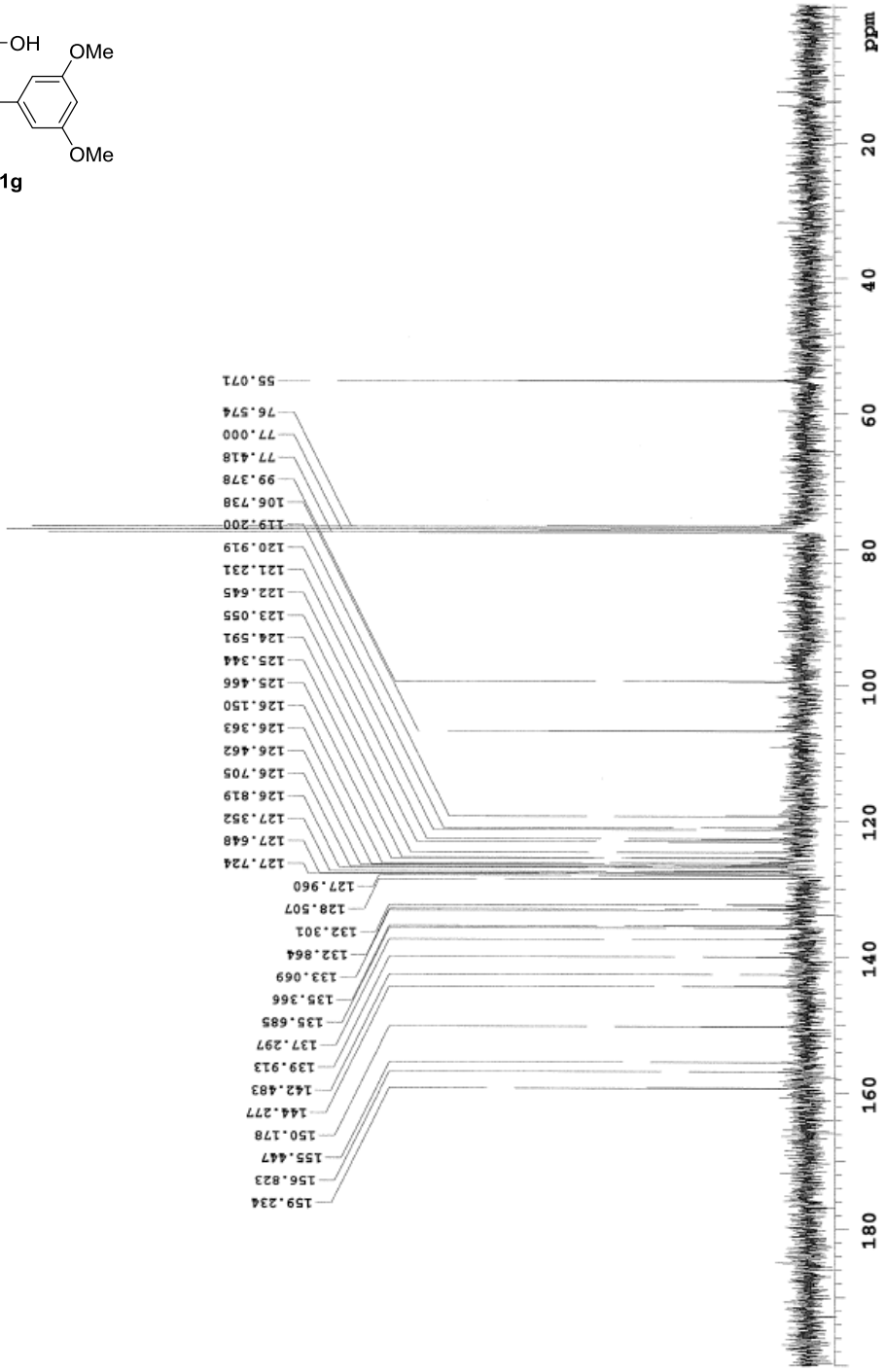
1.69
0.82
3.28
1.94
2.082.68
2.070.95
2.01
1.22
1.00


N
N
OH
OMe
OMe

1g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106.738
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120.919
121.231
122.645
123.055
124.591
125.344
125.466
126.150
126.363
126.462
126.705
126.819
127.352
127.648
127.724
127.960
128.507
132.301
132.864
133.069
135.366
135.685
137.297
139.913
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144.277
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155.447
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159.234
ppm
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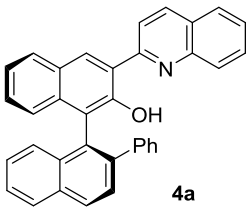
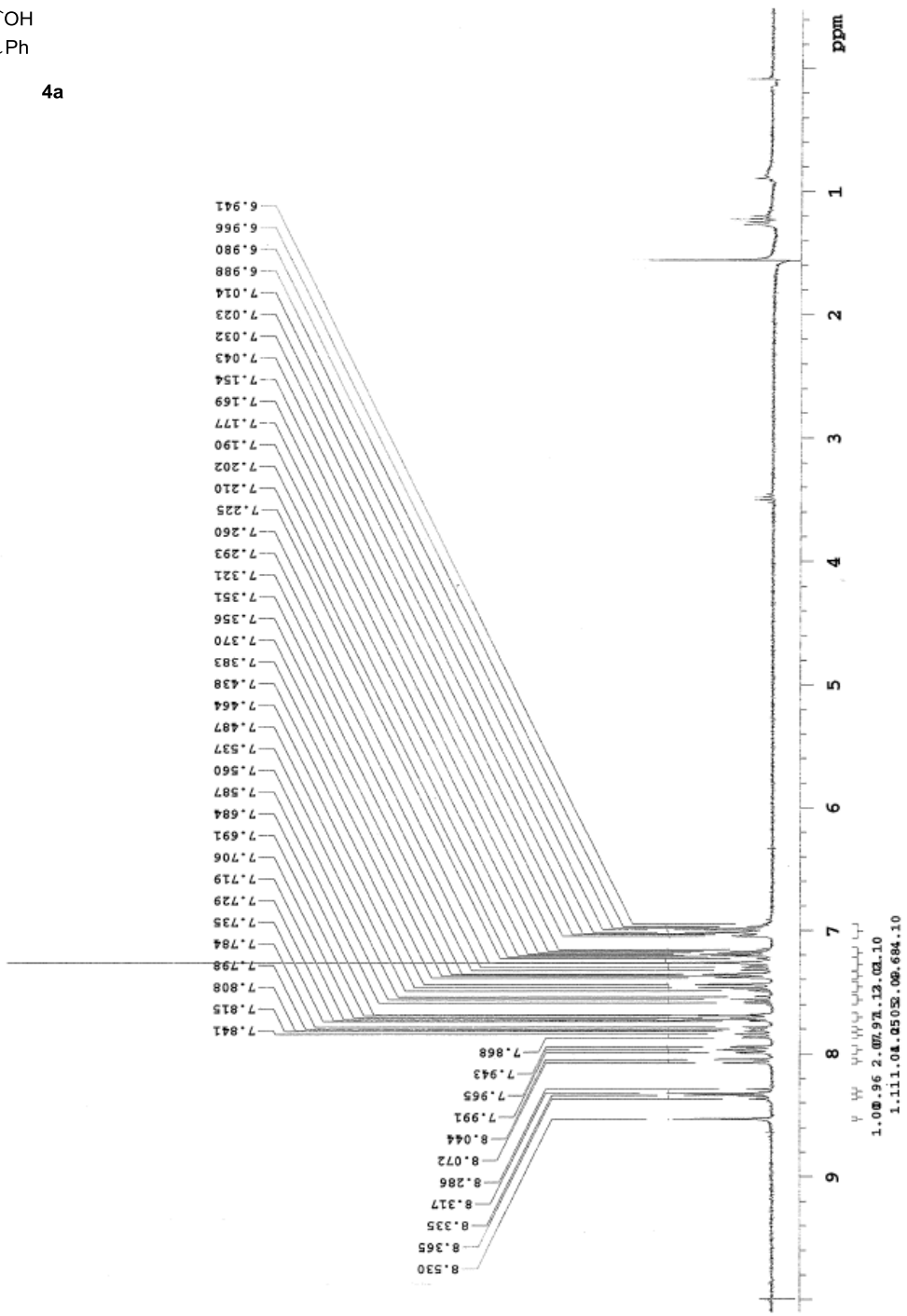
60
80
100
120
140
160
180


N
OH
Ph

4a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7.023
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7.043
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7.169
7.177
7.190
7.202
7.210
7.225
7.260
7.293
7.321
7.351
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7.370
7.383
7.438
7.464
7.487
7.537
7.560
7.587
7.684
7.691
7.706
7.719
7.729
7.735
7.784
7.798
7.808
7.815
7.841
7.868
7.943
7.965
7.991
8.044
8.072
8.286
8.317
8.335
8.365
8.530
ppm
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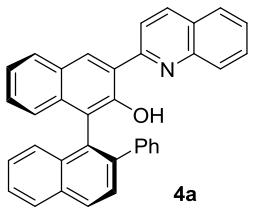
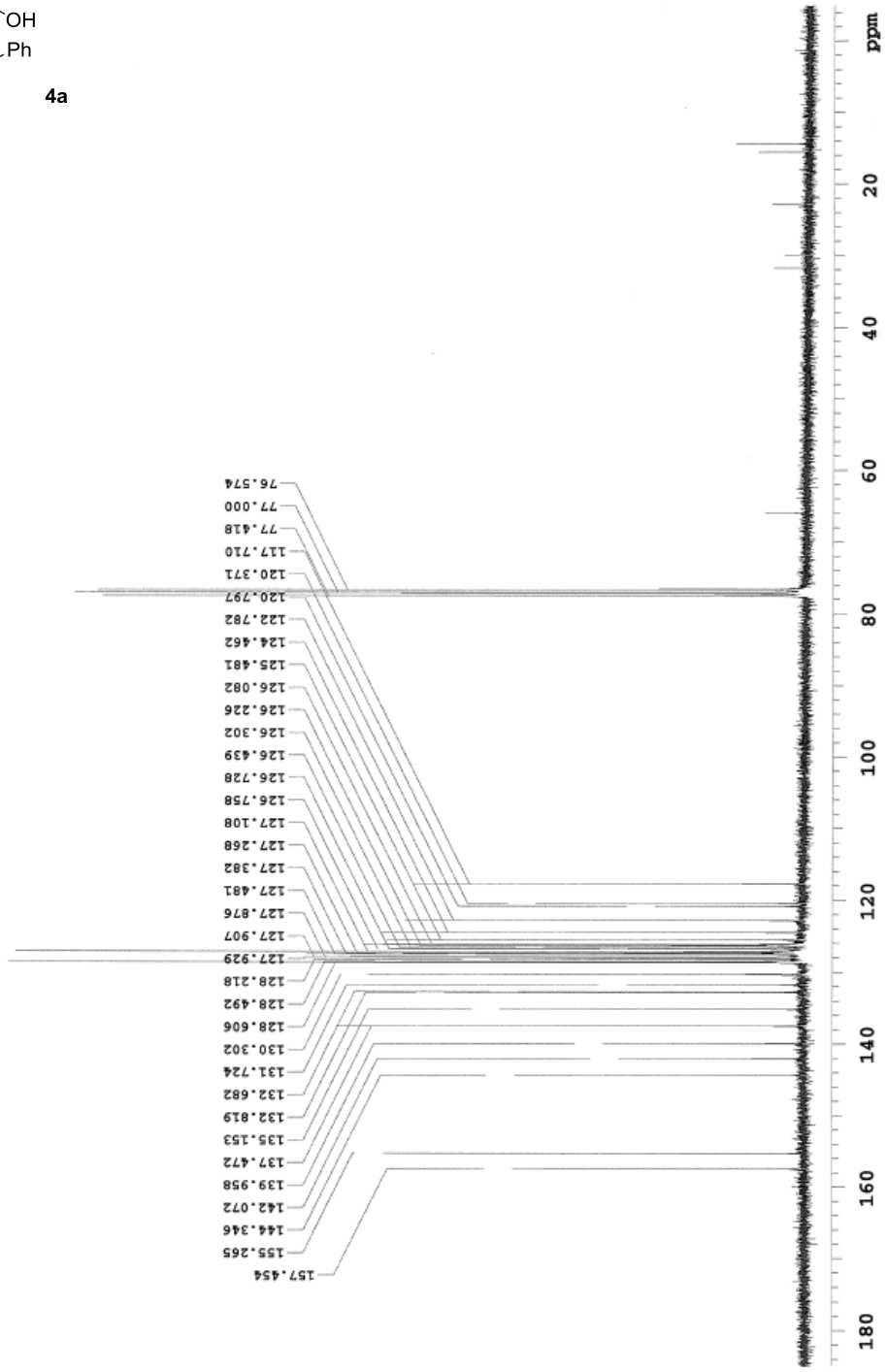
1.11 1.04 2.05 3.00 6.68 4.10


N
OH
Ph

4a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60
80
100
120
140
160
180
76.574
77.000
77.418
117.710
120.371
120.797
122.782
124.462
125.481
126.082
126.226
126.302
126.439
126.728
126.758
127.108
127.268
127.382
127.481
127.876
127.907
127.929
128.218
128.492
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139.958
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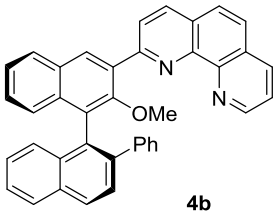
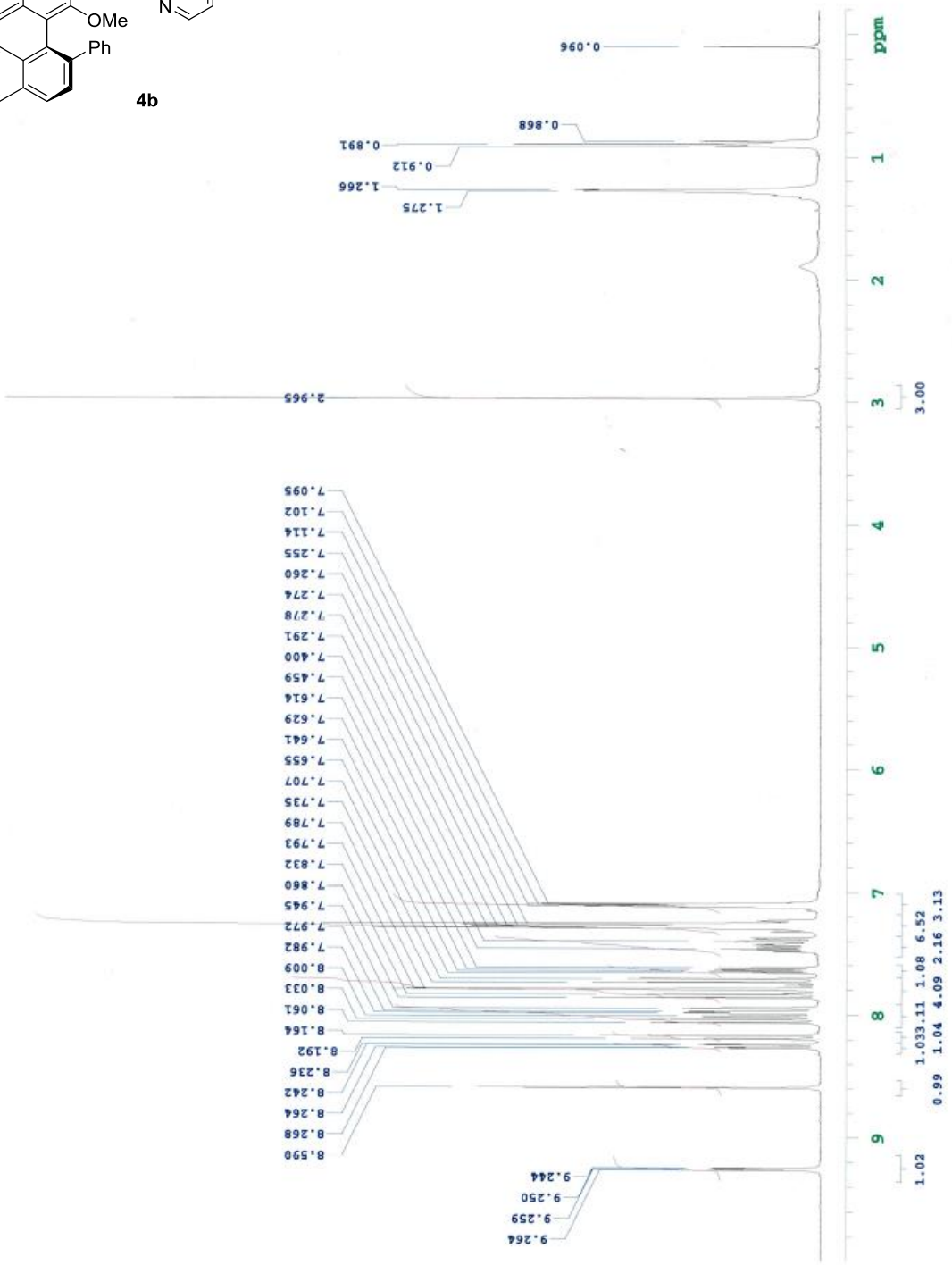
155.265
157.454


N
N
OMe
Ph

4b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7.095
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7.114
7.255
7.260
7.274
7.278
7.291
7.400
7.459
7.614
7.629
7.641
7.655
7.707
7.735
7.789
7.793
7.832
7.860
7.945
7.972
7.982
8.009
8.033
8.061
8.164
8.192
8.236
8.242
8.264
8.268
8.590
9.244
9.250
9.259
9.264
ppm
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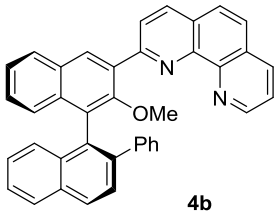
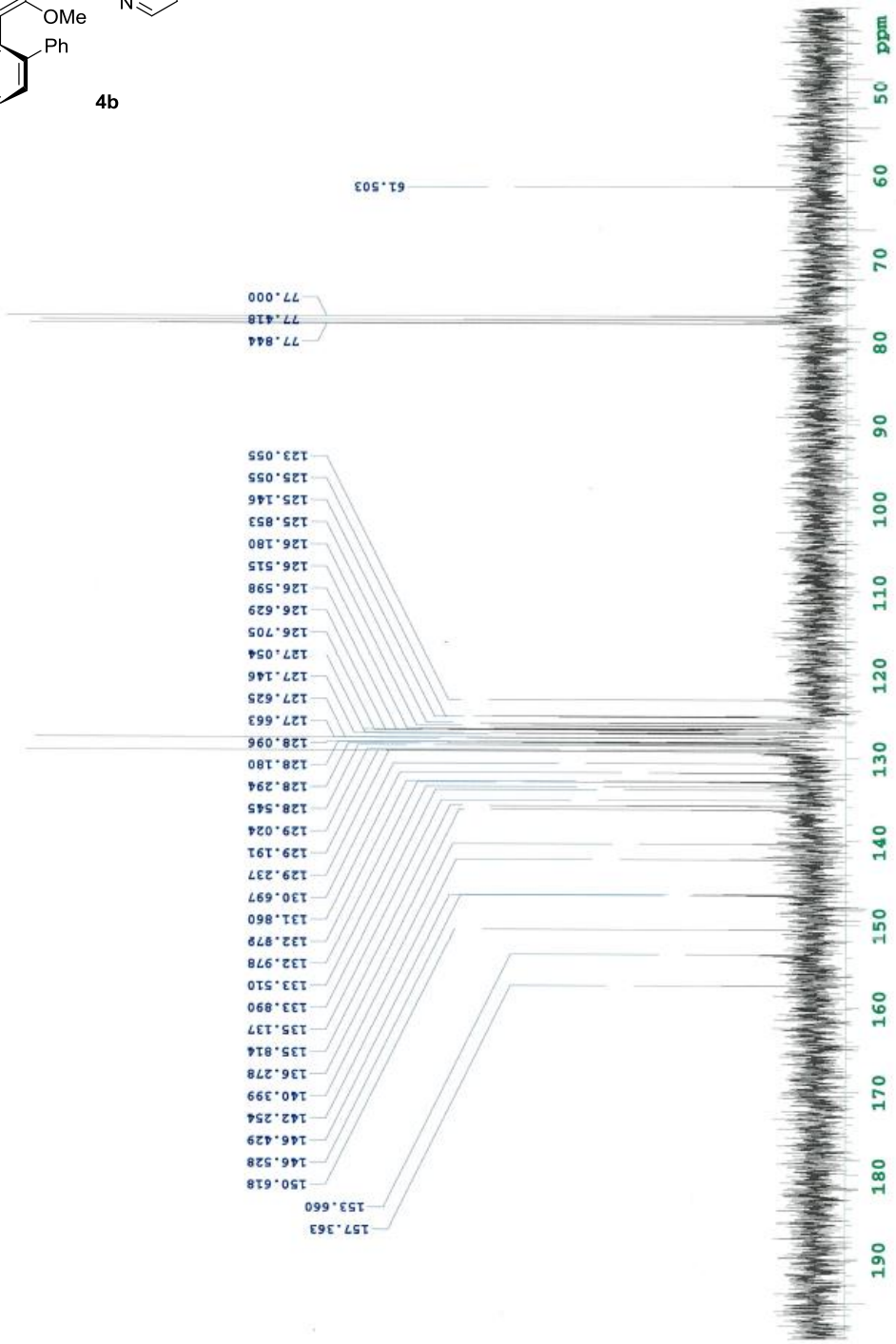
1.02
0.99 1.04 4.09 2.16 3.13
1.033.11 1.08 6.52


N
N
OMe
Ph

4b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125.055
125.146
125.853
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126.515
126.598
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126.705
127.054
127.146
127.625
127.663
128.096
128.180
128.294
128.545
129.024
129.191
129.237
130.697
131.860
132.879
132.978
133.510
133.890
135.137
135.814
136.278
140.399
142.254
146.429
146.528
150.618
153.660
157.363
ppm
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190