

Electronic Supplementary Information

Synthesis and Evaluation of New Chiral Nonracemic C₂-Symmetric and Unsymmetric 2,2'-Bipyridyl Ligands

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[†] M.P.A.L. performed all of the synthetic work and obtained all of the compound characterization data described herein.

[‡] N.D.D. determined the X-ray crystal structure of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18**.

1. General Experimental Details

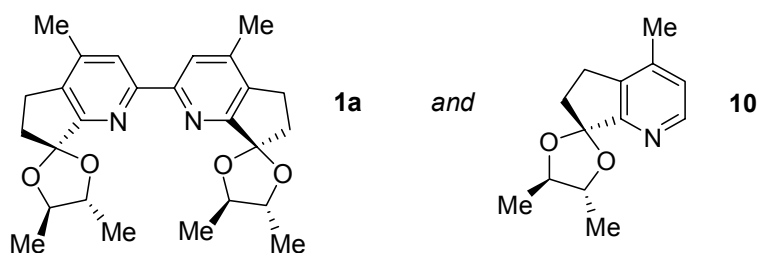
All non-aqueous reactions were performed under an atmosphere of dry nitrogen in oven- or flame-dried glassware, unless indicated otherwise. The reaction temperatures stated were those of the external bath. Diethyl ether (ether) and tetrahydrofuran (THF) were dried over sodium/benzophenone ketyl and distilled under an atmosphere of dry nitrogen immediately prior to use. Benzene and dichloromethane were dried over calcium hydride and distilled under an atmosphere of dry nitrogen immediately prior to use. All other solvents and reagents were purified by standard techniques or used as supplied.¹ Brine refers to a saturated aqueous solution of sodium chloride. Silica gel column chromatography (“flash chromatography”) was carried out using *Merck silica gel 60* (230 to 400 mesh).² Melting points were measured on a *Gallenkamp* capillary melting point apparatus and are uncorrected. Optical rotations were recorded on a *Perkin Elmer 341* polarimeter. All proton and carbon nuclear magnetic resonance spectra (¹H and ¹³C NMR, respectively) were recorded using a *Bruker AMX 400 FT* spectrometer (operating frequencies: ¹H, 400.13 MHz; ¹³C, 100.61 MHz) at ambient temperature. Chemical shifts (δ) for all compounds are listed in parts per million downfield from tetramethylsilane using the NMR solvent as an internal reference. The reference values used for deuterated chloroform (CDCl₃) were 7.26 and 77.16 ppm for ¹H and ¹³C NMR spectra, respectively. Infrared spectra (IR) were recorded as either KBr pellets (KBr) or as films (neat) using a *Perkin Elmer 599B* IR spectrophotometer. Low-resolution mass spectra (MS) were recorded on a *Hewlett Packard 5985* GC-mass spectrometer. The mode of ionization used was chemical ionization (CI) with isobutane. Analytical chiral high performance liquid chromatography (HPLC) was performed on a *Hewlett Packard Series 1050* instrument. The optical rotary dispersion spectrum of the bis-2,2'-bipyridyl ligand copper(I) chloride complex **18** was recorded on a *Jasco J-810* spectropolarimeter. The UV-visible spectrum of this complex was recorded on a *Varian Cary 300 UV-VIS* spectrophotometer.

(1) W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, 1997.

(2) W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

2. Experimental Procedures and Characterization Data

Preparation of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5*H*,5'*H*-2,2'-bi([1]pyrindinyl)-7,7'-dione (2*R*,3*R*)-2,3-butanediol *bis*-acetal (**1a**) and 4-methyl-6,7-dihydro-5*H*-[1]pyrindin-7-one (2*R*,3*R*)-2,3-butanediol acetal (**10**) from the 2-chloropyridine acetal (**3a**).

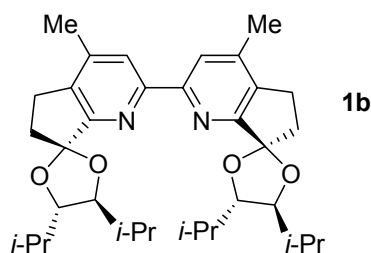


To a stirred solution of dibromobis(triphenylphosphine)nickel(II) (1.17 g, 1.58 mmol) in degassed tetrahydrofuran (30 mL) were added zinc dust (<10 microns, 310 mg, 4.74 mmol) and tetraethylammonium iodide (812 mg, 3.16 mmol). The reaction mixture was stirred at room temperature for 30 min and then a solution of the 2-chloropyridine acetal **3a**³ (800 mg, 3.16 mmol) in degassed tetrahydrofuran (12 mL) was added *via* a cannula. The resultant mixture was heated at 60 °C for 72 h and then allowed to cool to room temperature. The reaction mixture was poured into an aqueous solution of ammonium hydroxide (10% w/w, 200 mL) and was extracted with a mixture of ether and benzene (1:1, 3 x 100 mL). The combined organic extracts were washed with water (2 x 20 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford the crude product. Flash chromatography using chloroform as the eluant afforded the *title compound* **10** (242 mg, 35%) as a white crystalline solid and the *title compound* **1a** (269 mg, 39%) as a white crystalline solid. *Title compound 1a*: **M.p.** 292-294 °C, chloroform; $[\alpha]_D^{20}$ –53.7 (*c* 0.99, chloroform); ¹H NMR (CDCl₃) δ 1.35 (6H, d, *J* = 6.1 Hz, CHCH₃), 1.57 (6H, d, *J* = 6.0 Hz, CHCH₃), 2.33 (6H, s, ArCH₃), 2.41-2.49 (4H, m, ArCH₂CH₂), 2.83-2.89 (4H, m, ArCH₂), 3.84 (2H, dq, *J* = 6.0, 8.0 Hz, CHCH₃), 4.55 (2H, dq, *J* = 6.0, 7.8 Hz, CHCH₃), 8.21 (2H, s, ArH); ¹³C NMR (CDCl₃) δ 16.8, 17.6, 18.6, 24.3, 36.1, 79.0, 79.6, 114.4, 122.1, 135.5,

(3) For full experimental details regarding the preparation of the 2-chloropyridine acetals **3a-c**, see: (a) M. P. A. Lyle and P. D. Wilson, *Org. Lett.*, 2004, **6**, 855; (b) M. P. A. Lyle, A. A. Narine and P. D. Wilson, *J. Org. Chem.*, 2004, **69**, 5060.

144.5, 156.5, 160.8; **IR** (KBr) ν_{\max} 2982, 2970, 2935, 2896, 1591, 1432, 1423, 1379, 1321, 1293, 1204, 1181, 1162, 1095, 1076, 1059 cm^{-1} ; **MS** (CI) m/z (rel. intensity) 437 (M + H, 100), 365 (45), 167 (48); **Anal.** Calcd. for $\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_4$: C, 71.53; H, 7.39; N, 6.42. Found: C, 71.38; H, 7.22; N, 6.26. *Title compound 10*: **M.p.** 52-54 °C, chloroform; $[\alpha]_D^{20}$ - 14.9 (c 1.02, chloroform); **^1H NMR** (CDCl_3) δ 1.33 (3H, d, J = 6.1 Hz, CHCH_3), 1.41 (3H, d, J = 6.0 Hz CHCH_3), 2.25 (3H, s, ArCH_3), 2.33-2.42 (2H, m, ArCH_2CH_2), 2.79-2.86 (2H, m, ArCH_2), 3.78 (1H, dq, J = 6.1, 7.8 Hz, CHCH_3), 4.32 (1H, dq, J = 6.1, 8.0 Hz, CHCH_3), 6.99 (1H, d, J = 4.8 Hz, ArH), 8.40 (1H, d, J = 4.8 Hz, ArH); **^{13}C NMR** (CDCl_3) δ 16.7, 16.8, 18.2, 24.3, 36.2, 79.4, 114.1, 124.7, 135.9, 144.4, 149.4, 161.0; **IR** (KBr) ν_{\max} 2974, 2921, 2862, 1602, 1448, 1378, 1331, 1303, 1193, 1094, 926, 828 cm^{-1} ; **MS** (CI) m/z (rel. intensity) 220 (M + H, 100); **Anal.** Calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.07; H, 7.84; N, 6.32.

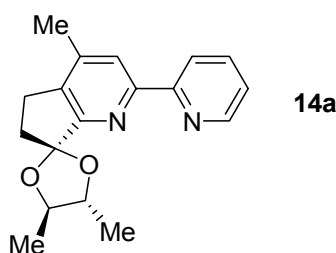
Preparation of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5H,5'H-2,2'-bi([1]pyrindinyl)-7,7'-dione (1S,2S)-1,2-diisopropyl-1,2-ethanediol bis-acetal (1b) from the 2-chloropyridine acetal (3b).



To a stirred solution of dibromobis(triphenylphosphine)nickel(II) (609 mg, 0.82 mmol) in degassed tetrahydrofuran (12 mL) were added zinc dust (<10 microns, 162 mg, 2.48 mmol) and tetraethylammonium iodide (424 mg, 1.65 mmol). The reaction mixture was stirred at room temperature for 30 min and then a solution of the 2-chloropyridine acetal **3b**³ (511 mg, 1.65 mmol) in degassed tetrahydrofuran (6 mL) was added *via* a cannula. The resultant mixture was heated at 60 °C for 72 h and then was allowed to cool to room temperature. The reaction mixture was poured into an aqueous solution of ammonium hydroxide (10% w/w, 200 mL) and was extracted with ether (3 x 50 mL). The combined organic extracts were washed with water (2 x 20 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo* to afford the crude product. Flash chromatography using hexanes:ether (10:1) as the eluant afforded the *title*

compound 1b (326 mg, 72%) as a white crystalline solid. **M.p.** 166-167 °C, hexanes/ether; $[\alpha]_D^{20}$ –44.3 (*c* 0.37, chloroform); $^1\text{H NMR}$ (CDCl_3) δ 0.99-1.08 (24H, m, CHCH_3), 1.82-1.95 (2H, m, CHCH_3), 2.31 (6H, s, ArCH_3), 2.39-2.45 (4H, m, ArCH_2CH_2), 2.46-2.58 (2H, m, CHCH_3), 2.81-2.87 (4H, m, ArCH_2), 3.72 (2H, dd, $J = 4.8, 7.8$ Hz, OCH), 4.18 (2H, dd, $J = 4.8, 6.4$ Hz, OCH), 8.21 (2H, s, ArH); $^{13}\text{C NMR}$ (CDCl_3) δ 17.8, 18.6, 19.0, 19.4, 19.9, 24.2, 31.5, 31.8, 37.1, 85.8, 86.1, 115.5, 122.2, 135.9, 144.4, 156.5, 160.3; **IR** (KBr) ν_{max} 2959, 2872, 1596, 1573, 1468, 1435, 1384, 1367, 1324, 1292, 1225, 1191, 1163, 1148, 1099, 1056, 1009, 921 cm^{-1} ; **MS** (MALDI-TOF) m/z 550 ($M + H$); **Anal.** Calcd. for $\text{C}_{34}\text{H}_{48}\text{N}_2\text{O}_4$: C, 74.42; H, 8.82; N, 5.10. Found: C, 74.60; H, 8.95; N, 5.30.

Preparation of 4-methyl-2-(2'-pyridyl)-6,7-dihydro-5H-[1]pyrindin-7-one (2R,3R)-2,3-butanediol acetal (2a) from the 2-chloropyridine acetal (3a).



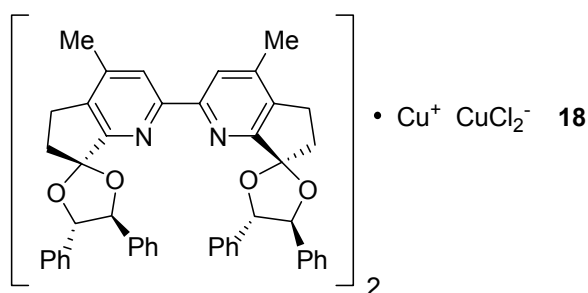
To a stirred solution the 2-chloropyridine acetal **3a**³ (175 mg, 0.690 mmol) and 2-(tri-*n*-butylstannyl)pyridine⁴ (472 mg, 0.759 mmol) in anhydrous, degassed dioxane (3 mL) at room temperature were added *tris*(dibenzylideneacetone)dipalladium(0) (16 mg, 17 μmol), a solution of tri-*t*-butylphosphine in tetrahydrofuran (0.10 M, 0.69 mL, 69 μmol) and anhydrous cesium fluoride (231 mg, 1.52 mmol). The resultant solution was heated at reflux for 24 h and then was allowed to cool to room temperature. The reaction mixture was filtered through a pad of silica gel using ethyl acetate as the eluant and the filtrate was then concentrated *in vacuo* to afford the crude product. Flash chromatography using hexanes:ether (4:1) as the eluant afforded the *title compound 2a* (147 mg, 72%) as a white crystalline solid. **M.p.** 164-165 °C, hexanes/ether; $[\alpha]_D^{20}$ –40.8 (*c* 1.04, chloroform); $^1\text{H NMR}$ (CDCl_3) δ 1.37 (3H, d, $J = 6.1$ Hz, CHCH_3), 1.52 (3H, d, J

(4) 2-(Tri-*n*-butylstannyl)pyridine was prepared from 2-bromopyridine according to a literature procedure, see: W. R. McWhinnie, R. C. Poller and M. Thevarasa, *J. Organomet. Chem.*, 1968, **11**, 499.

= 6.0 Hz, CHCH₃), 2.34 (3H, s, ArCH₃), 2.44-2.50 (2H, m, ArCH₂CH₂), 2.85-2.91 (2H, m, ArCH₂), 3.80-3.89 (1H, m, CHCH₃), 4.54-4.62 (1H, m, CHCH₃), 7.25-7.29 (1H, m, ArH), 7.76-7.84 (1H, m, ArH), 8.20 (1H, s, ArH), 8.45-8.49 (1H, m, ArH), 8.63-8.67 (1H, m, ArH); ¹³C NMR (CDCl₃) δ 16.7, 17.6, 18.4, 24.3, 36.0, 79.1, 79.7, 114.3, 121.3, 122.0, 123.5, 136.0, 136.9, 145.1, 148.9, 155.8, 156.7, 161.3; IR (KBr) ν_{max} 1586, 1565, 1441, 1376, 1316, 1191, 1096, 1079, 932, 896, 798 cm⁻¹; MS (CI) m/z (rel. intensity) 297 (M + H, 100); Anal. Calcd. for C₁₈H₂₀N₂O₂: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.68; H, 7.00; N, 9.17.

3. Preparation, Product Characterization and X-Ray Crystallographic Data of the *bis*-2,2'-Bipyridyl Ligand Copper(I) Chloride Complex (**18**)

Procedure for the preparation and crystallization of *bis*-[4,4'-dimethyl-6,6',7,7'-tetrahydro-5*H*,5'*H*-2,2'-bi([1]pyrindinyl)-7,7'-dione (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol *bis*-acetal] copper(I) chloride complex (**18**).



A solution of the bipyridyl ligand **1c** (35 mg, 51 μmol) and anhydrous copper(I) chloride (5.0 mg, 51 μmol) in a mixture of ethanol:dichloromethane (1:1, 3 mL) was stirred at room temperature for 4 h. The reaction mixture was then concentrated *in vacuo* to afford the crude product. This material was taken up in dichloromethane (2 mL) and was filtered through a plug of glass wool. Ether (3 mL) was then added to the filtrate and, upon slow evaporation of the solvent, the *title compound* **18** (27 mg, 68%) was obtained as bright red crystals that were suitable for X-ray crystallography. **M.p.** >220 °C (dec.), ether/dichloromethane; [α]₂₅₃²⁰ - 2500, [α]₃₆₅²⁰ - 4900, [α]₄₀₅²⁰ - 3400, [α]₅₄₆²⁰ - 1300, [α]₅₈₉²⁰ - 1300 (*c* 0.0030, chloroform); UV-vis λ_{max}

(chloroform) 287 ($\epsilon = 3.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 309 ($\epsilon = 3.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 472 ($\epsilon = 6.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) nm;); $^1\text{H NMR}$ (CDCl_3) δ 1.74 (12H, s, ArCH_3), 2.40-2.52 (4H, m, ArCH_2CHH), 2.59-2.73 (8H, m, ArCH_2CHH and ArCHH), 2.78-2.92 (4H, m, ArCHH), 3.79 (4H, d, $J = 8.5 \text{ Hz}$, CHPh), 4.35 (4H, d, $J = 8.5 \text{ Hz}$, CHPh), 6.51-6.59 (8H, m, ArH), 6.63-6.75 (8H, m, ArH), 6.81-6.92 (12H, m, ArH), 7.22-7.31 (12H, m, ArH), 7.35 (4H, s, ArH); $^{13}\text{C NMR}$ (CDCl_3) δ 19.0, 23.9, 37.3, 85.3, 85.5, 115.7, 123.3, 124.5, 127.7, 128.0, 128.2, 133.9, 137.5, 141.1, 145.8, 151.7; **IR** (KBr) ν_{max} 1603, 1496, 1315, 1167, 1140, 1056, 1023, 951, 807, 759 cm^{-1} ; **MS** (MALDI-TOF) m/z 1431 ($\text{M} - \text{CuCl}_2$), 747 ($\text{M} - \text{CuCl}_2 - \text{L}$); **Anal.** Calcd. for $\text{C}_{92}\text{H}_{80}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_8 \cdot \text{CH}_2\text{Cl}_2$: C, 67.59; H, 5.00; N, 3.39. Found: C, 68.07; H, 5.06; N, 3.69 (of note, the crystals of complex **18** readily desolvated).

X-ray crystallographic analysis of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex (18**).**

A single crystal, a red block that had the dimensions 0.17 x 0.40 x 0.94 mm^3 , was mounted on a glass fibre using epoxy adhesive. The data for this crystal of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18** was acquired at 293 K on a *Rigaku RAXIS-RAPID* curved image plate area detector with graphite monochromated Cu $K\alpha$ radiation. Indexing for the crystal was performed using four, 5° oscillations that were exposed for 300 seconds. A sweep of data was then collected using ω scans from 0.0° to 180.0° in 10° steps, at $\chi = 0.0^\circ$ and $\phi = 0.0^\circ$. A second sweep of data was collected using ω scans from 0.0° to 180.0° in 10° steps, at $\chi = 45.0^\circ$ and $\phi = 0.0^\circ$. A final sweep of data was collected using ω scans from 0.0° to 180.0° in 10° steps, at $\chi = 45.0^\circ$ and $\phi = 90.0^\circ$. The following data range was recorded: $4.65^\circ \leq 2\theta \leq 144.25^\circ$ and a total of fifty four images were collected. The exposure rate was 75 $\text{sec}/^\circ$ and in each case, the crystal-to-detector distance was 127.40 mm. A numerical absorption correction was then applied which resulted in the following transmission range: 0.4114 to 0.6854.⁵ The coordinates and anisotropic displacement parameters for the non-hydrogen atoms were then refined with the exception of Cl(5), Cl(6) and C(47). These three atoms of half occupancy were refined using isotropic parameters. Of note, hydrogen atoms were placed in calculated positions (d C-H 0.95

(5) J. de Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

Å) and their coordinate shifts were linked with those of the respective carbon atoms during refinement. Isotropic thermal parameters for the hydrogen atoms were initially assigned proportionately to the equivalent isotropic thermal parameters of their respective carbon atoms. Subsequently, the isotropic thermal parameters for the hydrogen atoms were constrained to have identical shifts during refinement. The programs used for all absorption corrections, data reduction and processing were from the *Rigaku CrystalClear* package. The structure was refined using *CRYSTALS*.⁶ Complex scattering factors for neutral atoms were used in the calculation of structure factors.⁷ ORTEP representations of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18** are provided below (Figures 3.1 and 3.2). Crystallographic data, fractional atomic coordinates and equivalent isotropic thermal displacement parameters, selected bond lengths as well as selected bond angles for the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18** are also listed below (Table 3.1, 3.2, 3.3 and 3.4, respectively).

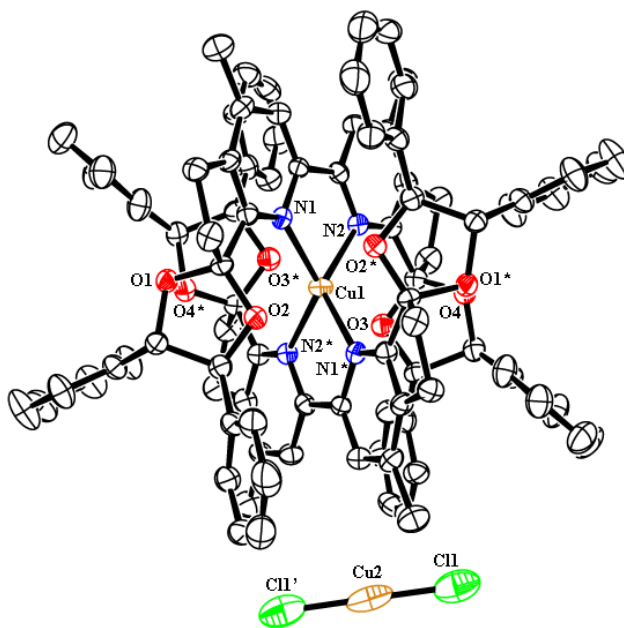


Figure 3.1. ORTEP representation of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18**.⁸

(6) D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS* Issue 12.50, Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 2003.

(7) International Union of Crystallography, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, England, 1952.

(8) The thermal ellipsoids are drawn at a 25% probability level and the atoms of the incorporated solvent molecule (CH_2Cl_2) as well as the hydrogen atoms have been removed for clarity. Symmetry transformations: (*) $-x - 2, -y - 1, z$; (') $-x - 3, -y - 1, z$.

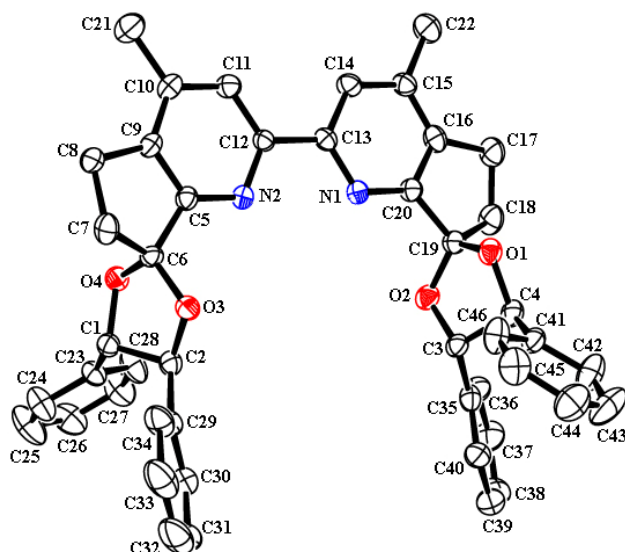


Figure 3.2. Partial ORTEP representation of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18** showing the carbon atom numbering scheme of the 2,2'-bipyridyl ligand.⁸

Table 3.1. Summary of Crystallographic Data for the *bis*-2,2'-Bipyridyl Ligand Copper(I) Chloride Complex **18**

Empirical formula	C ₉₃ H ₈₂ Cl ₄ Cu ₂ N ₄ O ₈
<i>FW</i> (g mol ⁻¹)	1648.35
Temperature (K)	293
Wavelength (Cu <i>K</i> α, Å)	1.54180
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2
<i>a</i> (Å)	14.7325(4)
<i>b</i> (Å)	15.2366(2)
<i>c</i> (Å)	19.0213(3)
α (°)	90
β (°)	90
γ (°)	90
<i>Z</i>	2
<i>U</i> (Å ³)	4269.77(15)
<i>D</i> _{calc} (g cm ⁻³)	1.285

2θ limits (°)	4.65-144.25
Reflections collected	28285
Independent reflections	6828
Reflections observed [$I = 2.5\sigma(I)$]	4566
Goodness-of-fit on F	0.601
R_1, R_w [$I = 2.5\sigma(I)$]	0.0532, 0.750

Table 3.2. Fractional Atomic Coordinates (Å) and Equivalent Isotropic Thermal Displacement Parameters [$U(\text{iso}), (\text{Å}^2)$] for the *bis*-2,2'-Bipyridyl Ligand Copper(I) Chloride Complex **18**⁹

atom	x	y	z	$U(\text{iso})$
Cu1	-1.0000	-0.5000	-0.74787(4)	0.0504
Cu2	-1.5000	-0.5000	-0.76716(8)	0.1386
Cl1	-1.4990(2)	-0.3648(3)	-0.76428(13)	0.1615
O1	-1.0381(3)	-0.7195(2)	-0.86114(17)	0.0593
O2	-1.0694(3)	-0.5825(2)	-0.90075(17)	0.0613
O3	-1.0397(2)	-0.4058(2)	-0.59490(16)	0.0543
O4	-0.9617(2)	-0.2825(2)	-0.62182(17)	0.0518
N1	-0.9054(3)	-0.5703(2)	-0.80400(16)	0.0447
N2	-0.8869(3)	-0.4603(2)	-0.69351(16)	0.0436
C1	-1.0541(4)	-0.2552(3)	-0.6092(2)	0.0498
C2	-1.1043(4)	-0.3416(3)	-0.6187(2)	0.0528
C3	-1.1556(4)	-0.6226(3)	-0.8818(3)	0.0522
C4	-1.1324(4)	-0.7206(3)	-0.8795(2)	0.0588
C5	-0.8787(4)	-0.4146(3)	-0.6328(2)	0.0479
C6	-0.9538(4)	-0.3690(3)	-0.5926(2)	0.0456
C7	-0.9148(4)	-0.3654(4)	-0.5184(2)	0.0639
C8	-0.8123(4)	-0.3587(4)	-0.5281(2)	0.0575
C9	-0.7980(4)	-0.4029(3)	-0.5974(2)	0.0505

(9) The occupancies for all atoms listed in this table are 1.0.

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C10	-0.7165(4)	-0.4310(3)	-0.6280(2)	0.0562
C11	-0.7244(4)	-0.4797(3)	-0.6898(2)	0.0564
C12	-0.8096(3)	-0.4960(3)	-0.71947(19)	0.0436
C13	-0.8201(4)	-0.5533(3)	-0.7818(2)	0.0471
C14	-0.7439(4)	-0.5890(3)	-0.8155(2)	0.0562
C15	-0.7527(4)	-0.6406(3)	-0.8752(3)	0.0564
C16	-0.8408(4)	-0.6547(4)	-0.8990(2)	0.0622
C17	-0.8719(5)	-0.7039(4)	-0.9627(3)	0.0772
C18	-0.9695(5)	-0.6718(4)	-0.9720(3)	0.0769
C19	-1.0014(4)	-0.6468(3)	-0.8980(2)	0.0527
C20	-0.9132(4)	-0.6192(3)	-0.8625(2)	0.0500
C21	-0.6252(5)	-0.4119(5)	-0.5955(3)	0.0821
C22	-0.6701(5)	-0.6755(5)	-0.9135(4)	0.0939
C23	-1.0785(4)	-0.1816(3)	-0.6576(2)	0.0578
C24	-1.1037(5)	-0.1012(4)	-0.6337(3)	0.0868
C25	-1.1216(7)	-0.0334(5)	-0.6787(4)	0.1213
C26	-1.1185(5)	-0.0464(5)	-0.7491(4)	0.0995
C27	-1.0920(5)	-0.1243(5)	-0.7749(3)	0.0950
C28	-1.0721(5)	-0.1929(4)	-0.7297(3)	0.0836
C29	-1.1927(4)	-0.3509(3)	-0.5795(3)	0.0614
C30	-1.2741(5)	-0.3279(4)	-0.6134(4)	0.0802
C31	-1.3551(6)	-0.3402(5)	-0.5775(6)	0.1098
C32	-1.3550(9)	-0.3736(6)	-0.5123(7)	0.1232
C33	-1.2777(8)	-0.3958(5)	-0.4796(5)	0.1094
C34	-1.1962(5)	-0.3859(4)	-0.5133(3)	0.0760
C35	-1.2313(4)	-0.5953(3)	-0.9303(3)	0.0606
C36	-1.2136(5)	-0.5690(4)	-0.9990(3)	0.0710
C37	-1.2844(6)	-0.5472(5)	-1.0418(4)	0.0921
C38	-1.3726(6)	-0.5498(5)	-1.0187(4)	0.0911

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C39	-1.3900(6)	-0.5756(5)	-0.9532(4)	0.0927
C40	-1.3200(5)	-0.5991(4)	-0.9075(3)	0.0717
C41	-1.1869(4)	-0.7712(3)	-0.8270(3)	0.0604
C42	-1.2522(6)	-0.8311(5)	-0.8497(4)	0.0979
C43	-1.3089(6)	-0.8702(6)	-0.7996(5)	0.1205
C44	-1.2974(6)	-0.8566(5)	-0.7308(5)	0.1054
C45	-1.2307(6)	-0.8003(4)	-0.7077(4)	0.0898
C46	-1.1760(5)	-0.7582(4)	-0.7552(3)	0.0799
Cl5	0.4148(5)	0.1049(4)	0.1749(3)	0.158(2)
Cl6	0.4107(6)	0.0982(6)	0.3254(4)	0.201(3)
C47	0.3545(16)	0.1399(16)	0.2415(12)	0.152(8)
H11	-1.0600	-0.2360	-0.5619	0.060
H21	-1.1153	-0.3507	-0.6674	0.063
H31	-1.1705	-0.6042	-0.8355	0.063
H41	-1.1397	-0.7454	-0.9250	0.071
H71	-0.9300	-0.4166	-0.4924	0.089
H72	-0.9364	-0.3150	-0.4942	0.089
H81	-0.7929	-0.2993	-0.5303	0.084
H82	-0.7805	-0.3881	-0.4915	0.084
H111	-0.6713	-0.5021	-0.7117	0.079
H141	-0.6853	-0.5768	-0.7971	0.075
H171	-0.8695	-0.7654	-0.9546	0.108
H172	-0.8358	-0.6896	-1.0024	0.108
H181	-1.0063	-0.7176	-0.9903	0.103
H182	-0.9717	-0.6227	-1.0028	0.103
H211	-0.5788	-0.4363	-0.6242	0.109
H212	-0.6226	-0.4375	-0.5500	0.109
H213	-0.6166	-0.3503	-0.5918	0.109
H221	-0.6883	-0.7100	-0.9526	0.128

H222	-0.6350	-0.6271	-0.9294	0.128
H223	-0.6347	-0.7103	-0.8824	0.128
H241	-1.1051	-0.0911	-0.5844	0.107
H251	-1.1404	0.0215	-0.6601	0.140
H261	-1.1336	0.0000	-0.7804	0.118
H271	-1.0873	-0.1334	-0.8242	0.125
H281	-1.0532	-0.2481	-0.7477	0.110
H301	-1.2722	-0.3054	-0.6600	0.101
H311	-1.4103	-0.3240	-0.5998	0.129
H321	-1.4120	-0.3818	-0.4898	0.132
H331	-1.2820	-0.4176	-0.4329	0.118
H341	-1.1423	-0.4044	-0.4902	0.087
H361	-1.1530	-0.5678	-1.0162	0.085
H371	-1.2725	-0.5286	-1.0886	0.109
H381	-1.4211	-0.5335	-1.0489	0.120
H391	-1.4511	-0.5787	-0.9374	0.118
H401	-1.3330	-0.6168	-0.8606	0.086
H421	-1.2601	-0.8411	-0.8987	0.104
H431	-1.3514	-0.9129	-0.8154	0.144
H441	-1.3394	-0.8821	-0.6989	0.122
H451	-1.2207	-0.7920	-0.6588	0.104
H461	-1.1308	-0.7182	-0.7396	0.092
H471	0.3522	0.2022	0.2410	0.12
H472	0.2948	0.1170	0.2379	0.12

Table 3.3. Bond Lengths (Å) for the *bis*-2,2'-Bipyridyl Ligand Copper(I) Chloride Complex **18**

Cu1-N3*	2.057(4)
Cu1-N2*	2.052(4)
Cu1-C13*	2.846(5)

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Cu1-N1	2.057(4)
Cu1-N2	2.052(4)
Cu1-C13	2.846(5)
Cu2-Cl1'	2.060(4)
Cu2-Cl1	2.060(4)
O1-C4	1.433(6)
O1-C19	1.418(6)
O2-C3	1.453(6)
O2-C19	1.402(6)
O3-C2	1.438(6)
O3-C6	1.384(6)
O4-C1	1.443(6)
O4-C6	1.435(6)
N1-C13	1.351(6)
N1-C20	1.344(6)
N2-C5	1.355(5)
N2-C12	1.355(6)
C1-C2	1.521(7)
C1-C23	1.494(7)
C2-C29	1.507(8)
C3-C4	1.533(7)
C3-C35	1.506(7)
C4-C41	1.495(8)
C5-C6	1.514(7)
C5-C9	1.378(7)
C6-C7	1.526(6)
C7-C8	1.525(8)
C8-C9	1.495(7)
C9-C10	1.402(8)

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C10-C11	1.395(7)
C10-C21	1.508(8)
C11-C12	1.398(7)
C12-C13	1.480(6)
C13-C14	1.402(7)
C14-C15	1.388(7)
C15-C16	1.391(8)
C15-C22	1.514(8)
C16-C17	1.495(7)
C16-C20	1.383(7)
C17-C18	1.529(9)
C18-C19	1.532(6)
C19-C20	1.522(7)
C23-C24	1.359(8)
C23-C28	1.386(7)
C24-C25	1.368(9)
C25-C26	1.355(10)
C26-C27	1.342(9)
C27-C28	1.384(8)
C29-C30	1.407(9)
C29-C34	1.368(8)
C30-C31	1.388(11)
C31-C32	1.341(14)
C32-C33	1.342(14)
C33-C34	1.370(11)
C35-C36	1.391(8)
C35-C40	1.379(8)
C36-C37	1.365(9)
C37-C38	1.372(11)

C38-C39	1.332(10)
C39-C40	1.395(9)
C41-C42	1.395(8)
C41-C46	1.389(8)
C42-C43	1.401(11)
C43-C44	1.336(11)
C44-C45	1.376(10)
C45-C46	1.372(9)
C15-C47	1.64(2)
C16-C47	1.91(2)

Table 3.4. Bond Angles (°) for the *bis*-2,2'-Bipyridyl Ligand Copper(I) Chloride Complex **18**

N1*-Cu1-N2*	82.23(15)
N1*-Cu1-C13*	26.20(14)
N2*-Cu1-C13*	56.08(14)
N1*-Cu1-N1	117.46(19)
N2*-Cu1-N1	131.17(14)
C13*-Cu1-N1	131.46(14)
N1*-Cu1-N2	131.17(14)
N2*-Cu1-N2	119.49(19)
C13*-Cu1-N2	141.85(13)
N1-Cu1-N2	82.23(15)
N1*-Cu1-C13	131.46(14)
N2*-Cu1-C13	141.85(13)
C13*-Cu1-C13	153.81(17)
N1-Cu1-C13	26.20(14)
N2-Cu1-C13	56.08(14)
C11'-Cu2-C11	176.95(17)
C4-O1-C19	105.0(4)

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C3-O2-C19	108.8(4)
C2-O3-C6	109.8(4)
C1-O4-C6	106.1(3)
Cu1-N1-C13	111.6(3)
Cu1-N1-C20	131.3(3)
C13-N1-C20	116.5(4)
Cu1-N2-C5	130.8(3)
Cu1-N2-C12	112.4(3)
C5-N2-C12	116.2(4)
O4-C1-C2	100.9(4)
O4-C1-C23	109.9(4)
C2-C1-C23	117.3(4)
C1-C2-O3	103.3(4)
C1-C2-C29	116.3(4)
O3-C2-C29	110.6(4)
O2-C3-C4	102.8(4)
O2-C3-C35	112.3(4)
C4-C3-C35	116.8(4)
C3-C4-O1	102.2(4)
C3-C4-C41	113.7(5)
O1-C4-C41	111.4(4)
N2-C5-C6	127.0(4)
N2-C5-C9	124.0(4)
C6-C5-C9	109.0(4)
C5-C6-O4	106.6(4)
C5-C6-O3	117.8(4)
O4-C6-O3	106.6(4)
C5-C6-C7	102.0(4)
O4-C6-C7	110.9(4)

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O3-C6-C7	112.8(4)
C6C7-C8	105.3(4)
C7-C8-C9	102.5(4)
C8-C9-C5	111.5(5)
C8-C9-C10	128.6(5)
C5-C9-C10	119.8(4)
C9-C10-C11	116.1(5)
C9-C10-C21	122.3(5)
C11-C10-C21	121.6(5)
C10-C11-C12	120.7(5)
C11-C12-N2	122.4(4)
C11-C12-C13	121.5(4)
N2-12-C13	116.1(4)
C12-C13-N1	117.5(4)
C12-C13-Cu1	75.4(3)
N1-C13-Cu1	42.2(2)
C12-C13-C14	120.7(4)
N1-C13-C14	121.8(4)
Cu1-C13-C14	163.7(4)
C13-C14-C15	121.3(5)
C14-C15-C16	116.1(5)
C14-C15-C22	121.2(6)
C16-C15-C22	122.6(5)
C15-C16-C17	128.8(5)
C15-C16-C20	119.8(4)
C17-C16-C20	111.5(5)
C16-C17-C18	102.8(5)
C17-C18-C19	105.1(5)
C18-C19-O1	112.2(4)

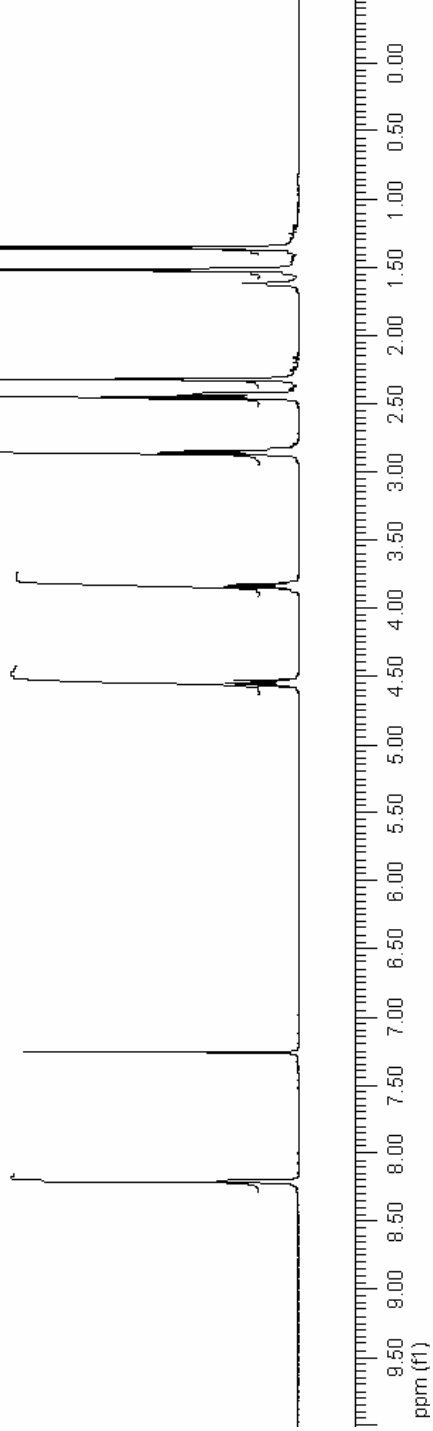
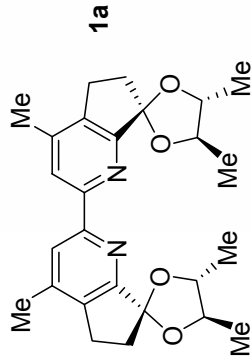
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C18-C19-O2	111.0(4)
O1-C19-O2	106.9(4)
C18-C19-C20	102.4(5)
O1-C19-C20	108.7(4)
O2-C19-C20	115.7(4)
C19-C20-C16	109.1(4)
C19-C20-N1	126.4(4)
C16-C20-N1	124.5(5)
C1-C23-C24	122.4(5)
C1-C23-C28	120.0(4)
C24-C23-C28	117.5(5)
C23-C24-C25	121.6(6)
C24-C25-C26	120.1(6)
C25-C26-C27	120.0(6)
C26-C27-C28	120.2(6)
C23-C28-C27	120.4(5)
C2-C29-C30	119.1(5)
C2-C29-C34	121.7(6)
C30-C29-C34	119.2(6)
C29-C30-C31	118.3(7)
C30-C31-C32	120.4(9)
C31-C32-C33	121.7(9)
C32-C33-C34	120.0(9)
C33-C34-C29	120.5(8)
C3-C35-C36	121.1(5)
C3-C35-C40	119.8(5)
C36-C35-C40	119.1(5)
C35-C36-C37	119.2(7)
C36-C37-C38	121.7(7)

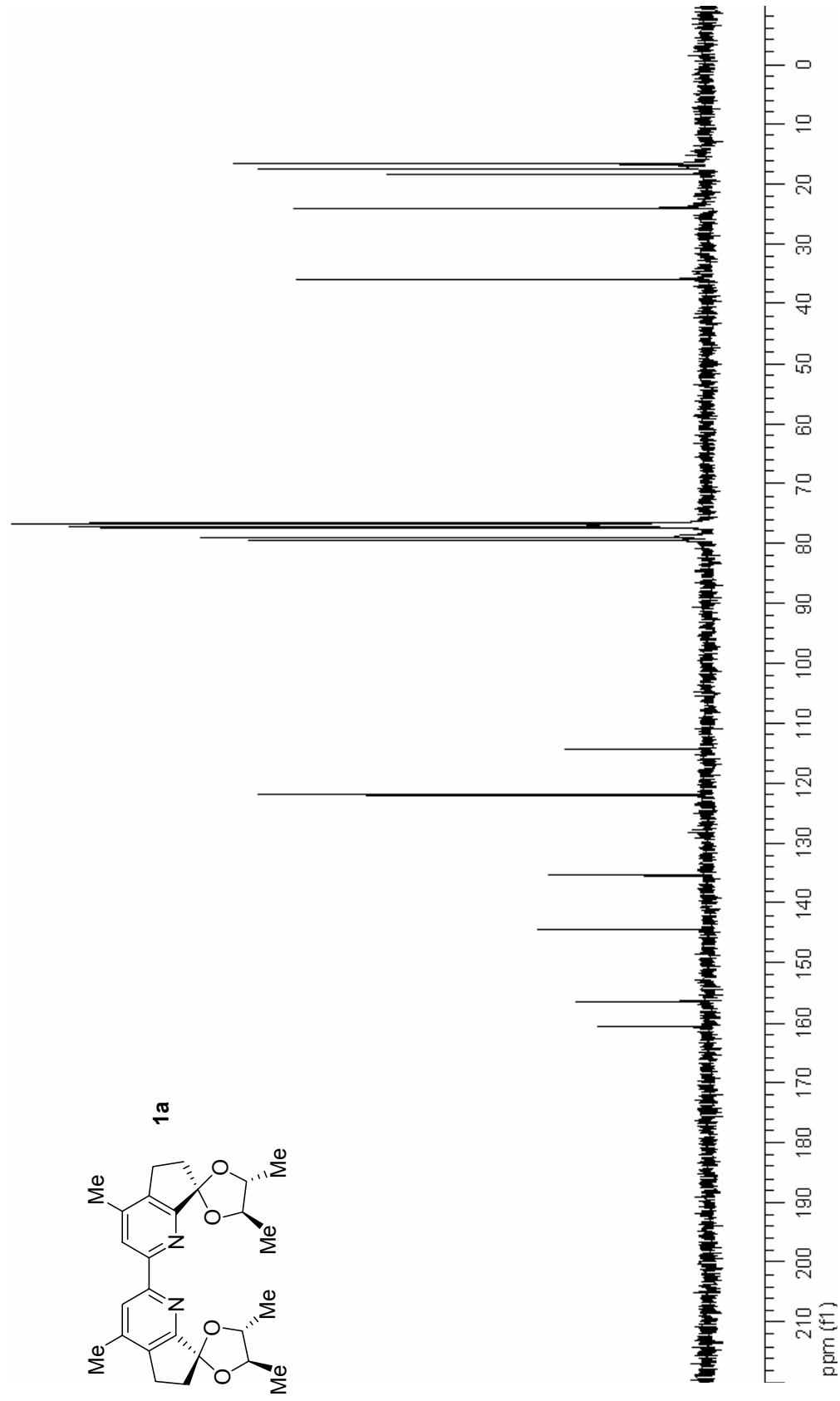
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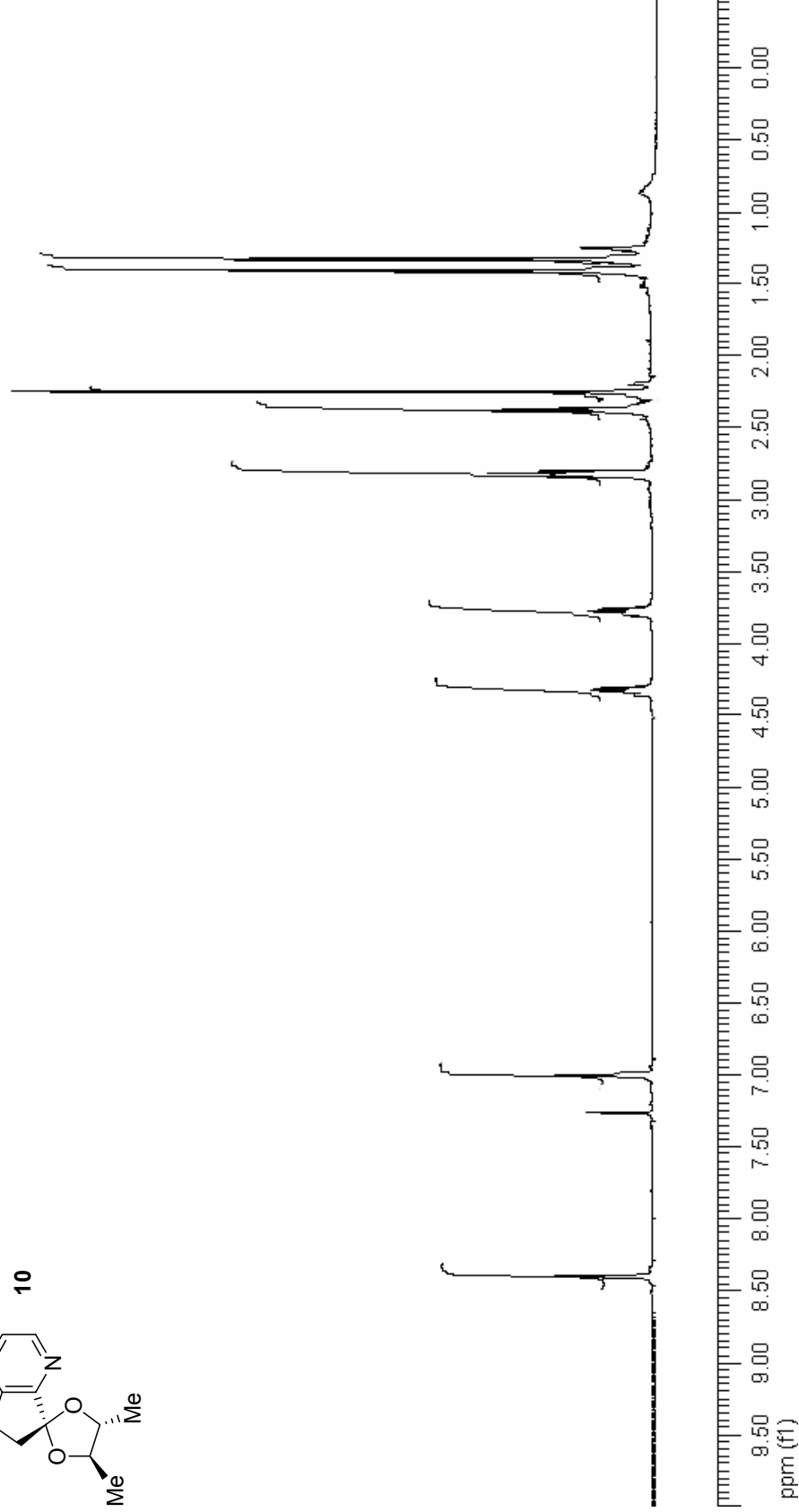
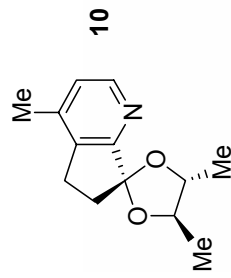
C37-C38-C39	119.4(6)
C38-C39-C40	121.1(7)
C39-C40-C35	119.6(6)
C4-C41-C42	120.1(5)
C4-C41-C46	121.4(5)
C42-C41-C46	118.5(6)
C41-C42-C43	118.6(7)
C42-C43-C44	121.7(7)
C43-C44-C45	120.1(7)
C44-C45-C46	120.0(6)
C41-C46-C45	120.9(6)
C16-C47-C15	107.7(13)

4. ^1H and ^{13}C NMR Spectra

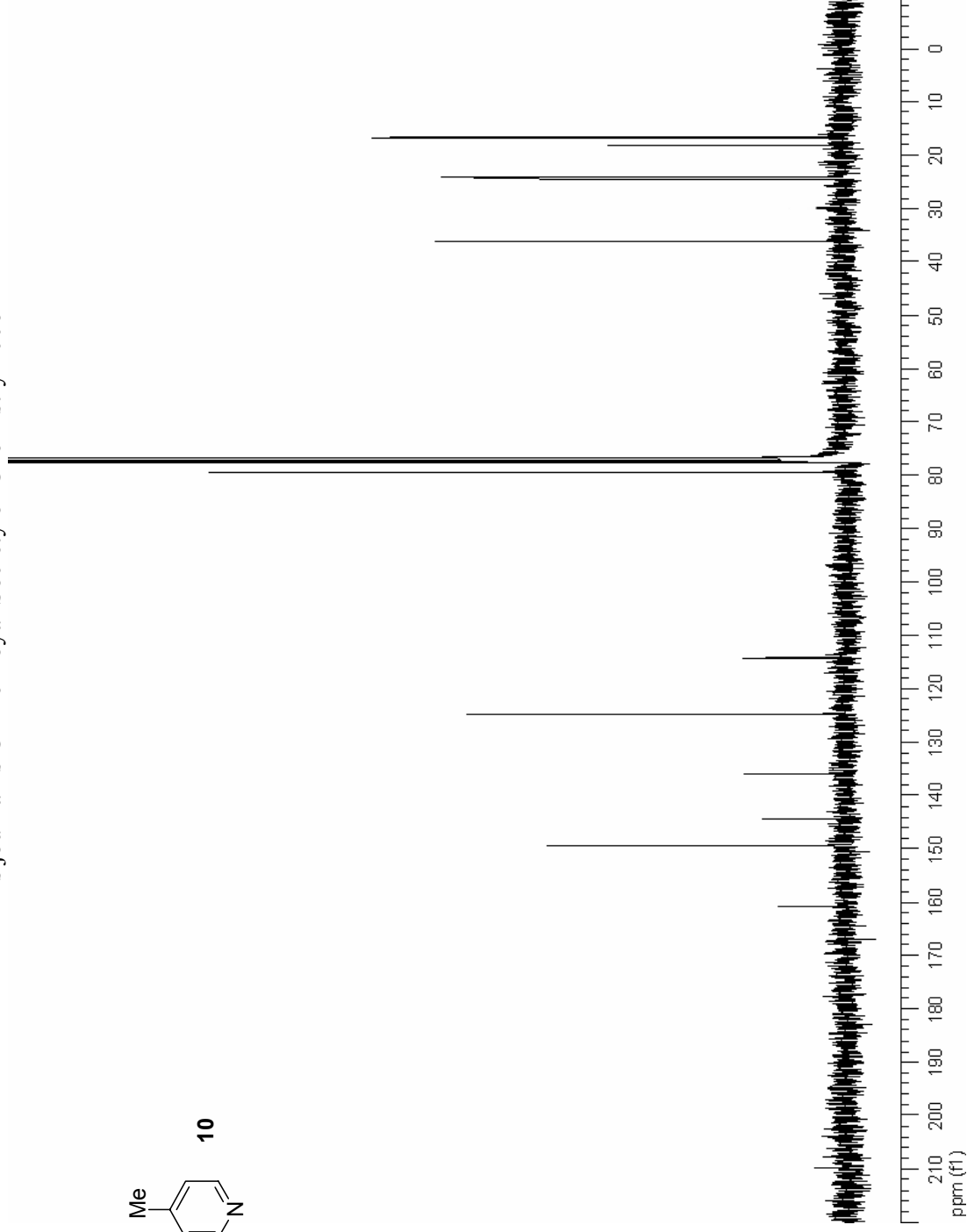
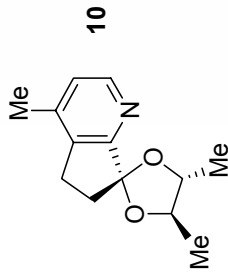


^1H NMR spectrum (CDCl₃) of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5*H*,5'*H*-2,2'-bi([1]pyrindinyl)-7,7'-dione
(2*R*,3*R*)-2,3-butanediol *bis*-acetal **1a**.

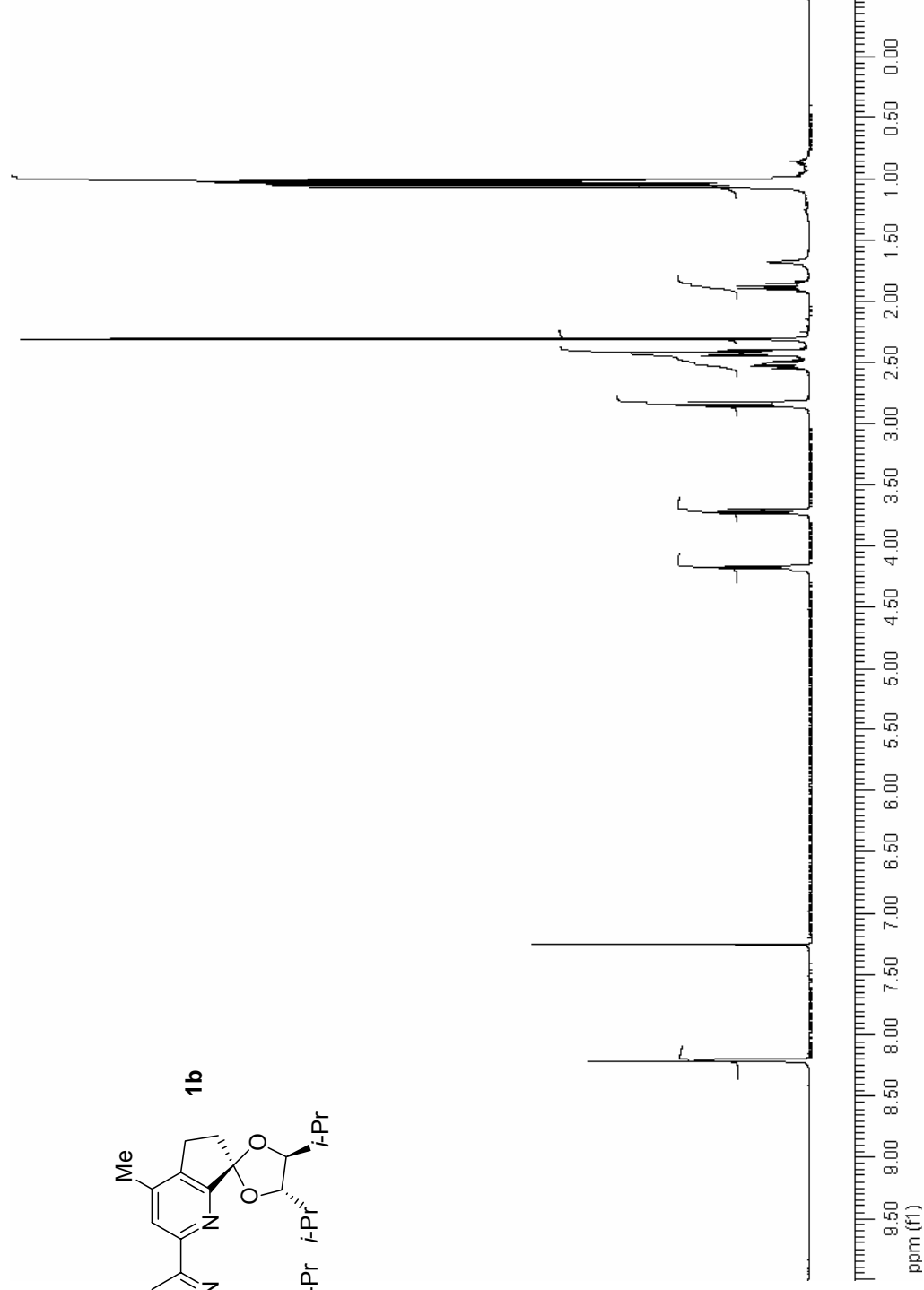
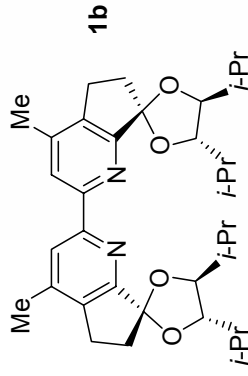




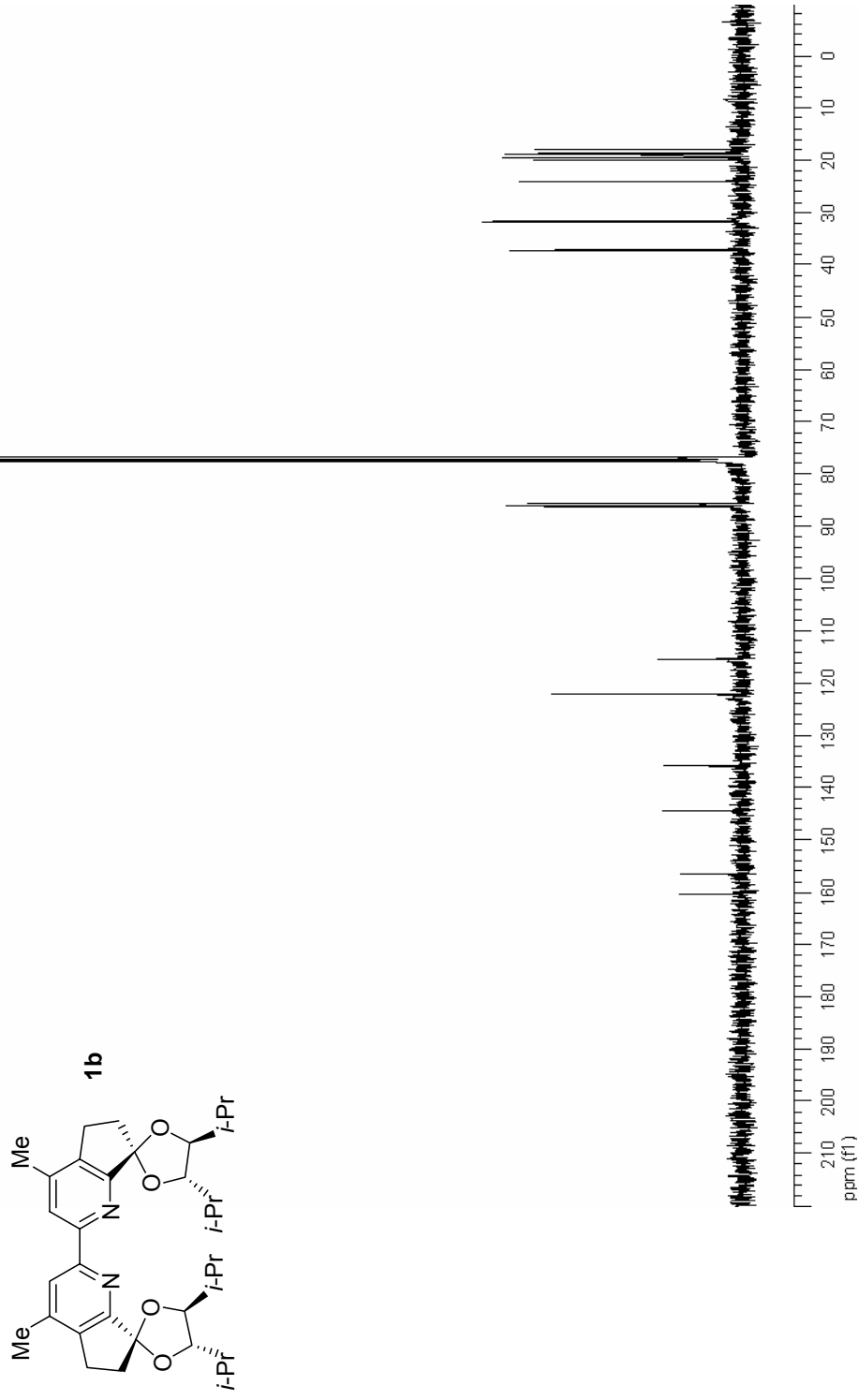
¹H NMR spectrum (CDCl₃) of 4-methyl-6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3-butanediol acetal **10**.

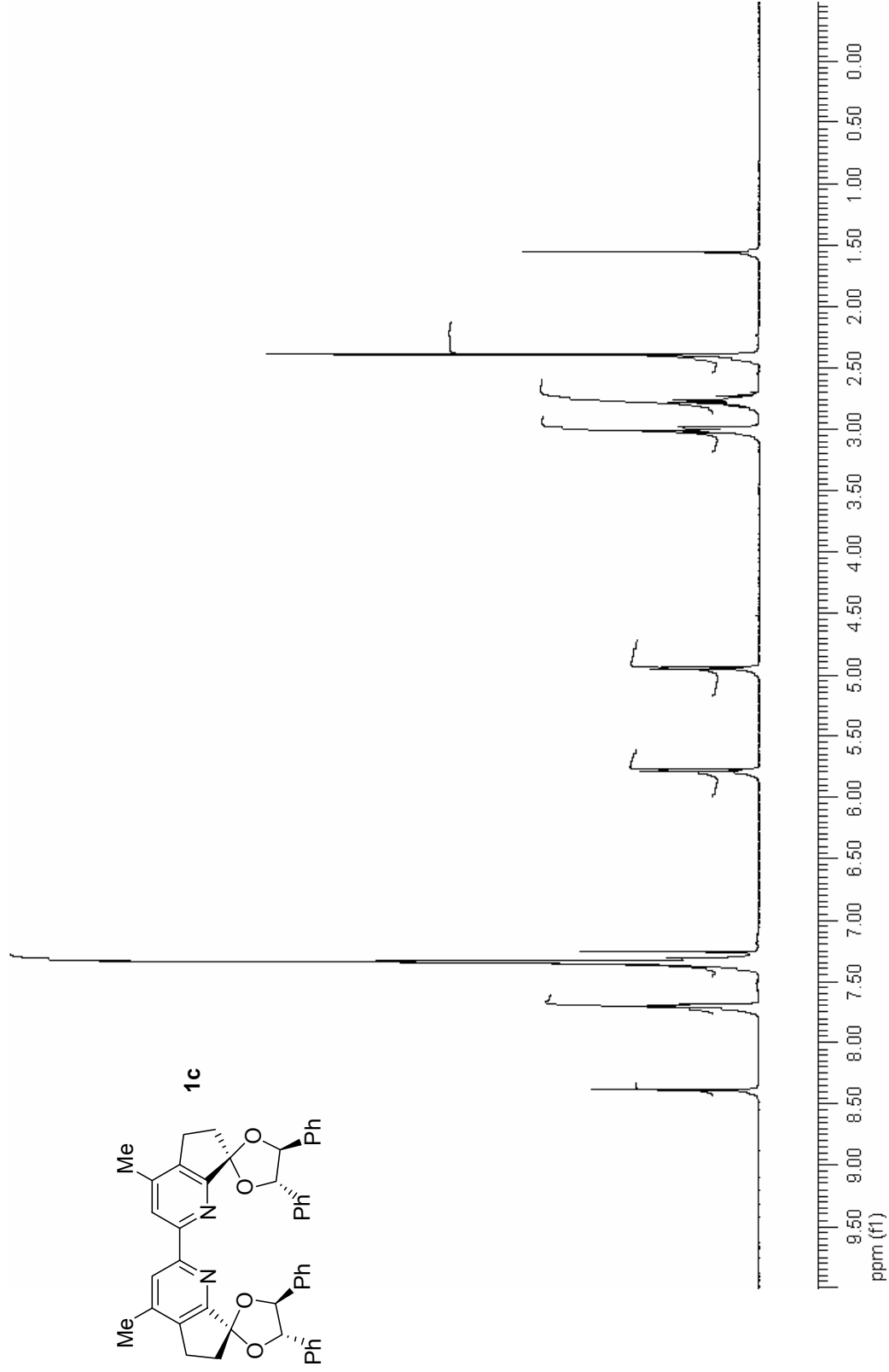


¹³C NMR spectrum (CDCl₃) of 4-methyl-1,6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3-butanediol acetal **10**.

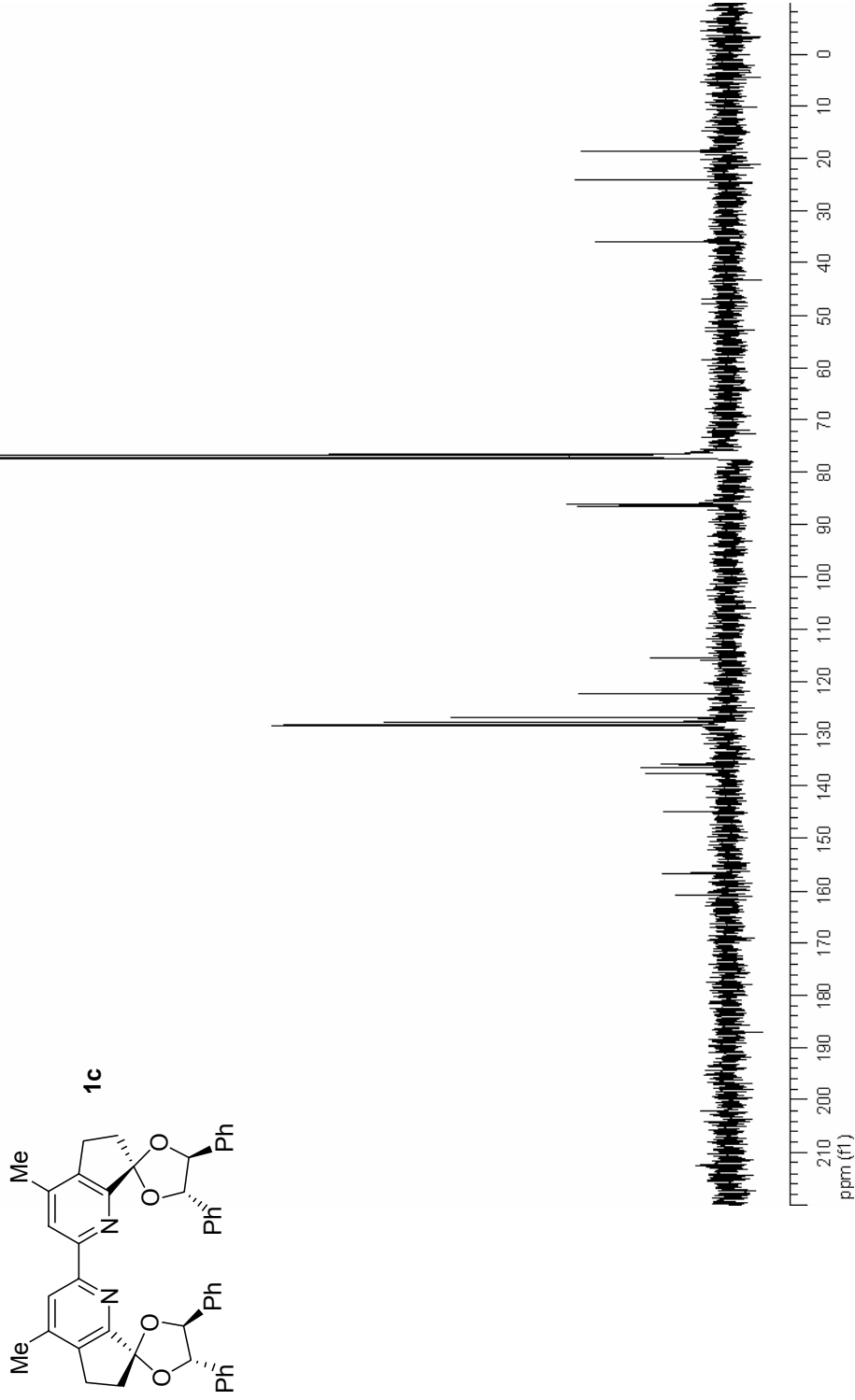


¹H NMR spectrum (CDCl₃) of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5H,5'H-2,2'-bi([1]pyrindinyl)-7,7'-dione
(1*S*,2*S*)-1,2-diisopropyl-1,2-ethanediol bis-acetal **1b**.

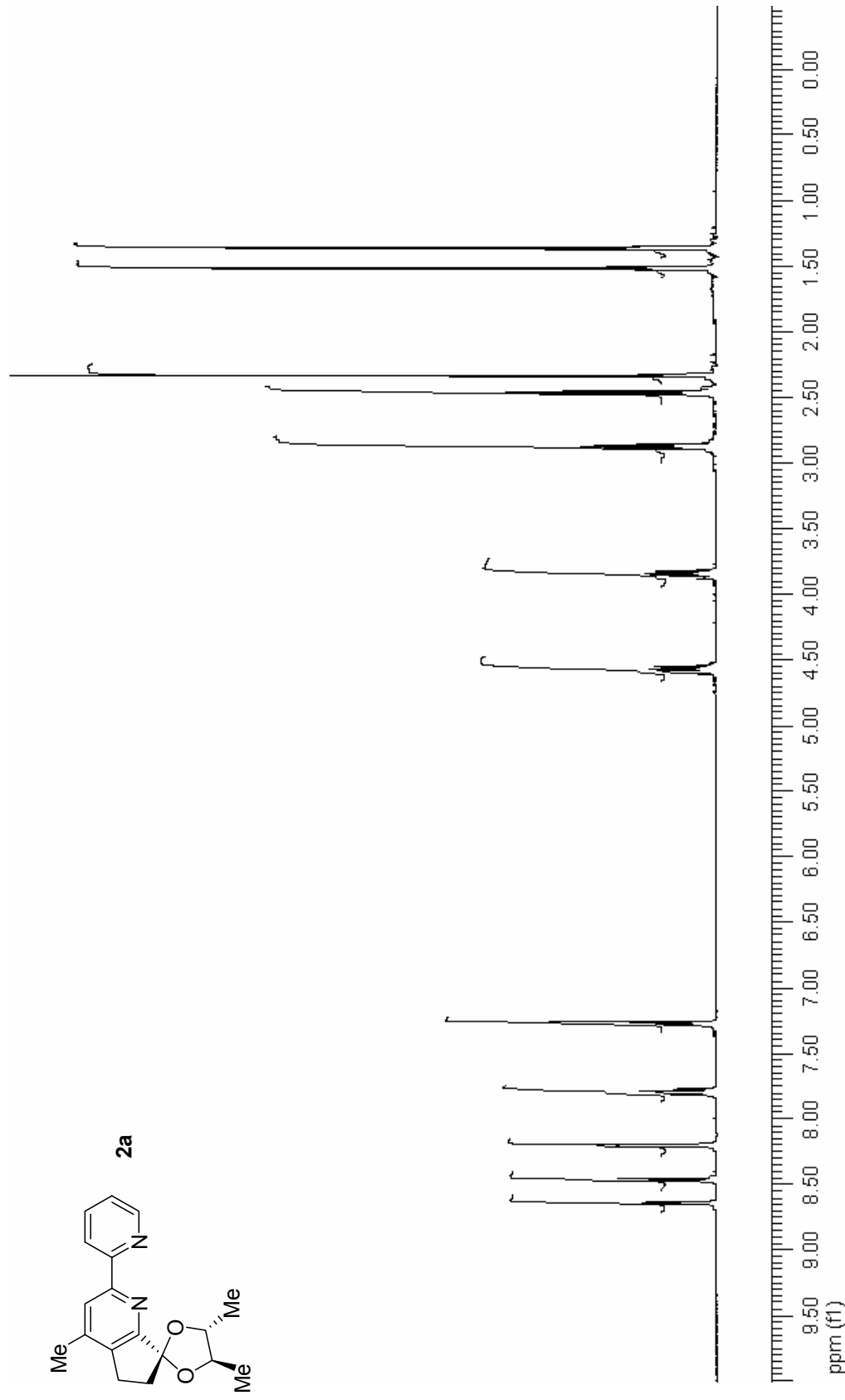




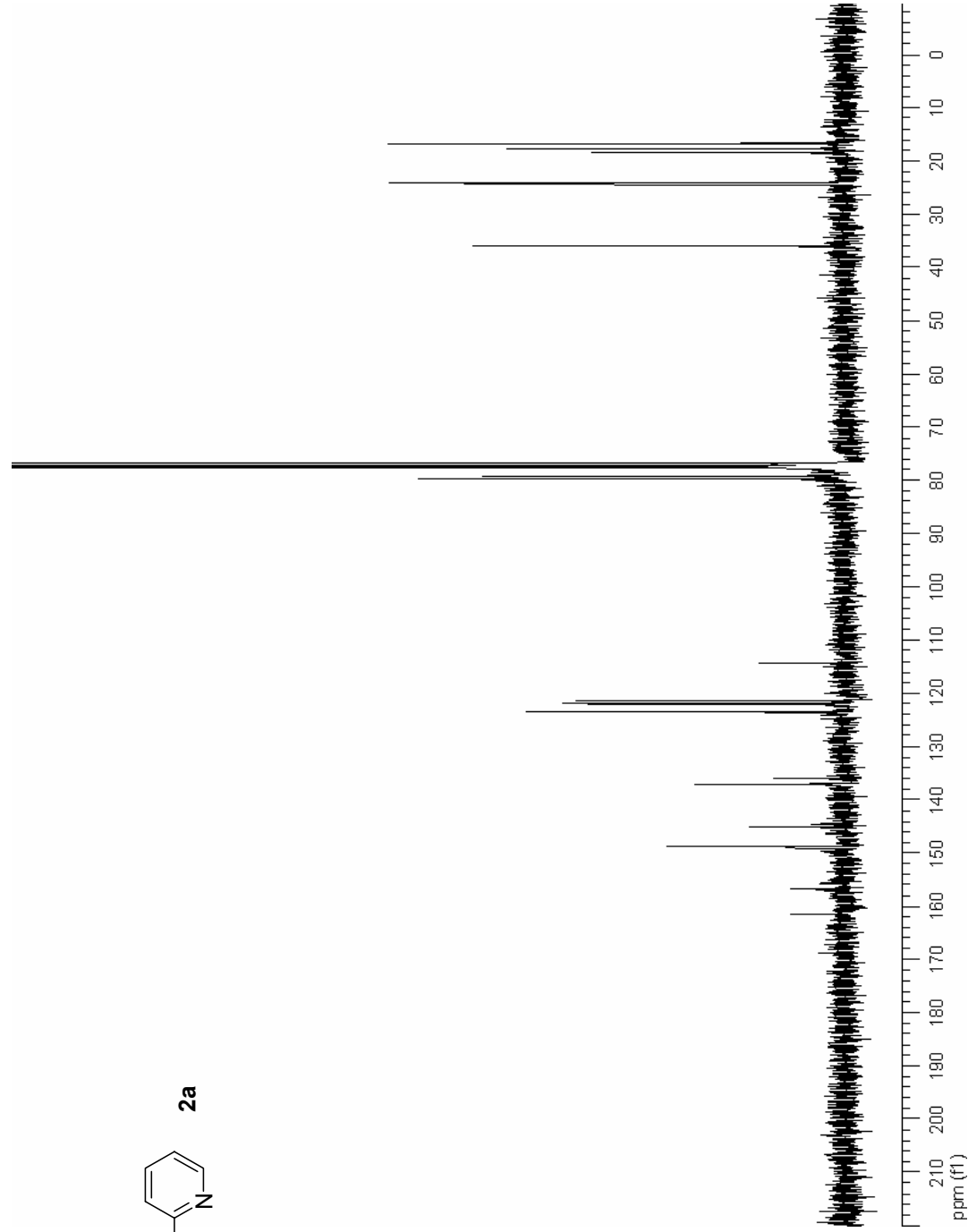
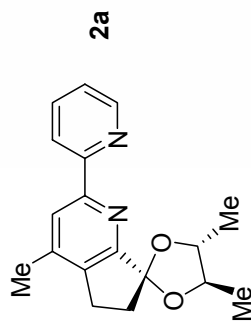
¹H NMR spectrum (CDCl₃) of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5H,5'H-2,2'-bi([1]pyrindinyl)-7,7'-dione
(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol bis-acetal **1c**.



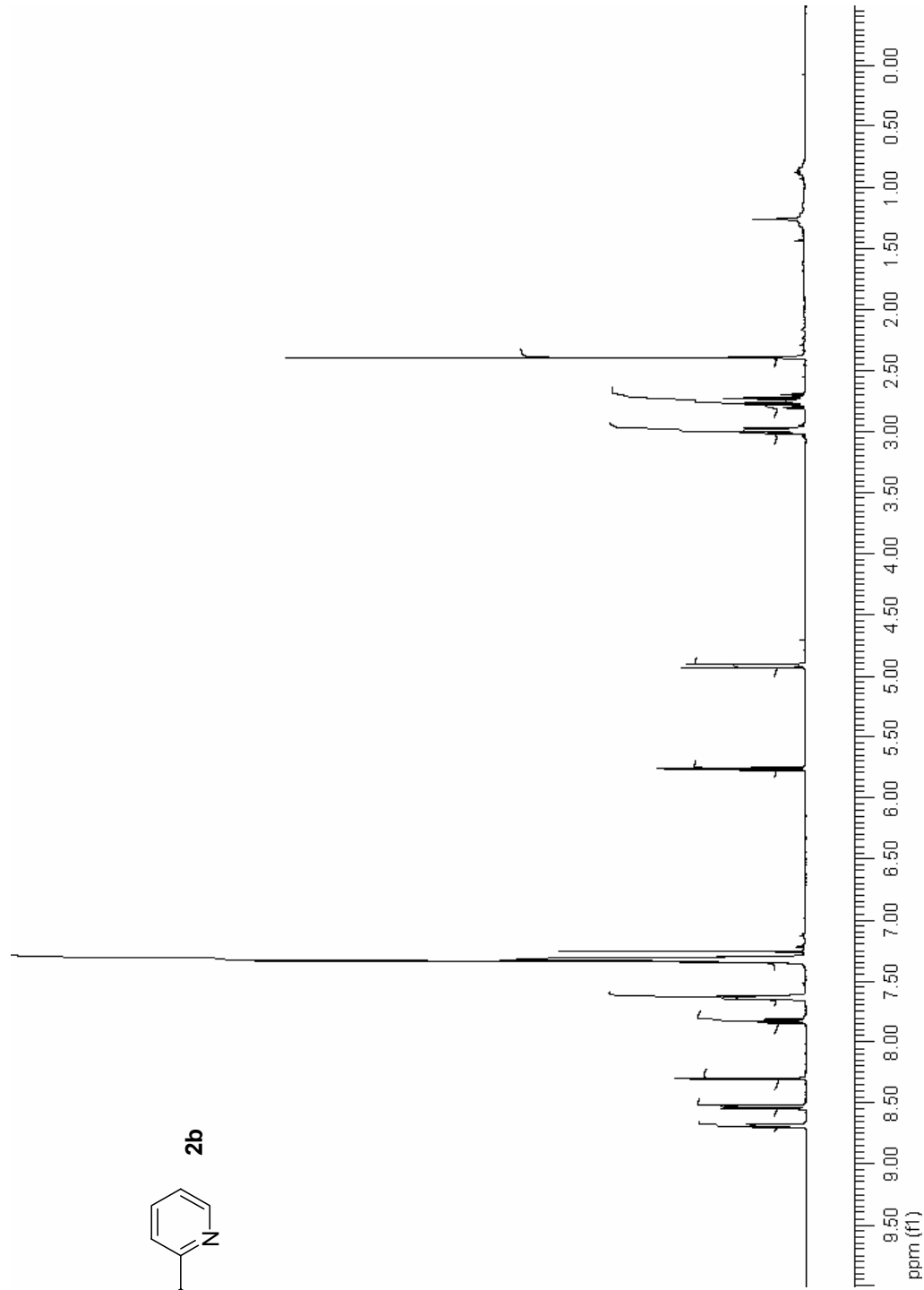
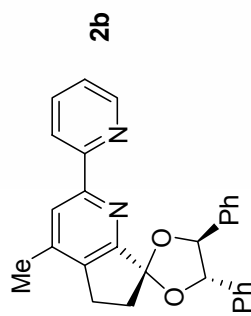
¹³C NMR spectrum (CDCl₃) of 4,4'-dimethyl-6,6',7,7'-tetrahydro-5H,5'H-2,2'-bi([1]pyrindinyl)-7,7'-dione
(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol *bis*-acetal **1c**.



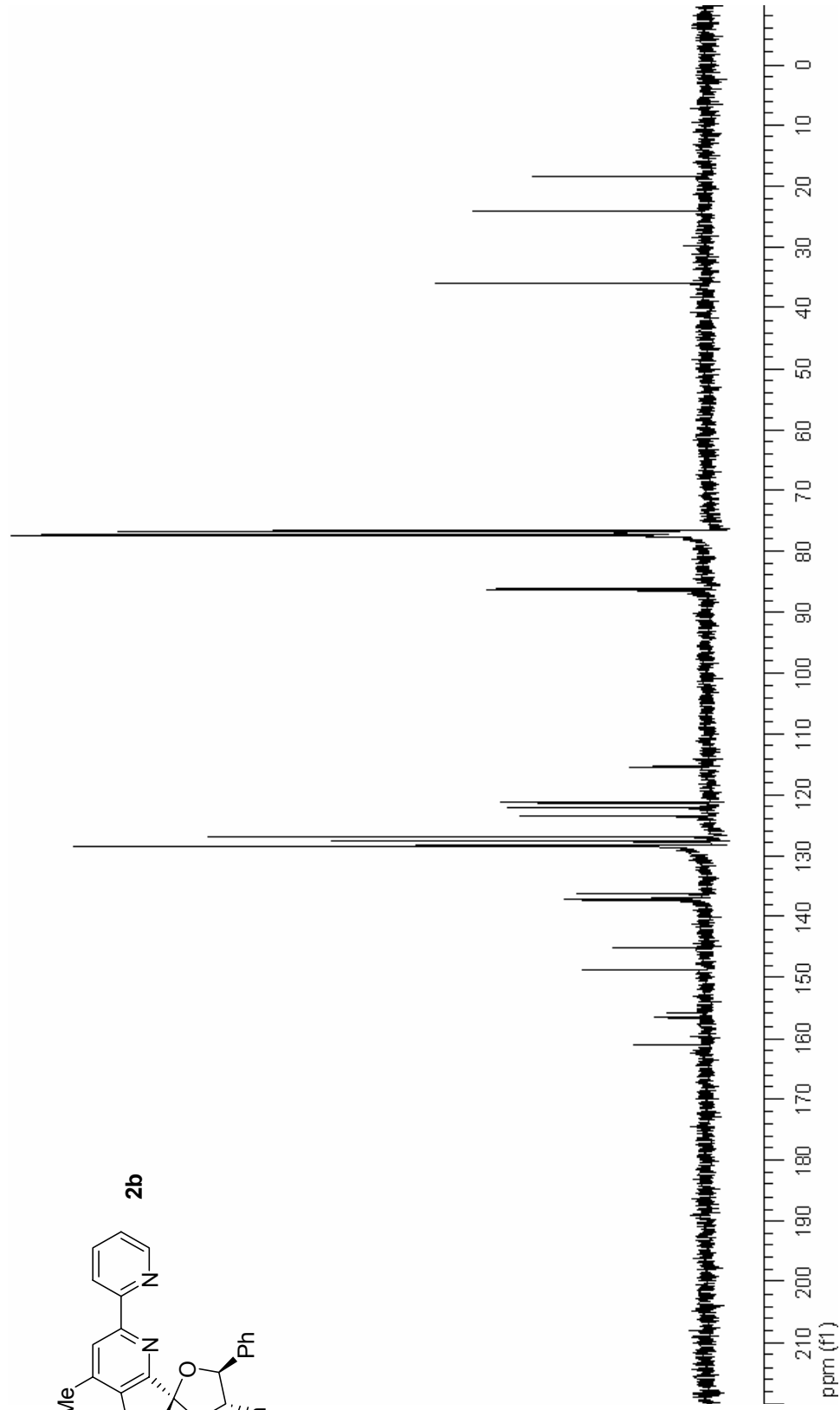
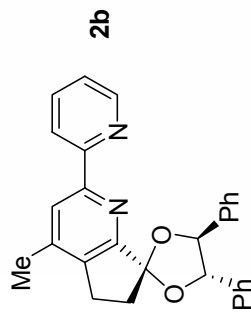
¹H NMR spectrum (CDCl₃) of 4-methyl-2-(2'-pyridyl)-6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3-butanediol acetal **2a**.



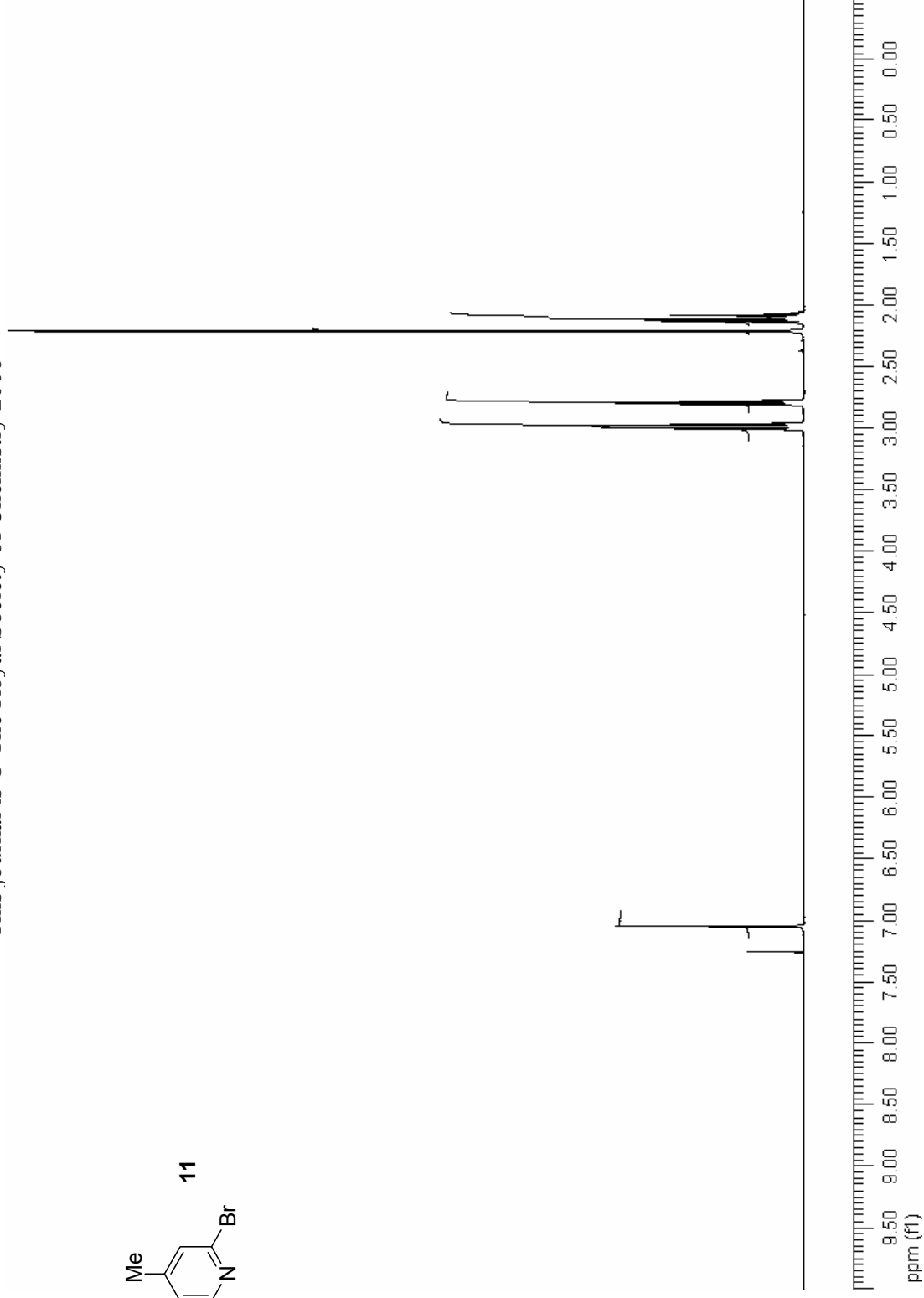
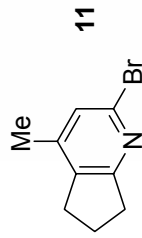
^{13}C NMR spectrum (CDCl₃) of 4-methyl-2-(2'-(2'-pyridyl)-6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3,3-butanediol) acetal **2a**.



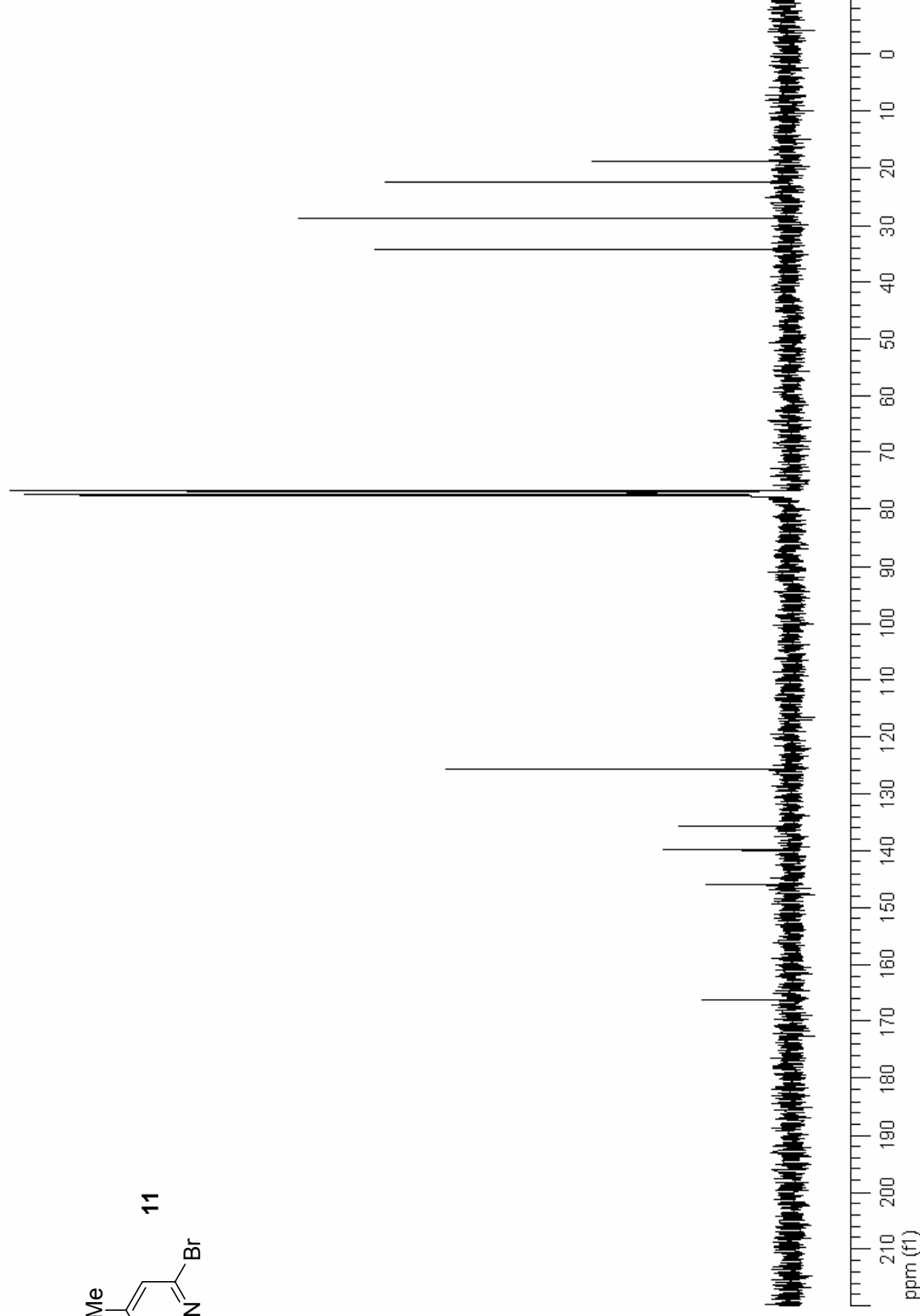
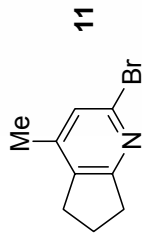
¹H NMR spectrum (CDCl₃) of 4-methyl-2-(2'-pyridyl)-6,7-dihydro-5*H*-[1]pyrindin-7-one (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol acetal **2b**.



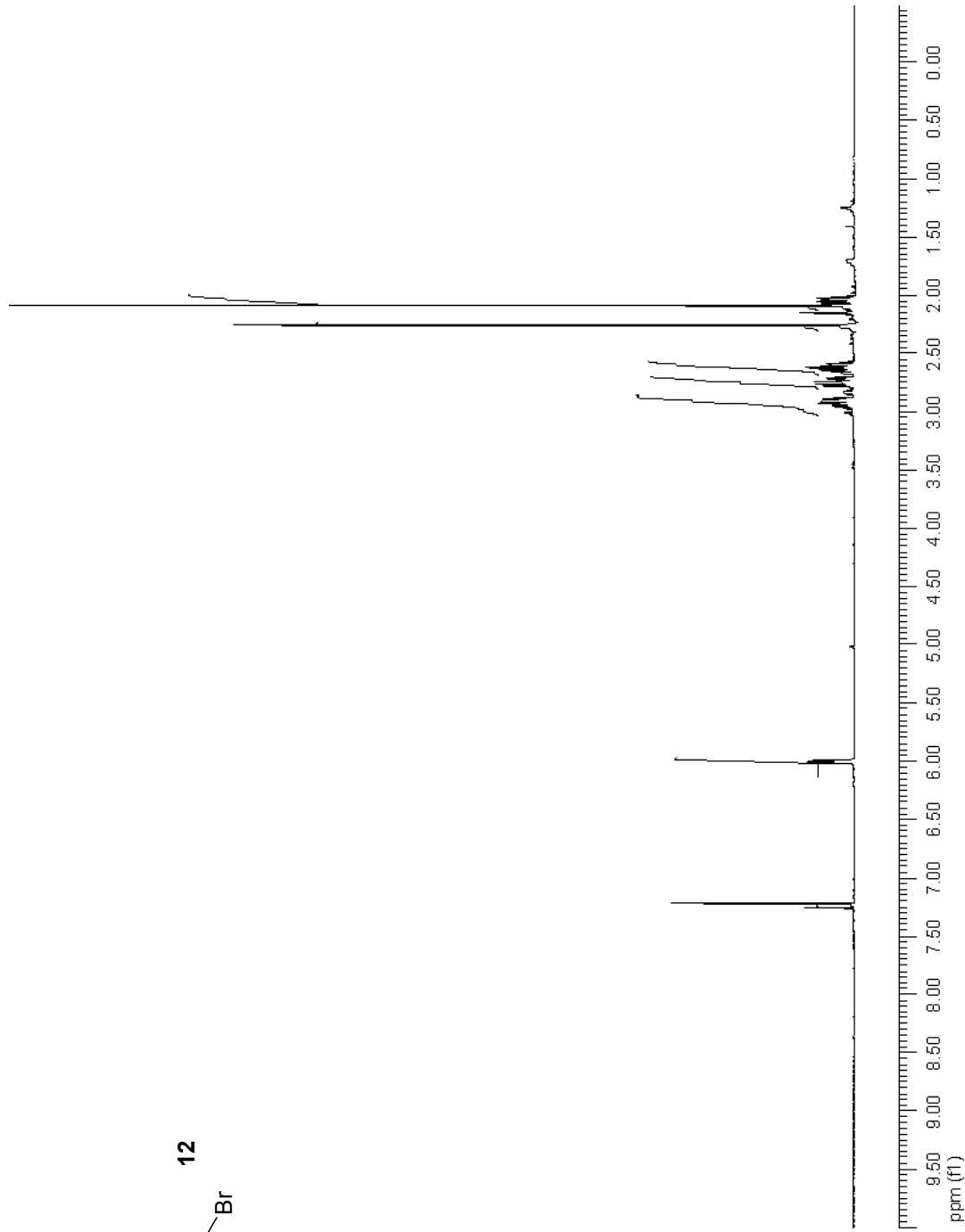
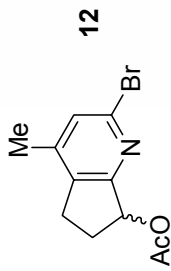
^{13}C NMR spectrum (CDCl_3) of 4-methyl-2-(2'-pyridyl)-6,7-dihydro-5H-[1]pyrindin-7-one
(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol acetal **2b**.



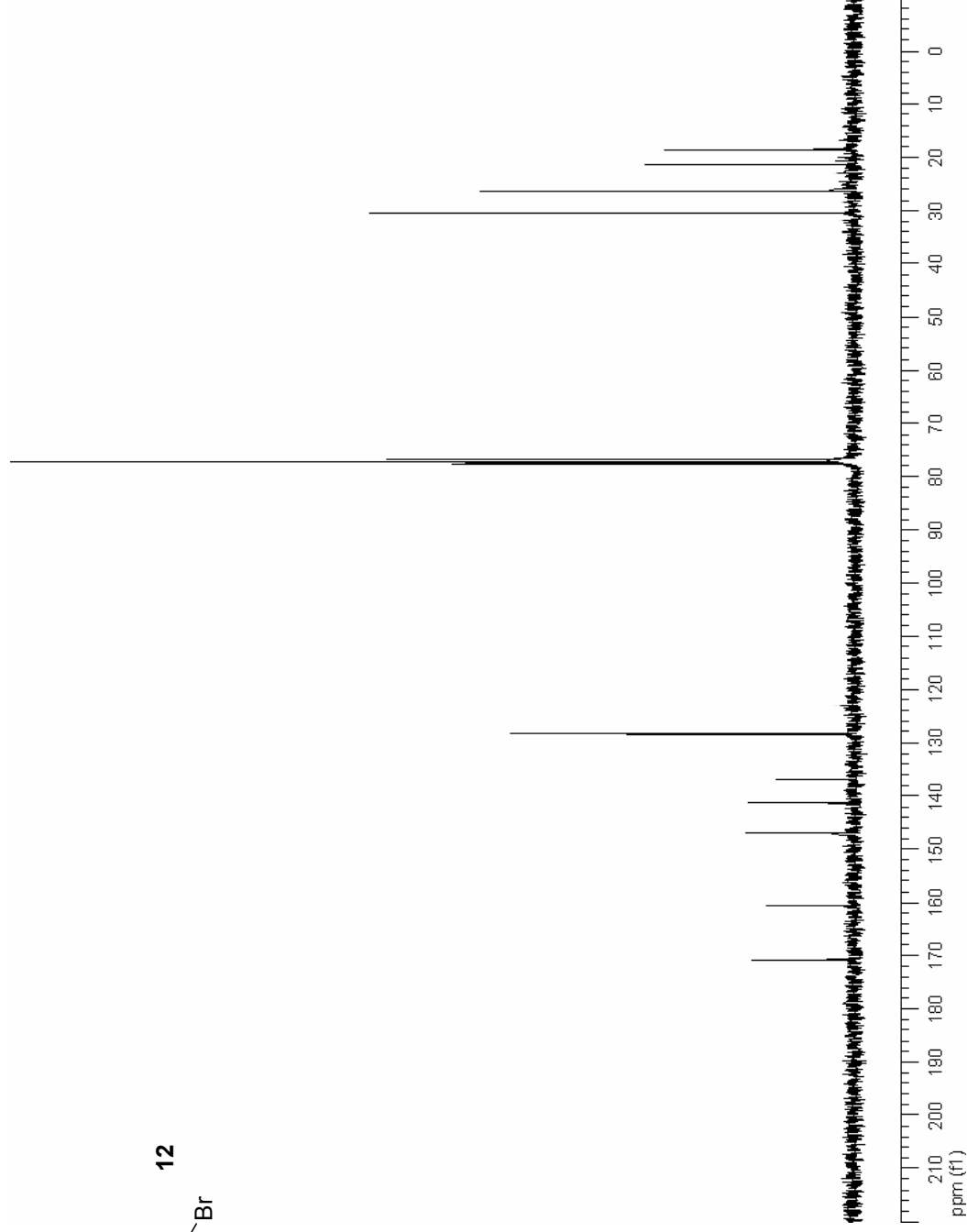
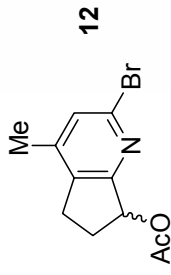
¹H NMR spectrum (CDCl₃) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindine **11**.

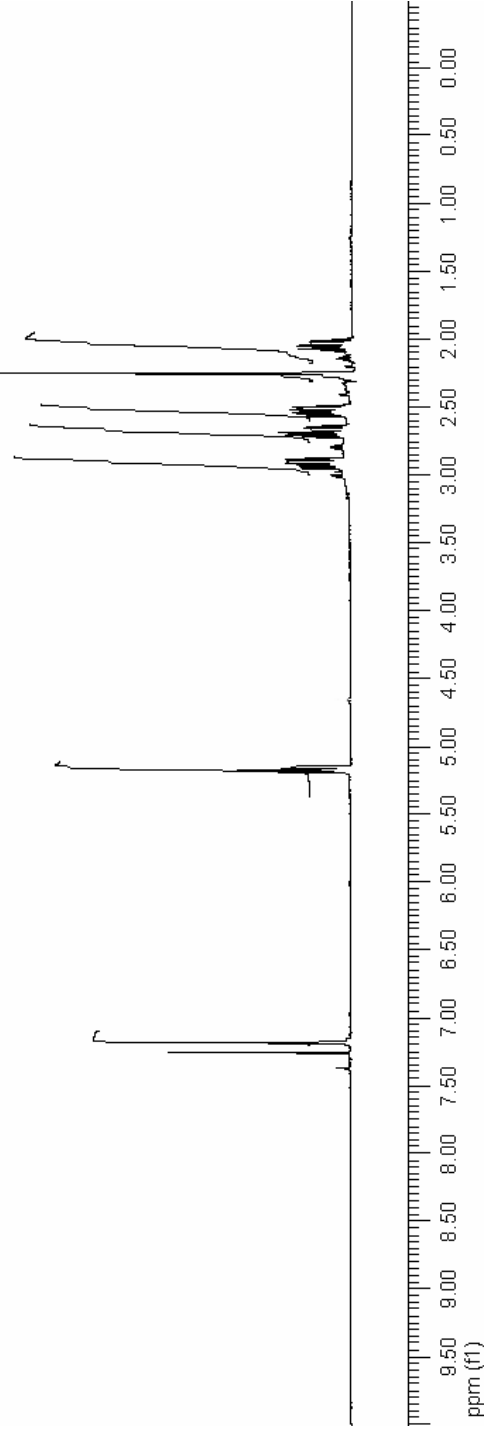
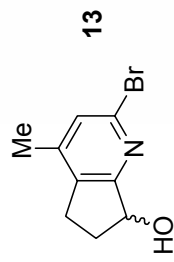


^{13}C NMR spectrum (CDCl_3) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindine **11**.

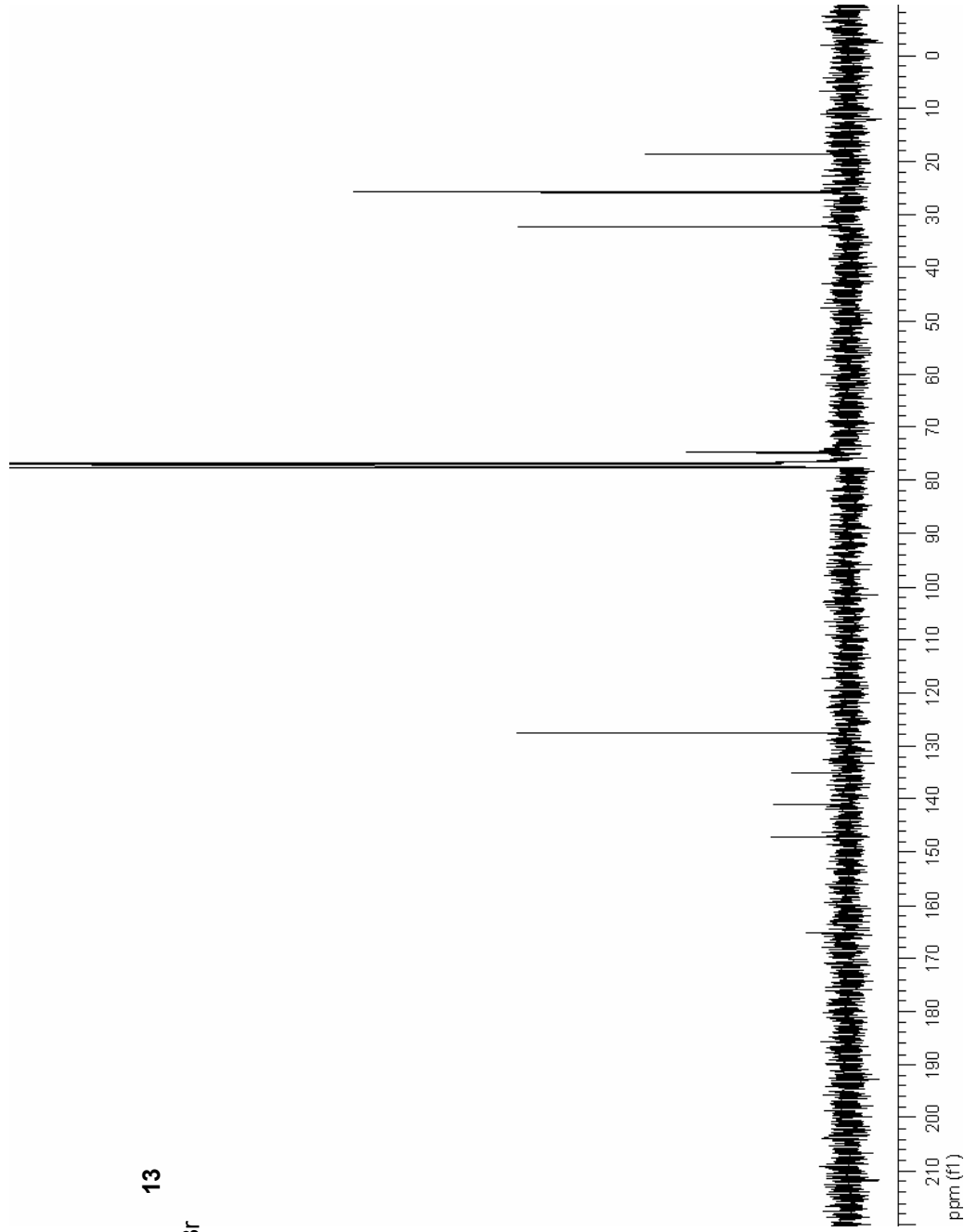
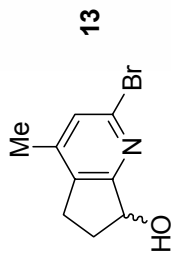


¹H NMR spectrum (CDCl₃) of (7*RS*)-7-acetoxy-2-bromo-4-methyl-6,7-dihydro-5*H*-[1]pyrindine **12**.

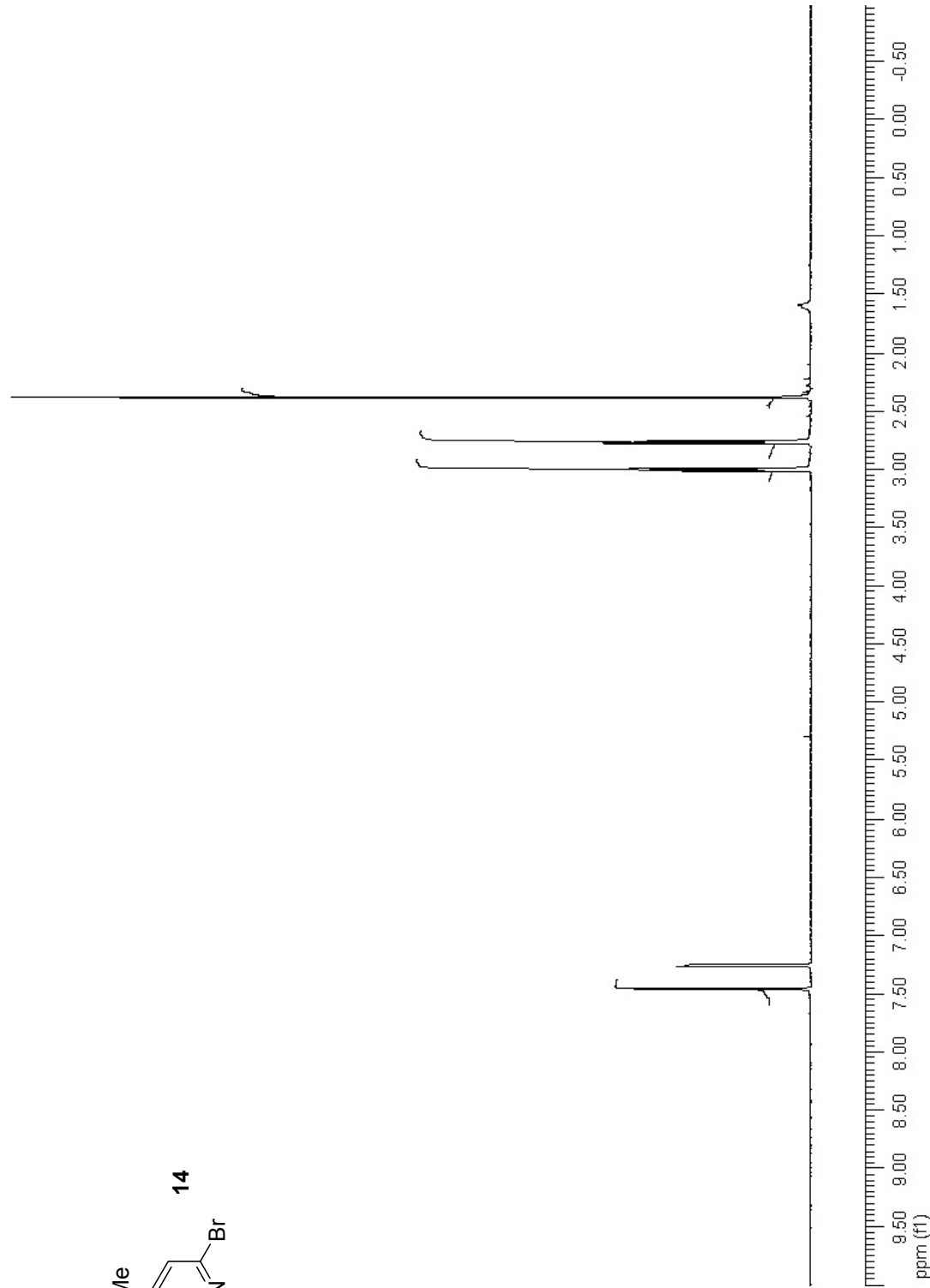
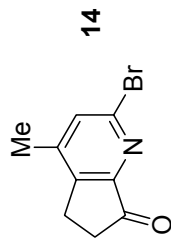




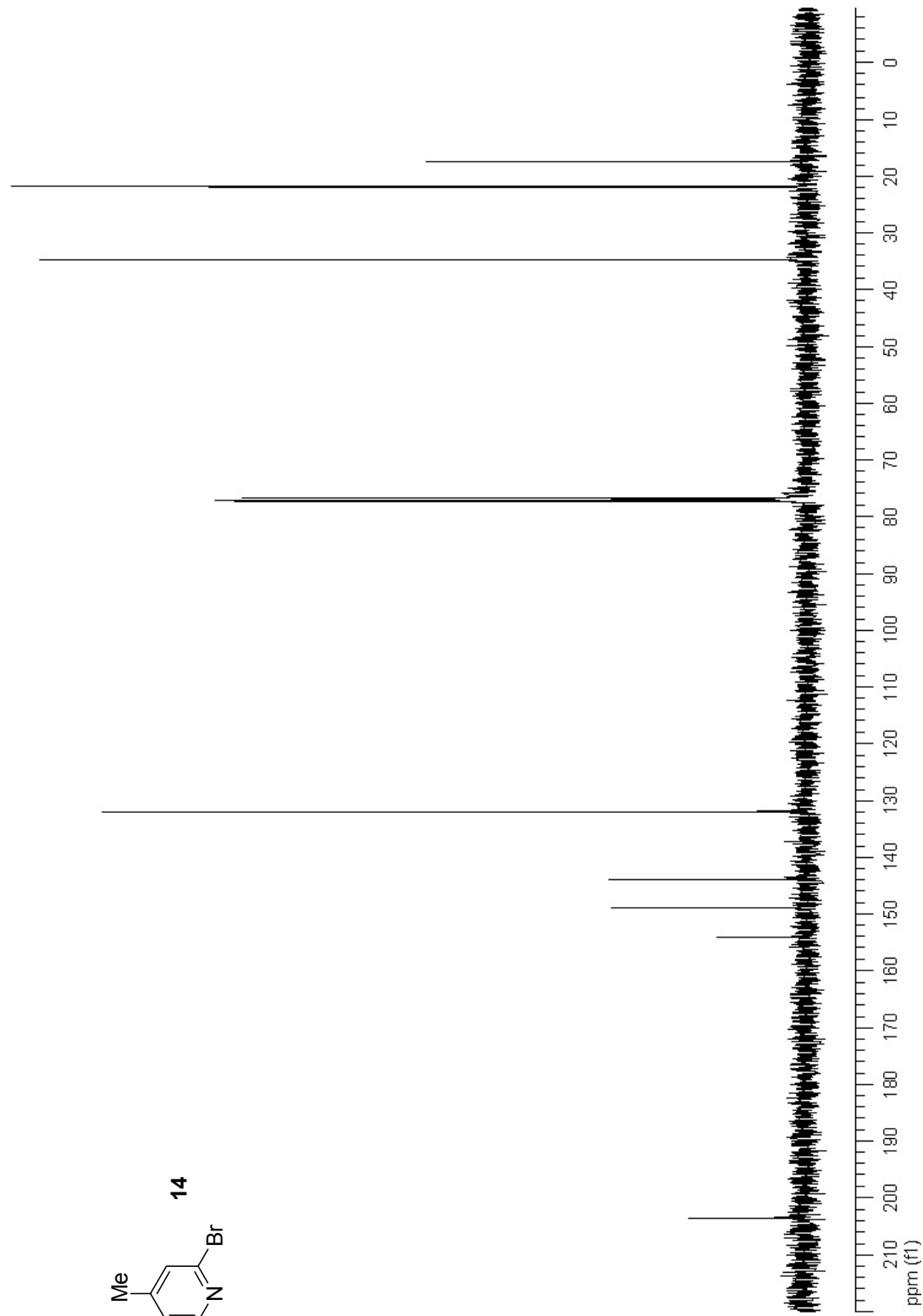
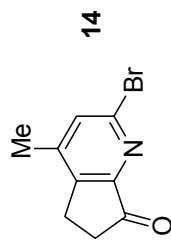
¹H NMR spectrum (CDCl₃) of (7*RS*)-2-bromo-4-methyl-6,7-dihydro-5*H*-[1]pyrindin-7-ol **13**.



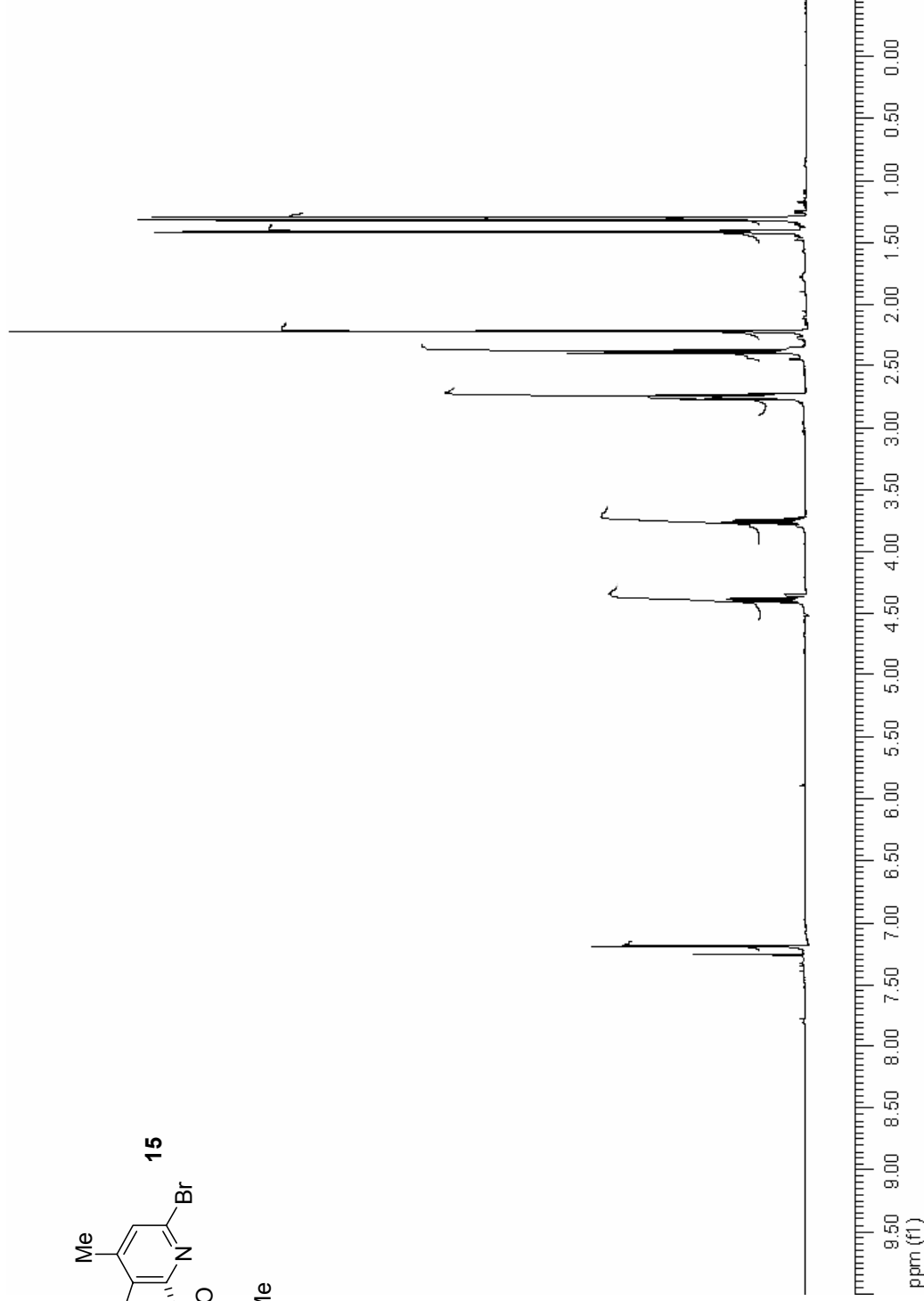
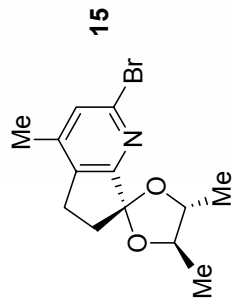
^{13}C NMR spectrum (CDCl_3) of (7*RS*)-2-bromo-4-methyl-6,7-dihydro-5*H*-[1]pyrindin-7-ol **13**.



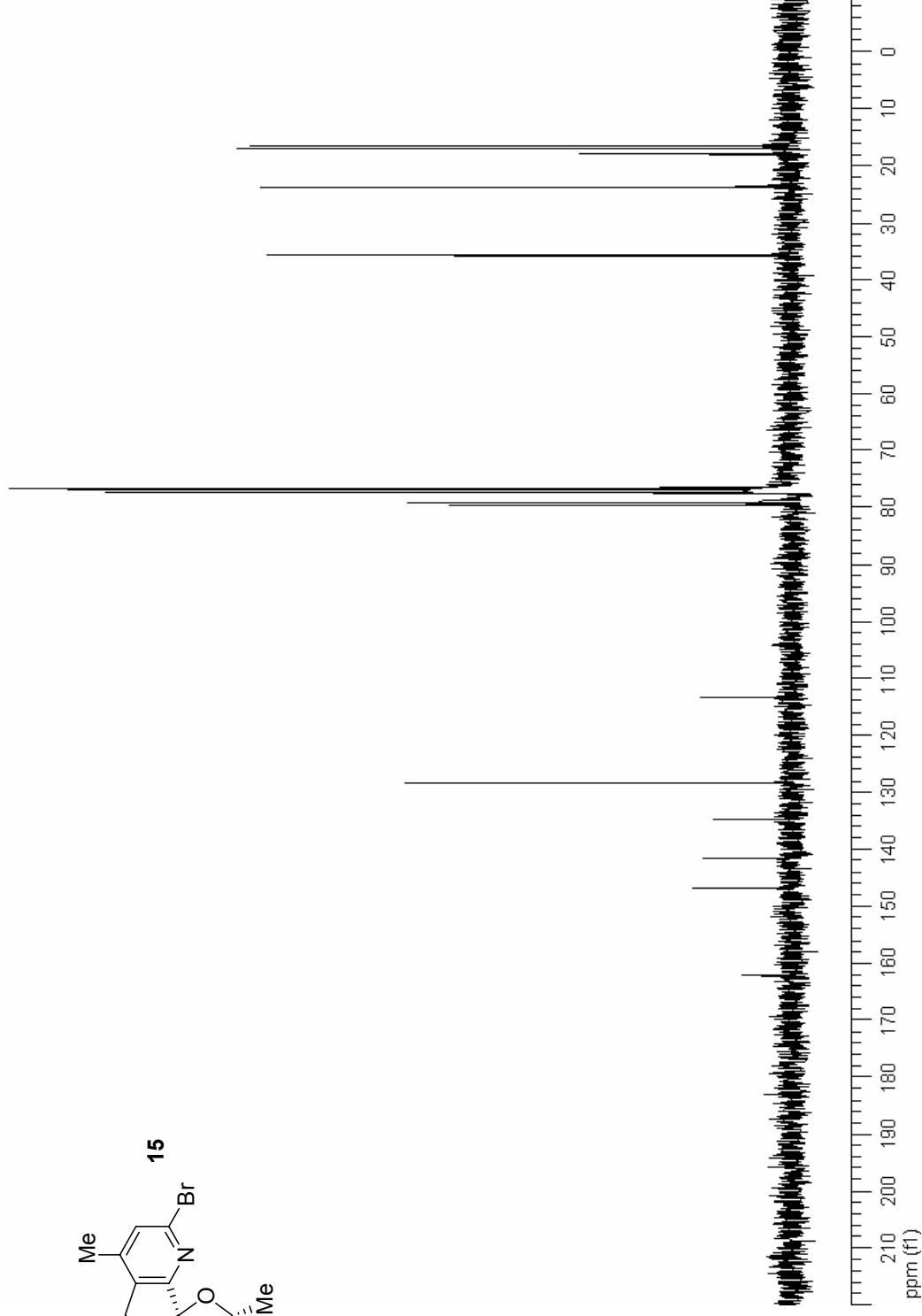
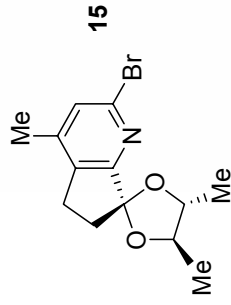
¹H NMR spectrum (CDCl₃) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-one **14**.



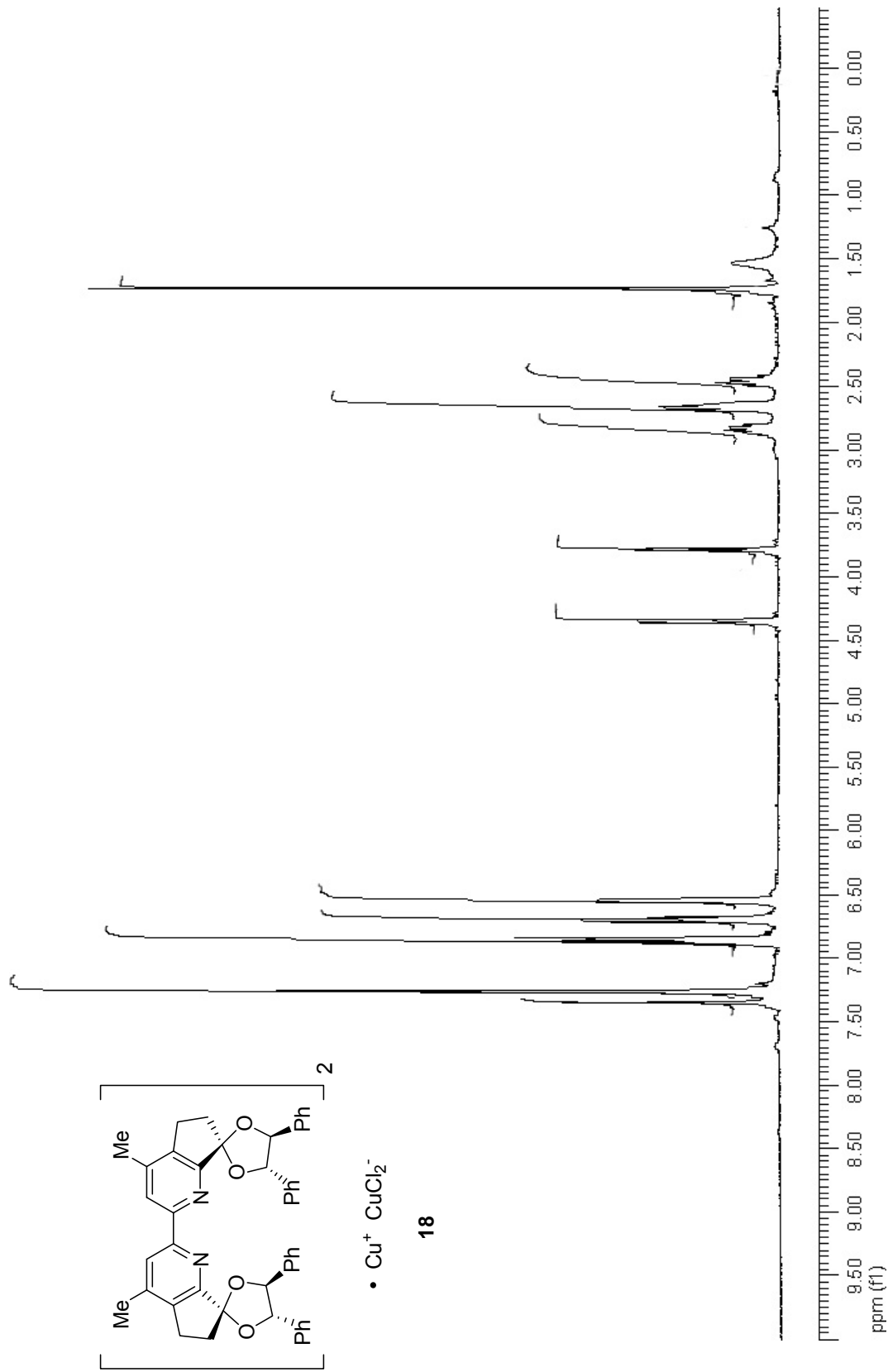
^{13}C NMR spectrum (CDCl_3) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-one **14**.



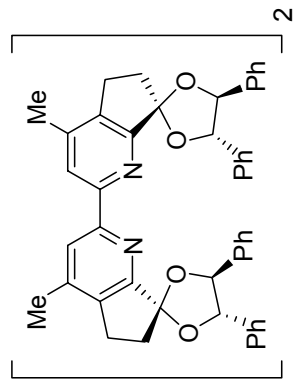
¹H NMR spectrum (CDCl₃) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3-butanediol acetal **15**.



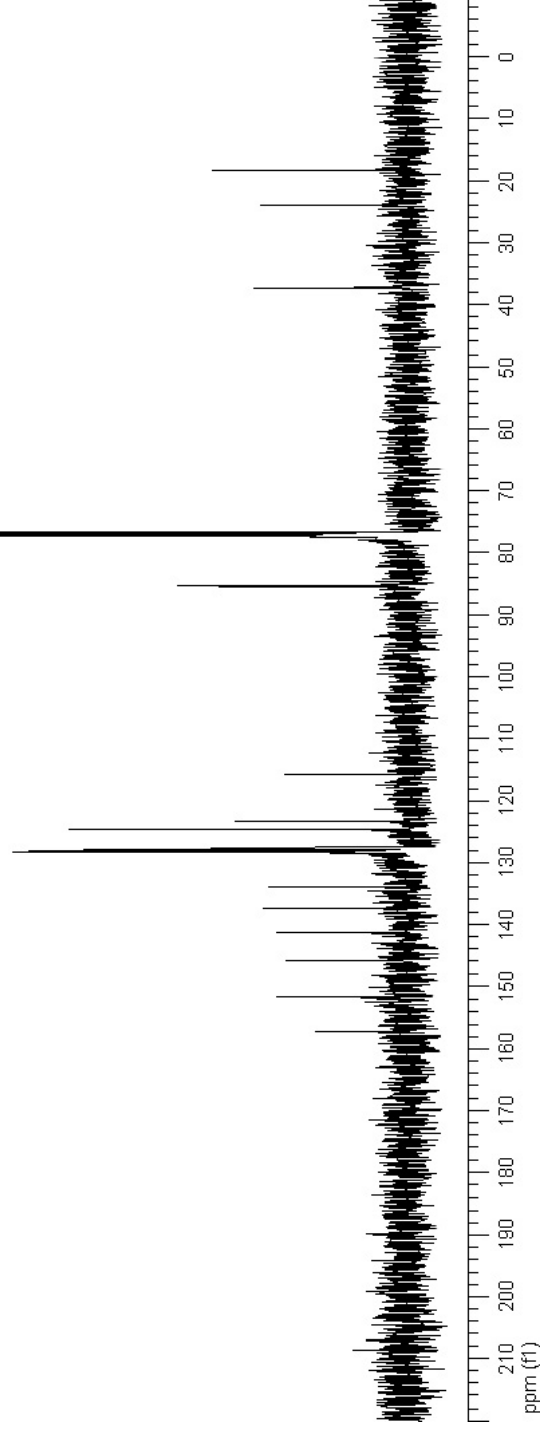
^{13}C NMR spectrum (CDCl₃) of 2-bromo-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-one (2*R*,3*R*)-2,3,3-butenediol acetal **15**.



¹H NMR spectrum (CDCl₃) of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18**.



18



¹³C NMR spectrum (CDCl₃) of the *bis*-2,2'-bipyridyl ligand copper(I) chloride complex **18**.