Supporting Information

for Chiral of Vanadium-based Catalysts for Asymmetric Epoxidation of Allylic Alcohols

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General. Infrared (IR) spectra were measured on a Shimadzu FTIR-9100 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR are expressed in ppm downfield relative to internal standard (tetramethylsilane at 0 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. ^{13}C NMR spectra were measured on a Varian Gemini-300 (75 MHz) spectrometer and are reported in ppm using solvent as the internal standard ($CDCl_3$ at 77.0 ppm). Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector and a capillary column of β-TA (0.25 mm x 25 m) using nitrogen as carrier gas. High performance liquid chromatography (HPLC) analyses were carried out on a Shimadzu LC-10AD instrument with a SPD-M10A UV detector using a chiral stationary column (Daicel, OD-H). Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Reaction products were purified by flash chromatography on

silica gel E. Merck 9385 or silica gel 60 extra pure. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm).

In experiments requiring dry solvents were freshly distilled from calcium hydride. Triethylamine was stored over KOH pellets. VO(acac) and $VO(O^iPr)_3$ were purchased from Wako Pure Chem. Ind., Ltd. and High Purity Chemicals, respectively. Hydroxylamines **3** and triphenylmethylhydroperoxide (TrOOH) were prepared according to the literature procedure.[1,2] Other hydroperoxides and simple chemicals were purchased.

All allylic alcohols and products in Table 1 and 2 have been previously isolated and characterized. References can be found elsewhere.[3]

Preparation of hydroxamic acid ligand 1a.[4] To a stirred solution of *N*-cyclohexylhydroxylamine (127 mg, 1.1 mmol) and Et_3N (0.35 mL, 2.5 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added dropwise a CH_2Cl_2 solution of 2'-methoxy-1,1'-binaphthyl-2-carboxyl chloride, which was prepared from **2**[5] (328 mg, 2.5 mmol) with oxalyl chloride (10 mL, 0.1 M, 1 mmol). After being stirred for 30 min, the reaction mixture was poured into 1N HCl (10 mL) and extracted with Et_2O by three thimes. The combined organic phase was washed with water and brine, and dried over Na_2SO_4. Evaporation of solvents followed by chromatographic purification (EtOAc / hexane = 1 : 2) gave the title compound as a powdered solid (359 mg, 84%). Hydroxamic acid **1a** can be further purified by recrystallization from chloroform / hexane: R_f = 0.37 (EtOAc / hexane = 1 : 1, $FeCl_3$ stain); $[\alpha]_D^{27}$ +50.3° (c 0.59, $CHCl_3$); ^{1}H NMR (THF-d_8) δ 8.44 (1H, br s, OH), 7.92-7.98 (3H, m, Ar-H), 7.79 (1H, d, J = 8.1 Hz, Ar-H), 7.43-7.54 (3H, m, Ar-H), 7.12-7.30 (5H, m, Ar-H), 3.74 (3H, s, CH_3), 3.51 (1H, br s, N-CH), 1.00-1.63 (10H, m, $5CH_2$); ^{13}C NMR ($CDCl_3$) δ 168.7 (C=O), 164.4 (C=O), 154.8 (2-Ar), 154.0 (2-Ar), 135.8, 134.1, 133.7, 133.2, 132.7, 132.6, 132.5, 131.8, 130.4, 130.3, 129.5, 128.6, 128.3, 128.2, 128.0, 127.6, 126.9, 126.7, 126.5, 126.4, 126.2, 125.9, 124.5, 124.2, 123.4, 121.2, 119.1, 113.8 (2'-Ar),

112.8 (2'-Ar), 77.2, 58.4, 57.8, 56.2, 53.7, 29.7 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 25.1 (CH_2), 25.0 (CH_2), 24.7 (CH_2); IR (KBr) 3100, 2856, 1625, 1599, 1558, 1508, 1468, 1310, 1250, 810, 752 cm^{-1}; Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 78.91; H, 6.51; N, 3.39.

Hydroxamic Acid 1b.[4] **1b** was prepared in the same manner described above (72% yield): R_f = 0.39 (EtOAc / hexane = 1 : 1, $FeCl_3$ stain); $[\alpha]_D^{27}$ +131.8° (c 0.50, $CHCl_3$); ^1H NMR (THF-d^8) δ 8.82, 8.11 (1H, br s, OH), 7.91-8.02 (3H, m, Ar-H), 7.84 (1H, d, J = 8.4 Hz, Ar-H), 7.57 (1H, br s, Ar-H), 7.42-7.47 (2H, m, Ar-H), 7.13-7.28 (9H, m, Ar-H), 6.82 (1H, br s, Ar-H), 4.68 (1H, d, J = 15.0 Hz, NCH_2), 4.43 (1H, br s, NCH_2), 3.59 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.4 (C=O), 165.5 (C=O), 154.1 (2-Ar), 153.7 (2-Ar), 135.5, 134.9, 134.8, 133.9, 133.7, 133.6, 133.2, 132.4, 131.1, 130.2, 130.0, 129.8, 129.1, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 127.1, 126.9, 126.8, 126.7, 126.4, 126.2, 125.8, 125.6, 125.3, 124.2, 123.5, 123.3, 120.1, 118.7, 113.4 (2'-Ar), 112.5 (2'-Ar), 56.5 (OCH_3), 55.5 (OCH_3), 53.0 ($PhCH_2$), 50.4 ($PhCH_2$); IR (KBr) 3061, 3010, 1624, 1598, 1510, 1433, 1356, 1250, 812, 750 cm^{-1}; Anal. Calcd for $C_{29}H_{23}NO_3$: C, 80.35; H, 5.35; N, 3.23. Found: C, 80.08; H, 5.52; N, 3.25.

Hydroxamic Acid 1c.[4] **1c** was also prepared in the manner described for **1a**. In this case **1c** was obtained in 70% yield together with a significant amount of *O*-acylated by-product **1c'** (22% yield). Rearrangement of **1c'** to **1c** was carried out by treatment of *t*-BuLi (2 equivalents) in THF while raising the temperature from –78 °C to 0 °C. Acidic work-up and purification of column chromatography on silica gel furnished **1c** in 86% yield: R_f = 0.38 (EtOAc / hexane = 1 : 2, $FeCl_3$ stain); $[\alpha]_D^{27}$ +121.5° (c 1.52, $CHCl_3$); ^1H NMR (C_6D_6) δ 8.40 (1H, br s, OH), 7.70-7.74 (4H, m, Ar-H), 7.62 (2H, d, J = 8.4 Hz, Ar-H), 7.36-7.48 (4H, m, Ar-H), 6.89-7.24 (12H, m, Ar-H), 6.68 (1H, d, J = 9.0 Hz, Ar-H), 2.59 (3H, br s, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.5 (C=O), 166.7 (C=O), 154.0 (2-Ar), 153.6 (2-Ar), 138.3, 135.2, 134.1,

133.9, 133.5, 133.3, 133.0, 132.5, 131.4, 130.1, 129.9, 129.7, 129.3, 128.6, 128.5, 128.2, 127.7, 127.6, 127.4, 127.1, 126.8, 126.6, 126.3, 124.9, 124.5, 123.7, 123.5, 120.2, 118.4, 113.3 (2'-Ar), 122.3 (2'-Ar), 66.4 (Ph-*C*H), 61.3 (Ph-*C*H), 56.5 (OCH_3), 54.8 (OCH_3); IR (KBr) 3300, 3025, 1650, 1625, 1598, 1503, 1460, 1250, 708, 650 cm^{-1}; Anal. Calcd for $C_{35}H_{27}NO_3$: C, 82.49; H, 5.34; N, 2.75. Found: C, 82.49; H, 5.41; N, 2.81. ***O*-Acylated By-Product 1c'[4]:** R_f = 0.57 (EtOAc / hexane = 1 : 2); $[\alpha]_D^{28}$ +12.0° (c 1.27, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.85-7.95 (5H, m, Ar-H), 7.68 (1H, d, *J* = 3.6 Hz, NH), 7.49-7.55 (1H, m, Ar-H), 7.14-7.35 (13H, m, Ar-H), 6.90 (1H, d, *J* = 8.4 Hz, Ar-H), 4.51 (1H, d, *J* = 3.6 Hz, CH), 3.56 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.0 (C=O), 154.2, 139.7, 139.6, 137.0, 135.1, 133.7, 132.7, 129.6, 128.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6, 125.7, 124.6, 123.5, 120.9 113.4 (2'-Ar), 68.6 (N-CH), 56.4 (CH_3); IR (KBr) 3061, 1728, 1622, 1595, 1510, 1460, 1335, 1271, 1252, 828, 754 cm^{-1}; Anal. Calcd for $C_{35}H_{27}NO_3$: C, 82.49; H, 5.34, N, 2.75. Found: C, 82.28; H, 5.49; N, 2.81.

General Procedure for the Asymmetric Epoxidation of Allylic Alcohols. To a solution of the chiral vanadium catalyst (9.8 mM, 12.7 μmol) readily prepared from **1** (19.1 μmol) and $VO(OPr^i)_3$ (3.0 μL, 12.7 μmol) in dry toluene (25°C, 1h) were added an allylic alcohol (0.254 mmol) and tritylhydroperoxide (105 mg, 0.381 mmol) at –20°C under argon atmosphere. After stirring the solution for 2-7 days at this temperature, the reaction was quenched by addition of *sat.* Na_2SO_3 aq (2 mL). Extraction of the product with ether, evaporation of solvents and chromatographic purification on silica gel afforded the corresponding 2,3-epoxy alcohol in a yield of 14-96%.

References and Notes

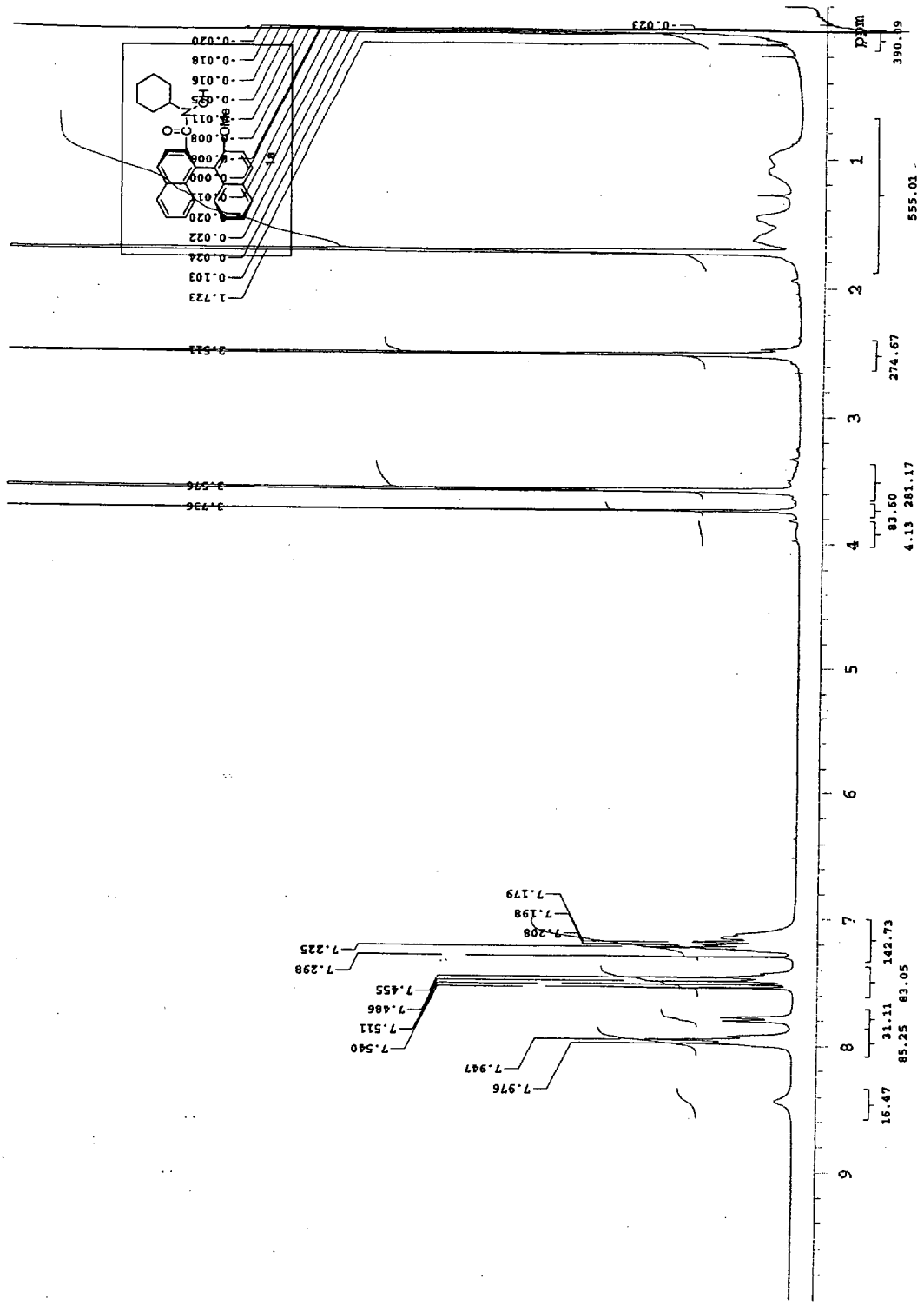
(1) Bissing, D. E.; Matuszak, C. A.; McEwen, W. E. *J. Am. Chem. Soc.* **1964**, *86*, 3824.

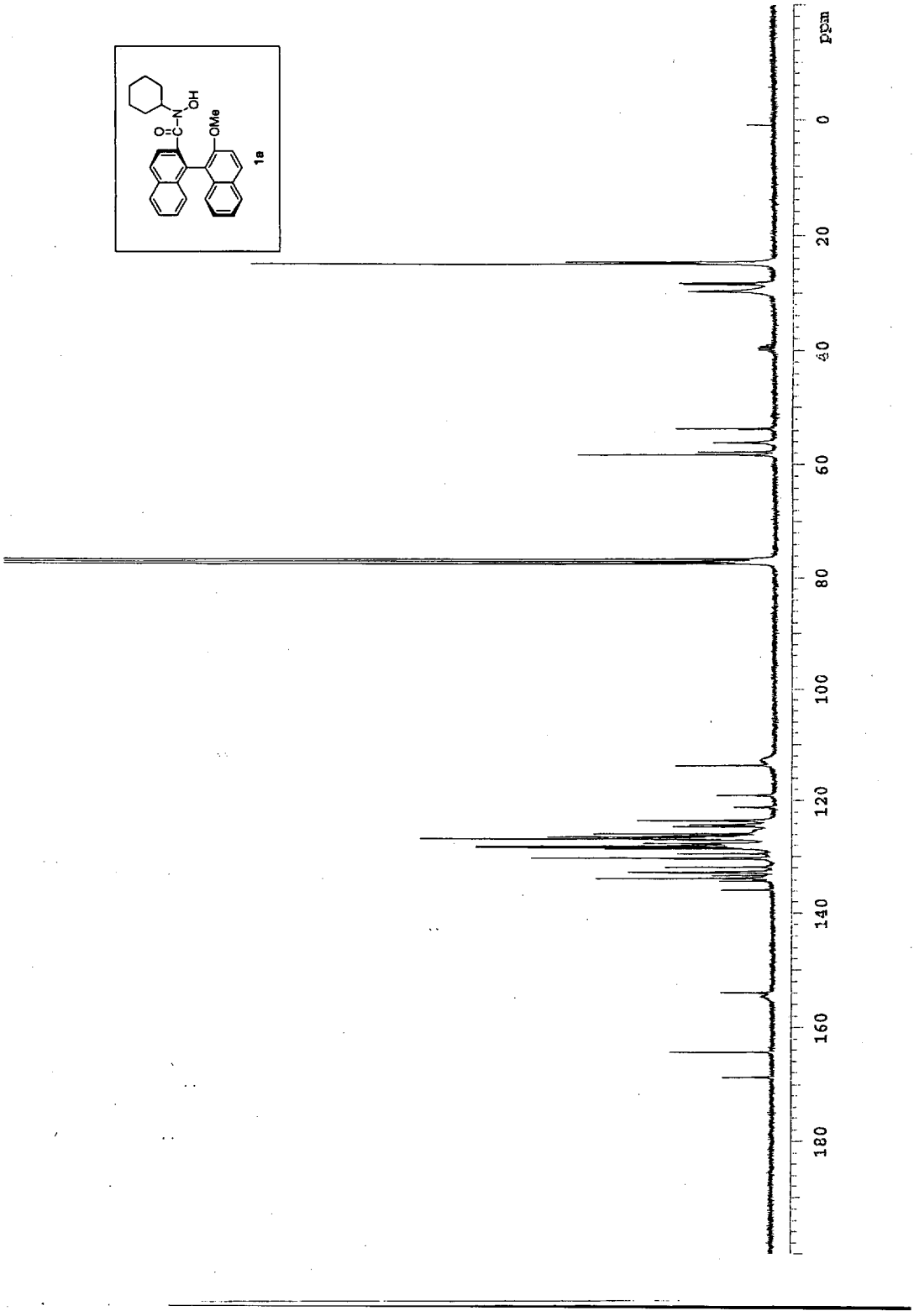
(2) Kawase, M.; Kikugawa, Y. *J. Chem. Soc., Perkin Trans. I* **1979**, 643.

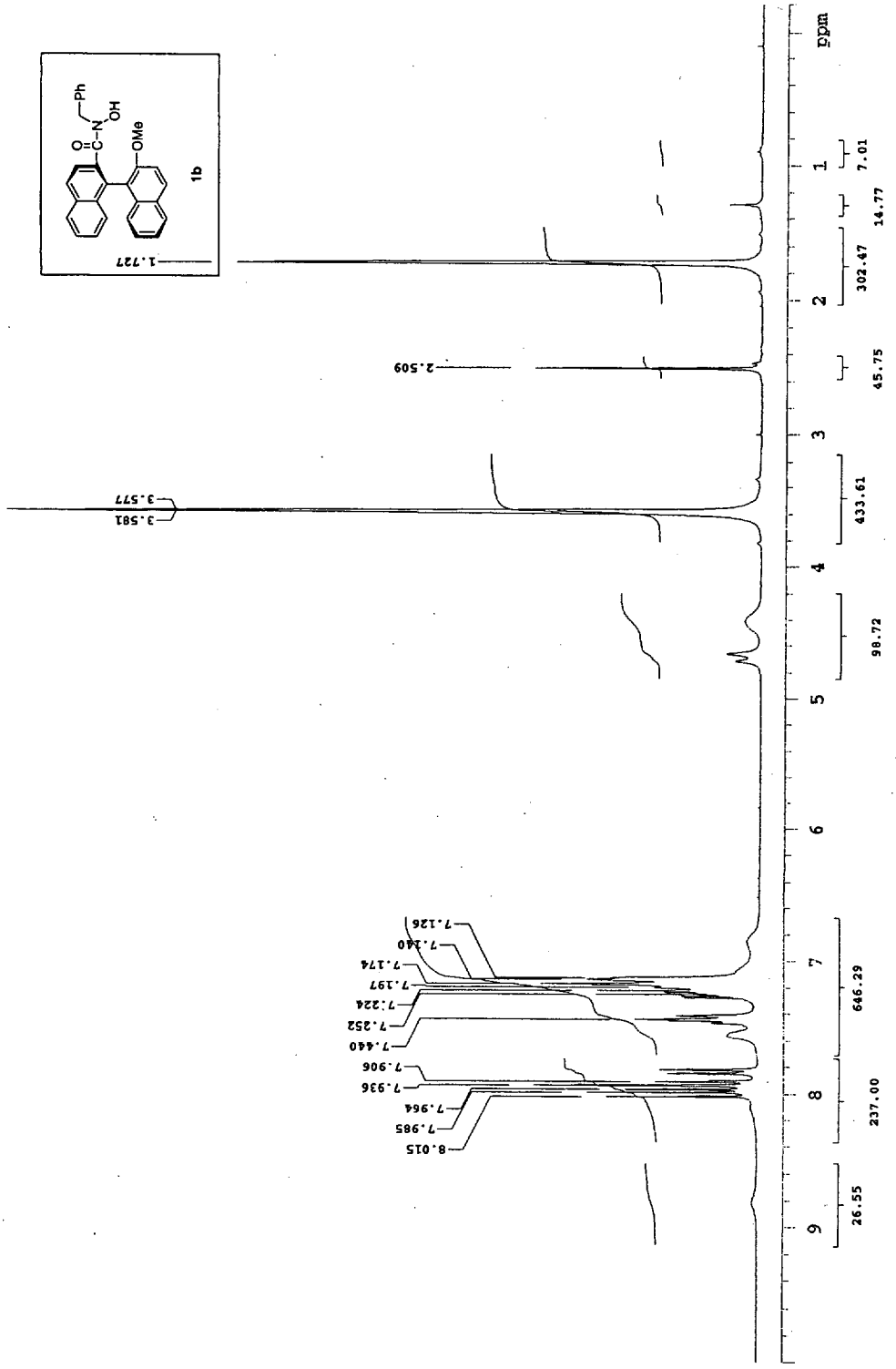
(3) Katsuki, T; Martin, V. S. *Org. React.***1996**, *48*, 1-299.

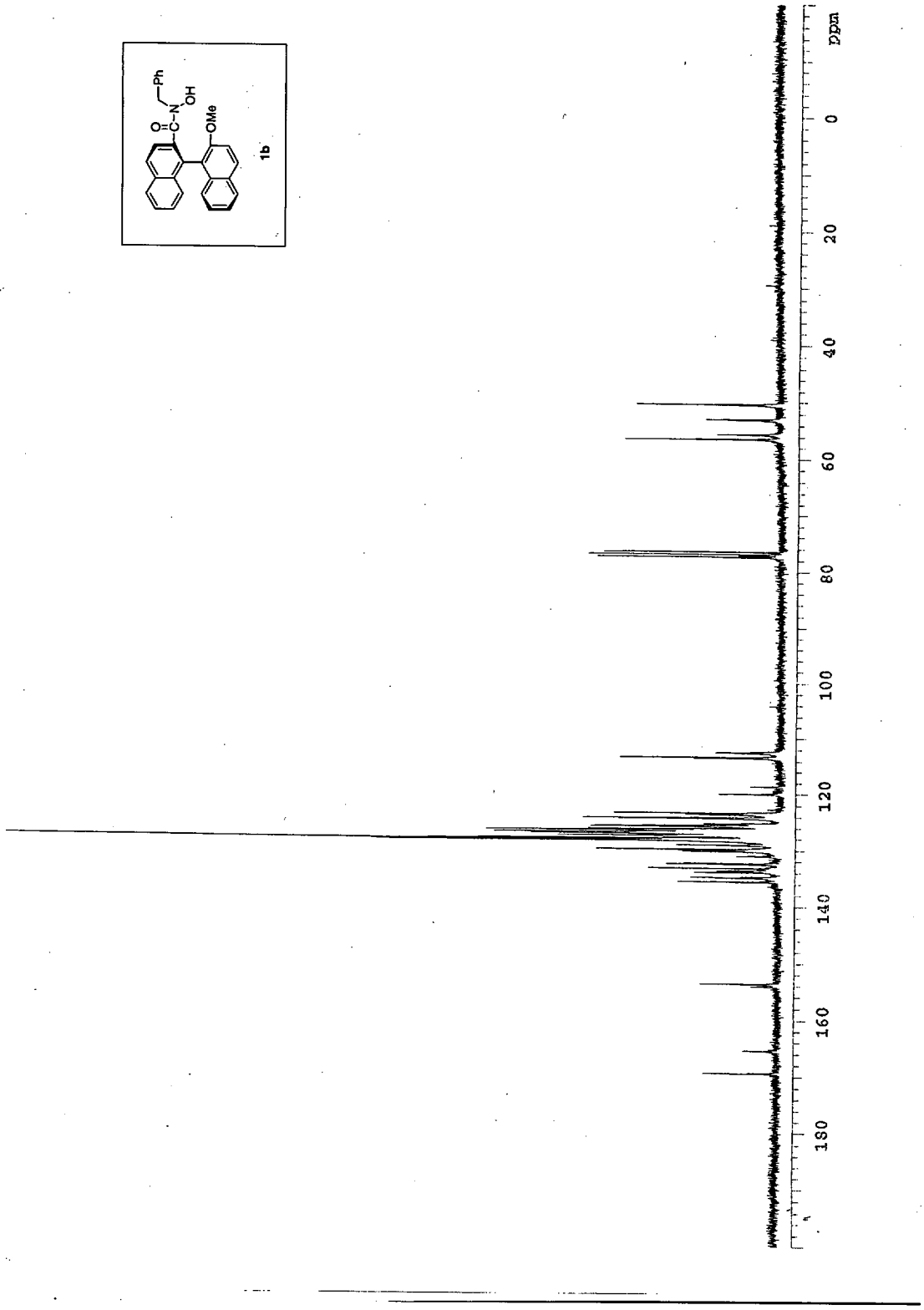
(4) Our attempt to measure ^{1}H and ^{13}C NMR spectra of **1a-1c** with varying temperature and solvent speculated the existence of at least two conformers of each hydroxamic acid **1** in solution state. Therefore, we tried to determined a solid state structure of **1c** by following X-ray analysis.

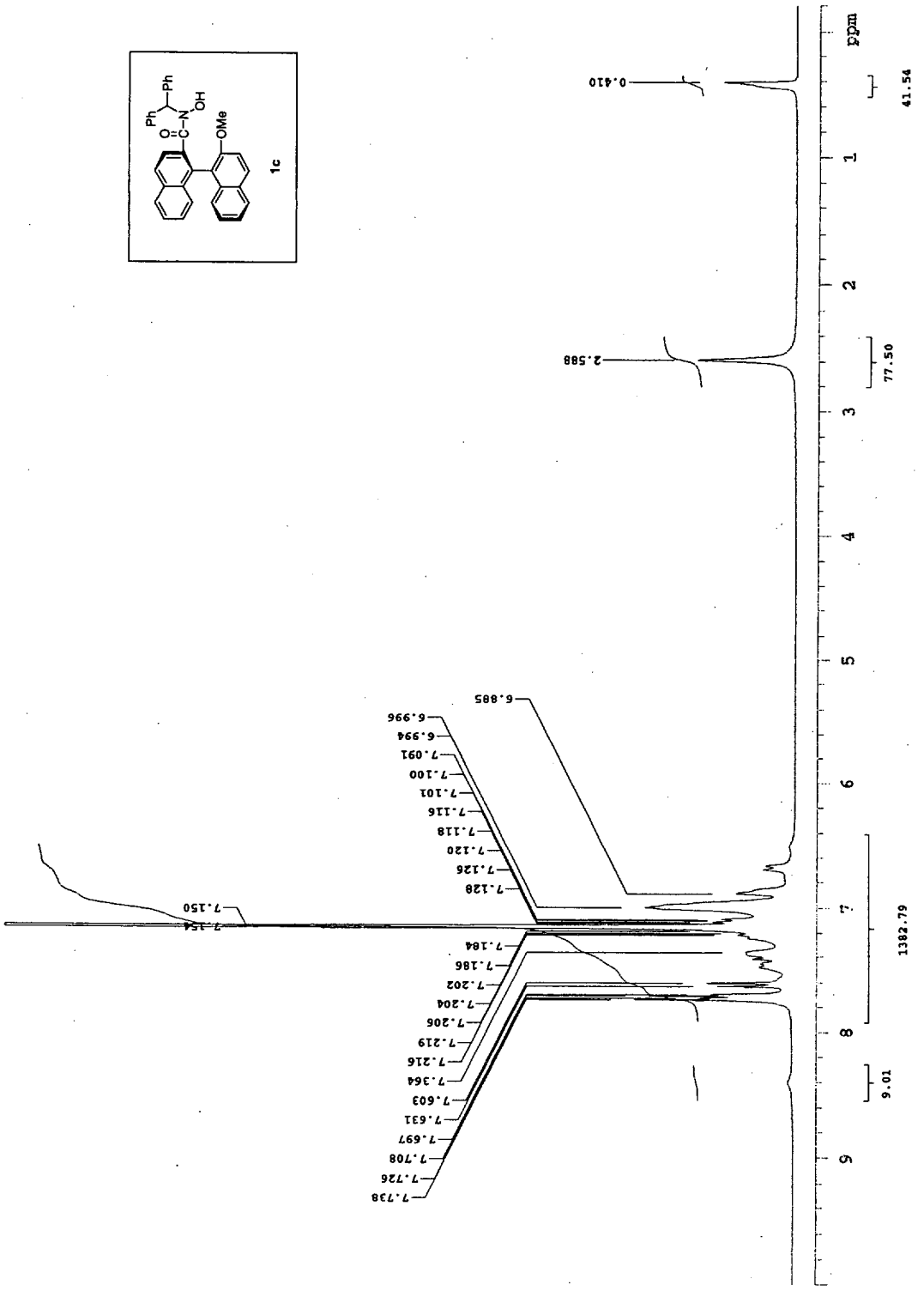
(5) (a) Miyano, S.; Okada, S.; Suzuki, T.; Handa, S.; Hashimoto, H *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2044. (b) Miyano, S.; Hotta, H.; Takeda, M.; Kabuto, C.; Hashimoto, H *Bull. Chem. Soc. Jpn.* **1989**, *52*, 1528.

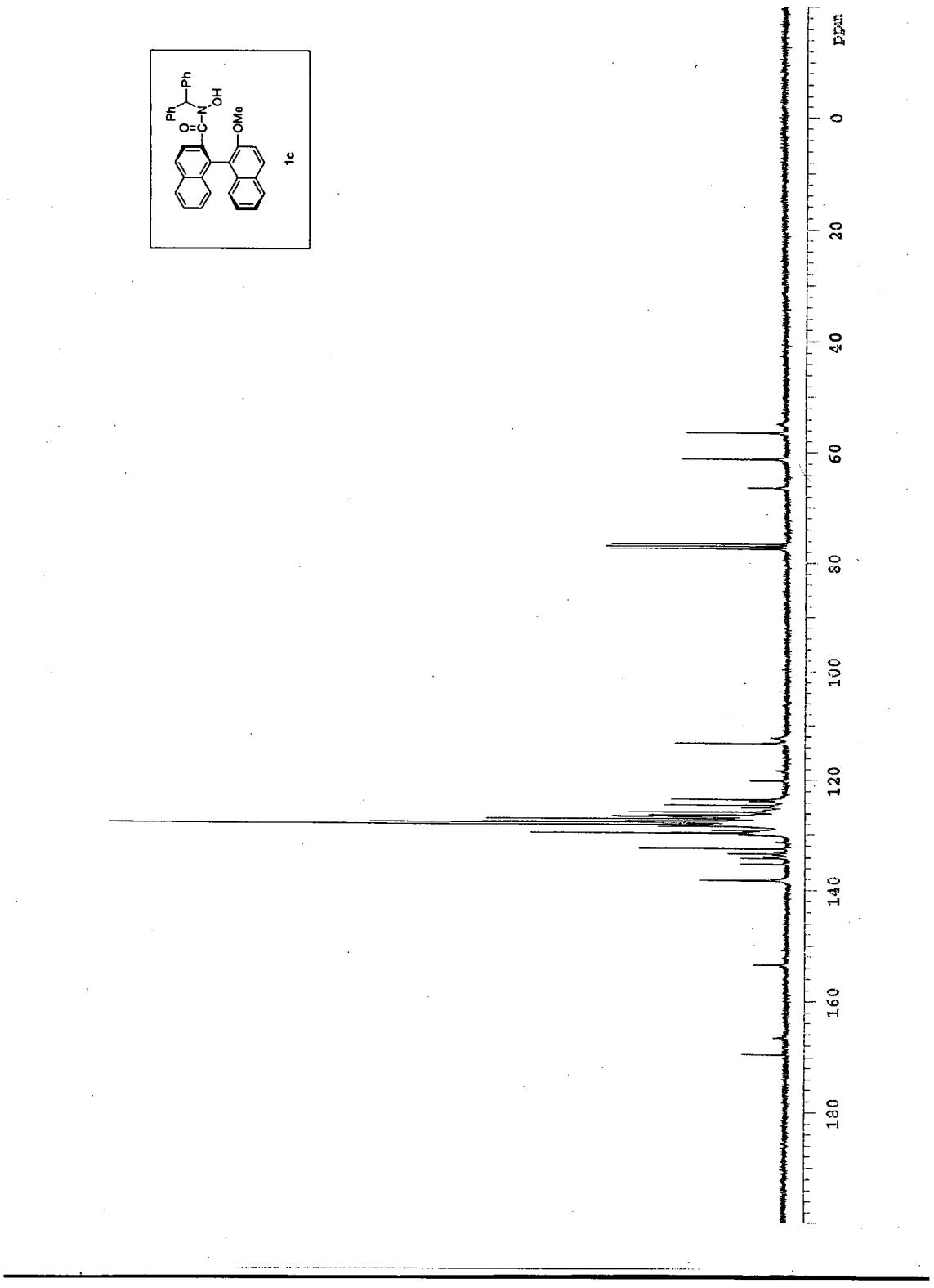


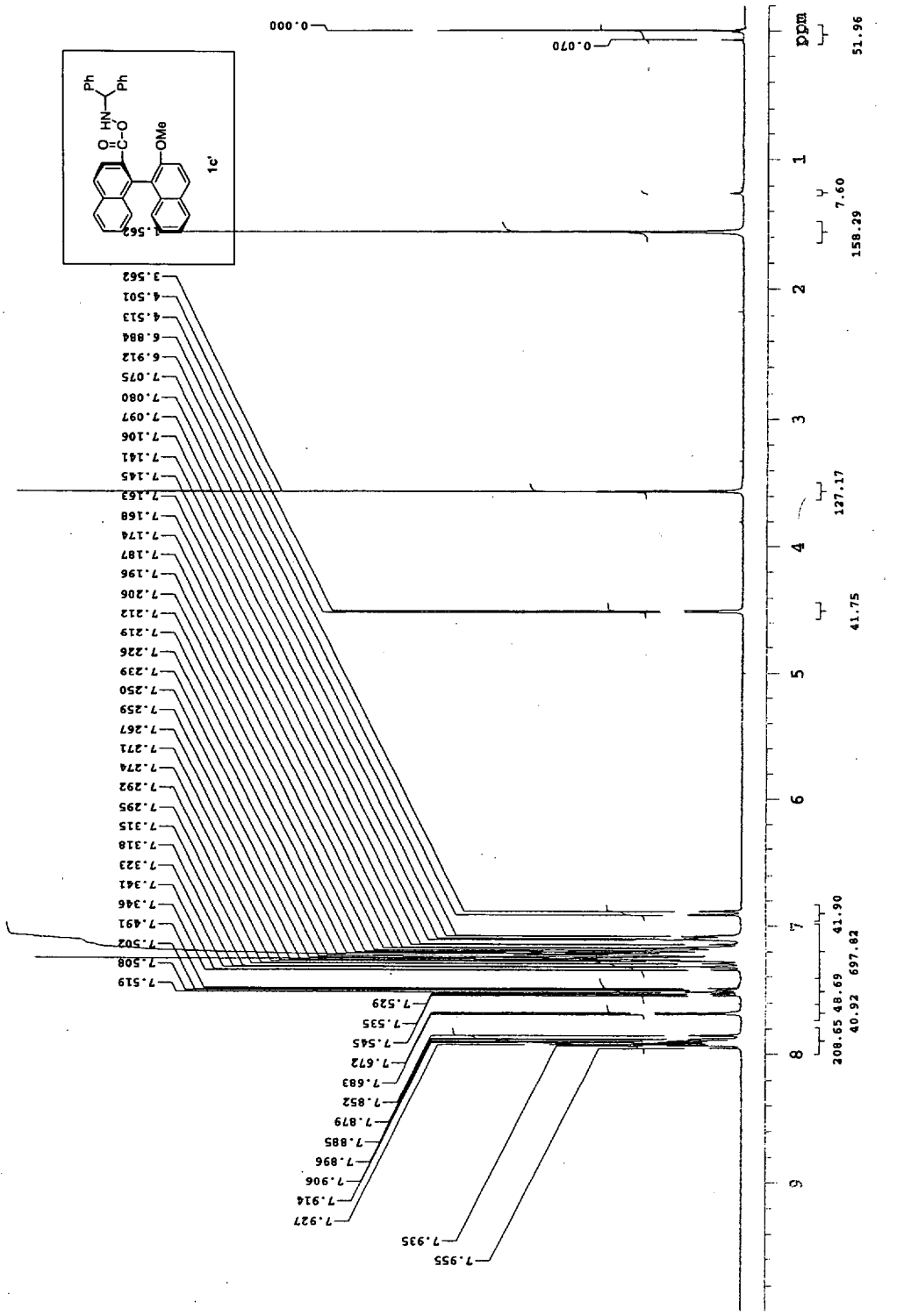


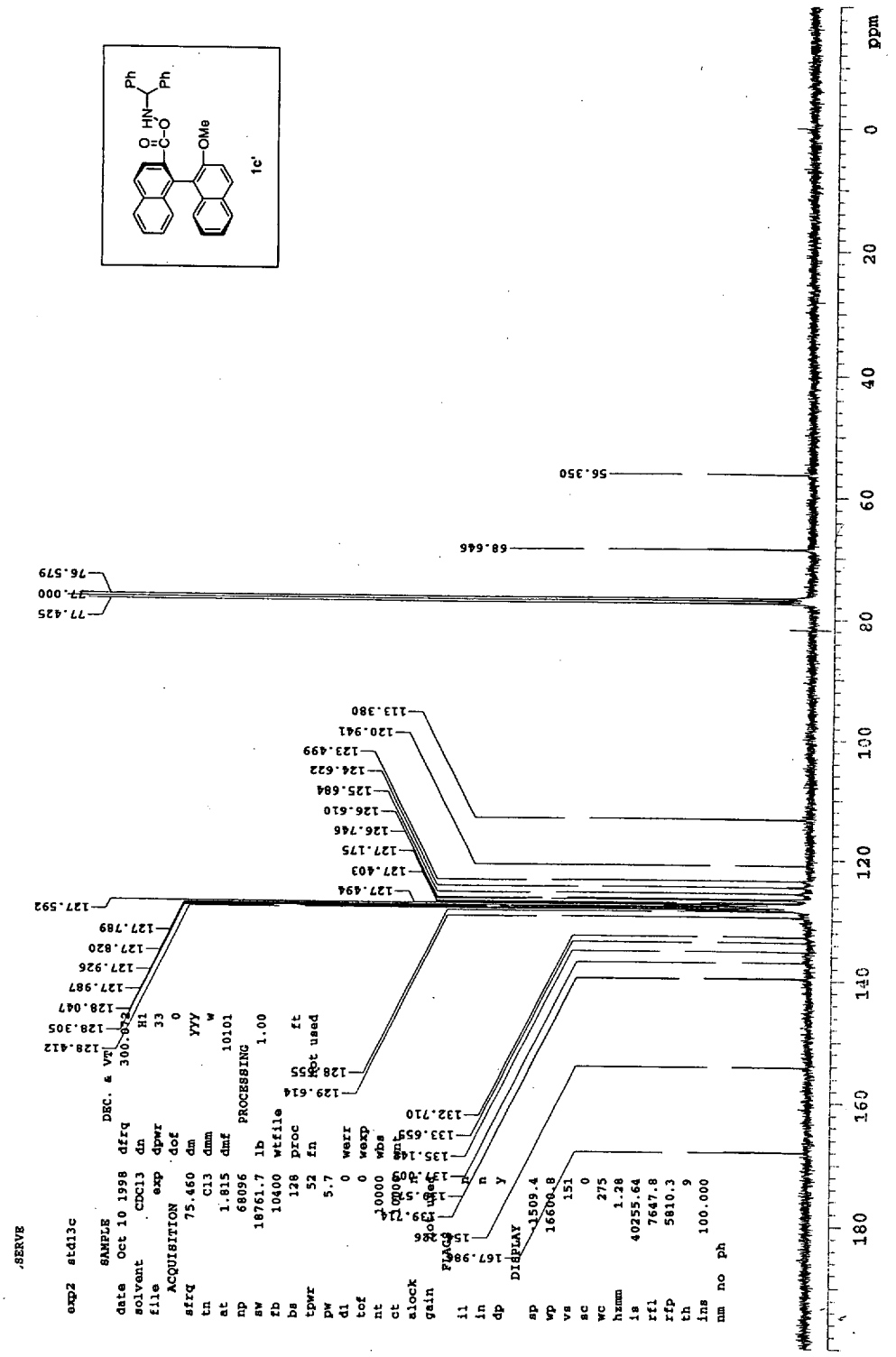












X-ray diffraction structural analysis of **1c**

The study of the structure of **1c** was undertaken to establish its three dimensional structure. Geometries are tabulated below. All Diagrams and calculations were performed using maXus (MacScience, Japan).

EXPERIMENTAL DETAILS

A. *Crystal Data*	
Formula	$C_{35}H_{27}N_1O_3$
Formula Weight	Mr = 509.60
Crystal Color, Habit	colorless, platy
Crystal Dimensions	1.38 x 0.63 x 0.125 mm
Temperature	298 *K*
Crystal System	Monoclinic
Space Group	$P2_1$
Unit Cell Dimensions	*a* = 12.4420 (13) Å
	b = 8.2220 (4) Å
	c = 13.6680 (14) Å
	β = 102.624(4) °
	V = 1364.4 (2) Å^3
Z value	2
D*x*	1.240 Mgm^{-3}
Absorption Coefficient,μ	0.0785 mm^{-1}
F(000)	536

B. *Data Collection and Reduction*	
Diffractometer	DIP Image plate
Radiation	Mo *K*α
	λ = 0.7107 Å
θ range for data collection	1-28 °
θ_{max}	25.45 °
Limiting indices	$0 \leq h \leq 15$, $0 \leq k \leq 10$, $-17 \leq l \leq 16$
Measured reflections	2919
Independent reflections	2919
Observed reflections	2193

Absorption Collection	none

C. *Solution and Refinement*

Structure Solution	Direct Methods (SIR)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weight	$\omega = 1.0/[\sigma^2(F_o) + 0.03.\ F_o{}^2]$
No. of Reflections	2193
No. of Parameters	459
Residuals: *R; ωR*	0.036; 0.038
S	0.916
$(\Delta/\sigma)_{max}$	0.1407
$\Delta\rho_{max}$	0.15 e Å^{-3}
$\Delta\rho_{min}$	-0.13 e Å^{-3}
Extinction Correction	none
All parameters of H atoms refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

atm	*x*	*y*	*z*	U_{eq}
O(1)	0.89530(7)	0.48000	0.03780(7)	0.0708(6)
O(2)	0.71340(7)	0.1762(2)	0.08160(7)	0.0710(5)
O(3)	0.82570(9)	0.6592(2)	0.19330(8)	0.0799(6)
N(4)	0.80070(8)	0.3804(2)	0.02070(8)	0.0644(6)
C(5)	0.87060(9)	0.3510(2)	0.27240(9)	0.0530(6)
C(6)	0.6790(1)	0.5826(2)	- 0.08230(9)	0.0579(7)
C(7)	0.7646(1)	0.4383(2)	0.27600(9)	0.0579(7)
C(8)	0.8829(1)	0.2724(2)	0.18580(9)	0.0543(7)
C(9)	0.6830(1)	0.3637(2)	0.32070(9)	0.0635(7)
C(10)	0.7918(1)	0.2707(2)	0.09250(9)	0.0563(7)
C(11)	0.9599(1)	0.3477(2)	0.35950(9)	0.0542(6)
C(12)	0.7475(1)	0.7090(2)	- 0.0998(1)	0.0671(8)
C(13)	0.9824(1)	0.1884(2)	0.1823(1)	0.0659(8)
C(14)	0.7592(1)	0.3486(2)	- 0.16600(9)	0.0609(7)
C(15)	1.06010(9)	0.2663(2)	0.35490(9)	0.0571(7)
C(16)	0.9538(1)	0.4232(2)	0.4517(1)	0.0680(8)
C(17)	0.5734(2)	0.6115(3)	0.2904(1)	0.092(1)
C(18)	0.6934(1)	0.2021(2)	0.3571(1)	0.0736(9)
C(19)	1.0681(1)	0.1858(2)	0.2651(1)	0.0683(8)
C(20)	1.1493(1)	0.2679(2)	0.4406(1)	0.0689(9)
C(21)	0.5722(1)	0.6216(2)	- 0.0748(1)	0.0760(9)
C(22)	0.7189(1)	0.4069(2)	- 0.07340(9)	0.0592(7)
C(23)	0.7455(1)	0.5942(2)	0.2378(1)	0.0641(7)
C(24)	0.6963(1)	0.3818(2)	- 0.2615(1)	0.0707(9)
C(25)	0.5867(1)	0.4523(2)	0.3290(1)	0.0788(9)
C(26)	0.6489(2)	0.6821(2)	0.2452(1)	0.082(1)
C(27)	1.0412(1)	0.4198(2)	0.5339(1)	0.0776(9)
C(28)	0.7261(2)	0.3208(3)	- 0.3467(1)	0.088(1)
C(29)	0.6052(2)	0.9050(3)	- 0.0976(1)	0.085(1)
C(30)	0.7103(2)	0.8696(2)	- 0.1062(1)	0.0775(9)
C(31)	0.8539(1)	0.2538(2)	- 0.1582(1)	0.0788(9)
C(32)	1.1402(1)	0.3419(2)	0.5281(1)	0.0743(9)
C(33)	0.5367(2)	0.7837(3)	- 0.0830(1)	0.091(1)

Table 1. (continued)

C(34)	0.5057(1)	0.3721(3)	0.3728(1)	0.098(1)
C(35)	0.6137(1)	0.1310(3)	0.3992(1)	0.092(1)
C(36)	0.5184(2)	0.2168(4)	0.4062(2)	0.104(1)
C(37)	0.8827(2)	0.1923(3)	- 0.2439(2)	0.094(1)
C(38)	0.8193(2)	0.2254(3)	- 0.3382(2)	0.095(1)
C(39)	0.8185(3)	0.8303(2)	0.1678(2)	0.110(1)
H(22)	0.653(1)	0.331(2)	- 0.064(1)	0.050(4)
H(24)	0.630(1)	0.449(2)	- 0.2700(9)	0.035(4)
H(16)	0.887(1)	0.465(2)	0.4620(9)	0.028(3)
H(18)	0.764(1)	0.139(2)	0.351(1)	0.052(4)
H(12)	0.828(1)	0.674(2)	- 0.108(1)	0.050(4)
H(13)	0.991(1)	0.139(2)	0.116(1)	0.053(4)
H(27)	1.028(1)	0.470(2)	0.601(1)	0.058(4)
H(32)	1.206(1)	0.337(2)	0.592(1)	0.065(5)
H(39A)	0.805(1)	0.888(2)	0.234(2)	0.084(6)
H(38)	0.844(1)	0.181(3)	- 0.409(2)	0.094(6)
H(34)	0.437(1)	0.430(2)	0.378(1)	0.069(5)
H(20)	1.214(1)	0.203(2)	0.433(1)	0.049(4)
H(39B)	0.888(2)	0.852(2)	0.142(1)	0.074(7)
H(21)	0.523(1)	0.534(2)	- 0.069(1)	0.062(5)
H(28)	0.676(1)	0.332(2)	- 0.415(1)	0.083(6)
H(19)	1.140(1)	0.124(2)	0.264(1)	0.073(5)
H(37)	0.960(2)	0.120(3)	- 0.229(1)	0.092(6)
H(17)	0.497(1)	0.684(2)	0.295(1)	0.089(6)
H(31)	0.899(1)	0.229(2)	- 0.086(1)	0.065(5)
H(26)	0.648(1)	0.789(3)	0.210(1)	0.080(6)
H(35)	0.628(1)	0.012(3)	0.429(1)	0.089(6)
H(36)	0.454(2)	0.168(3)	0.437(1)	0.104(7)
H(29)	0.576(1)	1.039(3)	- 0.106(1)	0.091(6)
H(30)	0.763(2)	0.951(3)	- 0.120(1)	0.101(7)
H(39C)	0.756(2)	0.848(3)	0.109(2)	0.120(9)
H(33)	0.462(1)	0.807(2)	- 0.079(1)	0.075(6)
H(1)	0.878(2)	0.559(3)	0.092(2)	0.116(8)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2. *Anisotropic thermal parameters* ($Å^2$)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
O(1)	0.0596(5)	0.0759(6)		0.0722(6)	-0.0189(5)	0.0042(5)	0.0108(5)
O(2)	0.0683(6)	0.0661(5)		0.0718(6)	-0.0104(5)	0.0109(5)	0.0066(5)
O(3)	0.0968(7)	0.0506(5)		0.0869(7)	0.0083(5)	0.0076(6)	0.0071(5)
N(4)	0.0633(6)	0.0706(6)		0.0543(6)	-0.0177(5)	0.0029(5)	0.0088(5)
C(5)	0.0563(7)	0.0489(6)		0.0524(7)	0.0051(5)	0.0129(6)	-0.0011(5)
C(6)	0.0541(7)	0.0695(7)		0.0489(7)	-0.0023(6)	0.0124(6)	-0.0005(6)
C(7)	0.0612(8)	0.0561(7)		0.0522(7)	0.0144(6)	0.0071(6)	-0.0090(6)
C(8)	0.0568(7)	0.0510(6)		0.0534(7)	0.0037(6)	0.0145(6)	0.0017(6)
C(9)	0.0549(7)	0.0783(9)		0.0546(7)	0.0080(7)	0.0091(6)	-0.0174(7)
C(10)	0.0594(7)	0.0551(6)		0.0518(7)	0.0040(6)	0.0170(6)	-0.0047(6)
C(11)	0.0567(7)	0.0498(6)		0.0531(7)	0.0032(5)	0.0120(6)	0.0028(6)
C(12)	0.0647(8)	0.0674(8)		0.0691(9)	-0.0030(7)	0.0214(7)	0.0021(7)
C(13)	0.0660(8)	0.0747(8)		0.0573(8)	0.0141(7)	0.0234(7)	0.0027(7)
C(14)	0.0628(7)	0.0608(7)		0.0566(8)	-0.0145(6)	0.0137(6)	-0.0015(6)
C(15)	0.0535(7)	0.0563(7)		0.0602(7)	0.0034(6)	0.0136(6)	0.0113(6)
C(16)	0.0711(9)	0.0667(8)		0.0613(9)	0.0113(7)	0.0088(8)	-0.0087(7)
C(17)	0.0735(10)	0.0968(12)		0.0945(12)	0.0298(10)	0.0045(9)	-0.0258(10)
C(18)	0.0675(9)	0.0777(9)		0.0746(9)	0.0046(7)	0.0220(8)	-0.0047(8)
C(19)	0.0599(8)	0.0782(9)		0.0636(9)	0.0172(7)	0.0197(7)	0.0094(7)
C(20)	0.0599(8)	0.0678(8)		0.0756(10)	0.0058(7)	0.0087(8)	0.0149(8)
C(21)	0.0603(9)	0.0928(10)		0.0724(10)	-0.0049(8)	0.0174(7)	-0.0050(8)
C(22)	0.0588(7)	0.0647(7)		0.0509(7)	-0.0104(6)	0.0090(6)	0.0022(6)
C(23)	0.0705(8)	0.0561(7)		0.0611(8)	0.0105(6)	0.0041(7)	-0.0085(6)
C(24)	0.0721(9)	0.0788(9)		0.0578(8)	-0.0086(8)	0.0090(7)	-0.0062(7)
C(25)	0.0602(9)	0.1018(11)		0.0706(9)	0.0165(8)	0.0073(7)	-0.0248(9)
C(26)	0.0883(11)	0.0681(9)		0.0823(11)	0.0307(9)	-0.0089(9)	-0.0144(9)
C(27)	0.0896(11)	0.0756(9)		0.0609(9)	0.0072(8)	0.0033(8)	-0.0089(7)
C(28)	0.1056(13)	0.0955(11)		0.0607(10)	-0.0208(10)	0.0123(9)	-0.0157(8)
C(29)	0.0867(12)	0.0879(11)		0.0777(10)	0.0179(10)	0.0012(9)	-0.0074(9)
C(30)	0.0860(11)	0.0657(9)		0.0763(10)	-0.0032(8)	0.0116(8)	0.0015(7)
C(31)	0.0841(10)	0.0759(9)		0.0719(10)	0.0038(8)	0.0184(9)	-0.0075(8)
C(32)	0.0752(10)	0.0698(8)		0.0692(10)	0.0042(7)	0.0005(8)	0.0068(8)
C(33)	0.0767(10)	0.1027(13)		0.0888(13)	0.0143(11)	0.0178(9)	-0.0112(10)

Table 2. (continued)

C(34)	0.0548(10)	0.1461(19)	0.0871(12)	0.0060(11)	0.0204(8)	-0.0359(13)
C(35)	0.0771(11)	0.1120(13)	0.0832(11)	-0.0076(10)	0.0310(9)	-0.0031(10)
C(36)	0.0784(12)	0.1327(18)	0.0946(13)	-0.0135(12)	0.0302(10)	-0.0180(13)
C(37)	0.0912(12)	0.0944(12)	0.0967(13)	0.0059(10)	0.0295(11)	-0.0174(10)
C(38)	0.1028(13)	0.0962(12)	0.0865(13)	-0.0175(10)	0.0318(11)	-0.0286(10)
C(39)	0.1934(24)	0.0518(8)	0.0886(14)	0.0139(11)	0.0441(16)	0.0068(8)

Table 3. *Bond distances* (Å)

O1	N4	1.411(2)	O2	C10	1.230(2)
O3	C23	1.384(2)	O3	C39	1.447(3)
N4	C10	1.355(2)	N4	C22	1.472(2)
C5	C7	1.512(2)	C5	C8	1.386(2)
C5	C11	1.440(2)	C6	C12	1.397(3)
C6	C21	1.392(2)	C6	C22	1.524(3)
C7	C9	1.432(2)	C7	C23	1.385(3)
C8	C10	1.510(2)	C8	C13	1.428(2)
C9	C18	1.415(3)	C9	C25	1.428(3)
C11	C15	1.428(2)	C11	C16	1.422(2)
C12	C30	1.396(3)	C13	C19	1.375(2)
C14	C22	1.536(2)	C14	C24	1.394(2)
C14	C31	1.397(3)	C15	C19	1.417(2)
C15	C20	1.427(2)	C16	C27	1.383(3)
C17	C25	1.407(3)	C17	C26	1.362(3)
C18	C35	1.380(3)	C20	C32	1.368(3)
C21	C33	1.401(3)	C23	C26	1.425(3)
C24	C28	1.391(3)	C25	C34	1.440(3)
C27	C32	1.406(3)	C28	C38	1.384(3)
C29	C30	1.370(3)	C29	C33	1.355(3)
C31	C37	1.393(3)	C34	C36	1.354(4)
C35	C36	1.401(3)	C37	C38	1.383(3)
O1	H1	1.04(3)	C12	H12	1.08(2)
C13	H13	1.01(2)	C16	H16	0.93(2)
C17	H17	1.14(2)	C18	H18	1.04(2)
C19	H19	1.03(2)	C20	H20	0.98(2)
C21	H21	0.96(2)	C22	H22	1.06(2)
C24	H24	0.98(2)	C26	H26	1.00(3)
C27	H27	1.06(2)	C28	H28	1.01(2)
C29	H29	1.16(3)	C30	H30	0.99(3)
C31	H31	1.04(2)	C32	H32	1.06(2)
C33	H33	0.96(2)	C34	H34	0.99(2)
C35	H35	1.06(3)	C36	H36	1.06(3)
C37	H37	1.10(2)	C38	H38	1.13(3)

Table 3. (continued)

C39	H39A	1.07(2)	C39	H39B	1.02(2)
C39	H39C	1.00(3)			

Table 4. *Bond angles* (°)

C23	O3	C39	117.9(2)	O1	N4	C10	117.6(1)
O1	N4	C22	116.8(2)	C10	N4	C22	125.5(2)
C7	C5	C8	120.6(2)	C7	C5	C11	120.2(2)
C8	C5	C11	119.2(2)	C12	C6	C21	118.0(2)
C12	C6	C22	121.2(2)	C21	C6	C22	120.8(2)
C5	C7	C9	121.0(2)	C5	C7	C23	120.4(2)
C9	C7	C23	118.6(2)	C5	C8	C10	121.5(2)
C5	C8	C13	120.8(2)	C10	C8	C13	117.6(2)
C7	C9	C18	122.2(2)	C7	C9	C25	120.1(2)
C18	C9	C25	117.7(2)	O2	C10	N4	121.4(2)
O2	C10	C8	122.5(2)	N4	C10	C8	116.1(2)
C5	C11	C15	119.7(2)	C5	C11	C16	122.9(2)
C15	C11	C16	117.4(2)	C6	C12	C30	120.5(2)
C8	C13	C19	120.1(2)	C22	C14	C24	119.5(2)
C22	C14	C31	122.2(2)	C24	C14	C31	118.2(2)
C11	C15	C19	119.0(2)	C11	C15	C20	119.3(2)
C19	C15	C20	121.7(2)	C11	C16	C27	121.8(2)
C25	C17	C26	122.0(2)	C9	C18	C35	121.7(2)
C13	C19	C15	121.1(2)	C15	C20	C32	121.6(2)
C6	C21	C33	120.2(2)	N4	C22	C6	111.2(2)
N4	C22	C14	112.7(2)	C6	C22	C14	112.9(2)
O3	C23	C7	116.2(2)	O3	C23	C26	122.4(2)
C7	C23	C26	121.4(2)	C14	C24	C28	121.0(2)
C9	C25	C17	118.5(2)	C9	C25	C34	118.4(2)
C17	C25	C34	123.1(2)	C17	C26	C23	119.5(2)
C16	C27	C32	120.4(2)	C24	C28	C38	120.4(2)
C30	C29	C33	120.0(2)	C12	C30	C29	120.4(2)
C14	C31	C37	120.4(2)	C20	C32	C27	119.5(2)
C21	C33	C29	121.0(2)	C25	C34	C36	122.1(2)
C18	C35	C36	120.7(3)	C34	C36	C35	119.4(2)
C31	C37	C38	120.9(2)	C28	C38	C37	119.1(2)
N4	O1	H1	100.8(13)	C6	C12	H12	116.2(8)
C30	C12	H12	123.2(8)	C8	C13	H13	119.0(9)
C19	C13	H13	120.7(9)	C11	C16	H16	121.0(8)

Table 4. (continued)

C27	C16	H16	116.7(8)	C25	C17	H17	119.8(10)
C26	C17	H17	118.2(10)	C9	C18	H18	117.2(9)
C35	C18	H18	121.1(9)	C13	C19	H19	121.2(10)
C15	C19	H19	117.7(10)	C15	C20	H20	114.7(9)
C32	C20	H20	123.5(9)	C6	C21	H21	118.1(11)
C33	C21	H21	121.6(11)	N4	C22	H22	102.4(8)
C6	C22	H22	108.6(8)	C14	C22	H22	108.4(9)
C14	C24	H24	120.5(8)	C28	C24	H24	118.5(8)
C17	C26	H26	131.2(10)	C23	C26	H26	109.3(10)
C16	C27	H27	116.9(8)	C32	C27	H27	122.5(8)
C24	C28	H28	121.1(11)	C38	C28	H28	118.0(11)
C30	C29	H29	118.6(10)	C33	C29	H29	121.4(10)
C12	C30	H30	115.6(14)	C29	C30	H30	123.9(14)
C14	C31	H31	117.0(9)	C37	C31	H31	122.6(9)
C20	C32	H32	120.3(9)	C27	C32	H32	120.1(9)
C21	C33	H33	118.4(11)	C29	C33	H33	120.6(12)
C25	C34	H34	120.0(10)	C36	C34	H34	117.9(10)
C18	C35	H35	118.7(10)	C36	C35	H35	120.6(10)
C34	C36	H36	116.5(13)	C35	C36	H36	124.2(13)
C31	C37	H37	114.5(11)	C38	C37	H37	124.6(11)
C28	C38	H38	119.2(10)	C37	C38	H38	121.6(10)
O3	C39	H39A	103.8(11)	O3	C39	H39B	104.0(12)
O3	C39	H39C	109.1(15)	H39A	C39	H39B	121.5(15)
H39A	C39	H39C	112.4(18)	H39B	C39	H39C	105.2(18)

Table 5. *Torsional angles* (°)

C39	O3	C23	C7	-169.7(3)	C39	O3	C23	C26	9.7(2)
O1	N4	C10	O2	-177.7(2)	O1	N4	C10	C8	2.6(2)
O1	N4	C22	C6	-56.9(2)	O1	N4	C22	C14	71.0(2)
C22	N4	C10	O2	3.4(2)	C10	N4	C22	C6	122.0(2)
C22	N4	C10	C8	-176.3(2)	C10	N4	C22	C14	-110.1(2)
C8	C5	C7	C9	99.6(2)	C7	C5	C8	C10	0.0(2)
C7	C5	C8	C13	-179.4(2)	C8	C5	C7	C23	-81.8(2)
C11	C5	C7	C9	-80.0(2)	C7	C5	C11	C15	-179.3(2)
C7	C5	C11	C16	0.4(2)	C11	C5	C7	C23	98.7(2)
C11	C5	C8	C10	179.5(2)	C11	C5	C8	C13	0.2(2)
C8	C5	C11	C15	1.1(2)	C8	C5	C11	C16	-179.2(3)
C21	C6	C12	C30	2.0(2)	C12	C6	C21	C33	-1.1(2)
C12	C6	C22	N4	71.1(2)	C12	C6	C22	C14	-56.7(2)
C22	C6	C12	C30	-179.0(3)	C21	C6	C22	N4	-110.0(2)
C21	C6	C22	C14	122.2(2)	C22	C6	C21	C33	179.9(3)
C5	C7	C9	C18	-4.5(2)	C5	C7	C9	C25	176.0(2)
C5	C7	C23	O3	2.8(2)	C5	C7	C23	C26	-176.6(3)
C9	C7	C23	O3	-178.5(2)	C23	C7	C9	C18	176.9(3)
C23	C7	C9	C25	-2.6(2)	C9	C7	C23	C26	2.1(2)
C5	C8	C10	O2	-80.7(2)	C5	C8	C10	N4	99.0(2)
C5	C8	C13	C19	-0.6(2)	C13	C8	C10	O2	98.6(2)
C13	C8	C10	N4	-81.7(2)	C10	C8	C13	C19	-180.0(3)
C7	C9	C18	C35	-179.4(3)	C7	C9	C25	C17	1.4(2)
C7	C9	C25	C34	178.9(3)	C18	C9	C25	C17	-178.1(3)
C18	C9	C25	C34	-0.6(2)	C25	C9	C18	C35	0.1(2)
C5	C11	C15	C19	-2.0(2)	C5	C11	C15	C20	178.1(2)
C5	C11	C16	C27	-179.3(3)	C16	C11	C15	C19	178.3(2)
C16	C11	C15	C20	-1.7(2)	C15	C11	C16	C27	0.5(2)
C6	C12	C30	C29	-1.4(2)	C8	C13	C19	C15	-0.3(2)
C24	C14	C22	N4	-172.8(2)	C24	C14	C22	C6	-45.8(2)
C22	C14	C24	C28	-175.3(3)	C31	C14	C22	N4	11.3(2)
C31	C14	C22	C6	138.3(2)	C22	C14	C31	C37	174.7(3)
C31	C14	C24	C28	0.7(2)	C24	C14	C31	C37	-1.2(2)
C11	C15	C19	C13	1.6(2)	C11	C15	C20	C32	1.8(2)

Table 5. (continued)

C20	C15	C19	C13	-178.5(3)	C19	C15	C20	C32	-178.2(3)
C11	C16	C27	C32	0.6(2)	C26	C17	C25	C9	0.4(2)
C25	C17	C26	C23	-1.0(2)	C26	C17	C25	C34	-176.9(3)
C9	C18	C35	C36	0.8(2)	C15	C20	C32	C27	-0.6(2)
C6	C21	C33	C29	-0.4(2)	O3	C23	C26	C17	-179.6(3)
C7	C23	C26	C17	-0.2(2)	C14	C24	C28	C38	0.0(2)
C9	C25	C34	C36	0.2(2)	C17	C25	C34	C36	177.6(4)
C16	C27	C32	C20	-0.6(2)	C24	C28	C38	C37	-0.3(2)
C33	C29	C30	C12	-0.1(2)	C30	C29	C33	C21	1.1(2)
C14	C31	C37	C38	0.9(2)	C25	C34	C36	C35	0.7(2)
C18	C35	C36	C34	-1.2(2)	C31	C37	C38	C28	-0.1(2)
H1	O1	N4	C10	-73.6(13)	H1	O1	N4	C22	105.4(13)
C23	O3	C39	H39A	47.7(11)	C23	O3	C39	H39B	175.7(12)
C23	O3	C39	H39C	-72.4(16)	O1	N4	C22	H22	-172.7(9)
C10	N4	C22	H22	6.2(9)	C21	C6	C12	H12	-177.4(9)
C12	C6	C21	H21	174.3(12)	C12	C6	C22	H22	-177.0(9)
C22	C6	C12	H12	1.5(9)	C21	C6	C22	H22	1.9(9)
C22	C6	C21	H21	-4.7(12)	C5	C8	C13	H13	-175.9(10)
C10	C8	C13	H13	4.7(10)	C7	C9	C18	H18	0.4(10)
C25	C9	C18	H18	179.9(10)	C5	C11	C16	H16	9.1(10)
C15	C11	C16	H16	-171.1(10)	C6	C12	C30	H30	-178.4(15)
H12	C12	C30	C29	178.0(10)	H12	C12	C30	H30	1.0(17)
C8	C13	C19	H19	179.1(12)	H13	C13	C19	C15	174.9(11)
H13	C13	C19	H19	-5.6(16)	C24	C14	C22	H22	74.6(9)
C22	C14	C24	H24	4.9(9)	C31	C14	C22	H22	-101.3(9)
C22	C14	C31	H31	-3.0(11)	C31	C14	C24	H24	-179.1(10)
C24	C14	C31	H31	-179.0(11)	C11	C15	C19	H19	-177.9(12)
C11	C15	C20	H20	175.9(10)	C19	C15	C20	H20	-4.1(10)
C20	C15	C19	H19	2.1(11)	C11	C16	C27	H27	-174.8(10)
H16	C16	C27	C32	172.6(9)	H16	C16	C27	H27	-2.9(13)
C25	C17	C26	H26	174.8(15)	H17	C17	C25	C9	179.4(11)
H17	C17	C25	C34	2.0(11)	H17	C17	C26	C23	-180.0(11)
H17	C17	C26	H26	-4.1(18)	C9	C18	C35	H35	-176.6(13)
H18	C18	C35	C36	-179.0(10)	H18	C18	C35	H35	3.5(16)

Table 5. (continued)

C15	C20	C32	H32	177.2(11)	H20	C20	C32	C27	-174.2(11)
H20	C20	C32	H32	3.6(15)	C6	C21	C33	H33	179.0(13)
H21	C21	C33	C29	-175.6(13)	H21	C21	C33	H33	3.8(17)
O3	C23	C26	H26	3.7(12)	C7	C23	C26	H26	-176.9(12)
C14	C24	C28	H28	171.7(13)	H24	C24	C28	C38	179.8(10)
H24	C24	C28	H28	-8.5(16)	C9	C25	C34	H34	-178.2(12)
C17	C25	C34	H34	-0.8(12)	C16	C27	C32	H32	-178.4(11)
H27	C27	C32	C20	174.6(11)	H27	C27	C32	H32	-3.2(15)
C24	C28	C38	H38	-177.7(12)	H28	C28	C38	C37	-172.3(13)
H28	C28	C38	H38	10.4(17)	C33	C29	C30	H30	176.6(16)
C30	C29	C33	H33	-178.4(13)	H29	C29	C30	C12	-178.1(12)
H29	C29	C30	H30	-1.4(19)	H29	C29	C33	C21	179.0(12)
H29	C29	C33	H33	-0.4(17)	C14	C31	C37	H37	179.3(12)
H31	C31	C37	C38	178.5(12)	H31	C31	C37	H37	-3.0(16)
C25	C34	C36	H36	-179.4(14)	H34	C34	C36	C35	179.1(12)
H34	C34	C36	H36	-1.0(17)	C18	C35	C36	H36	178.9(15)
H35	C35	C36	C34	176.2(13)	H35	C35	C36	H36	-3.7(19)
C31	C37	C38	H38	177.1(12)	H37	C37	C38	C28	-178.4(13)
H37	C37	C38	H38	-1.2(18)					

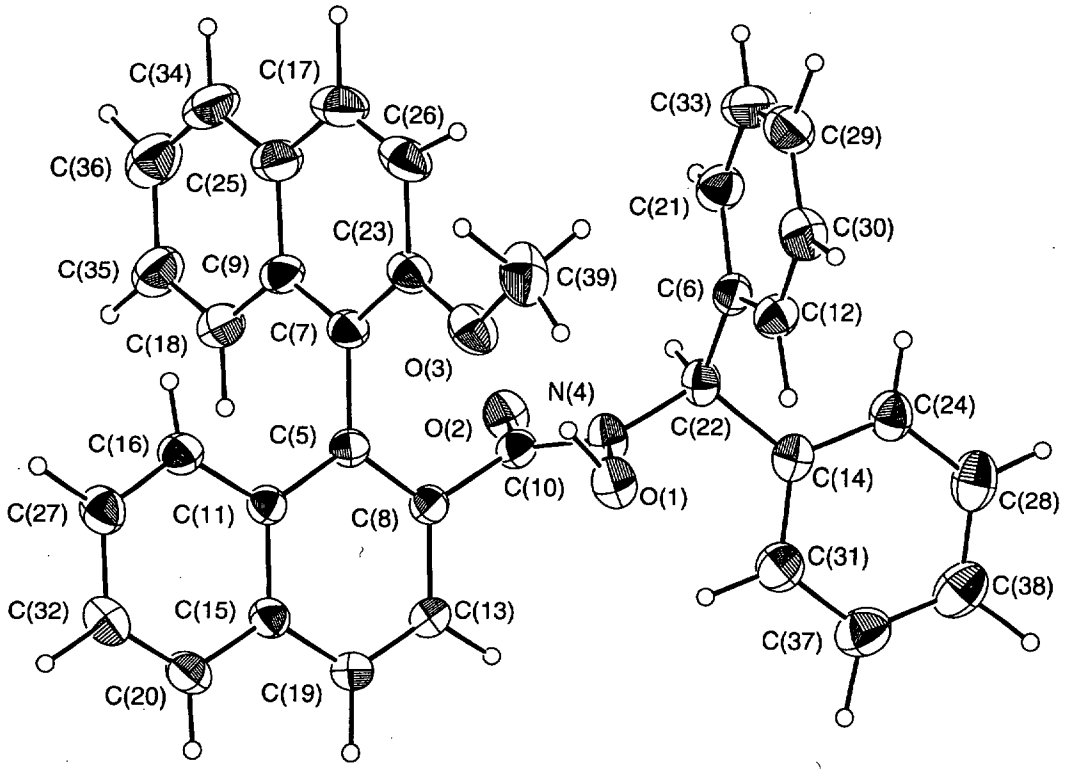


Figure 1. ORTEP diagram of Ligand **1c.**

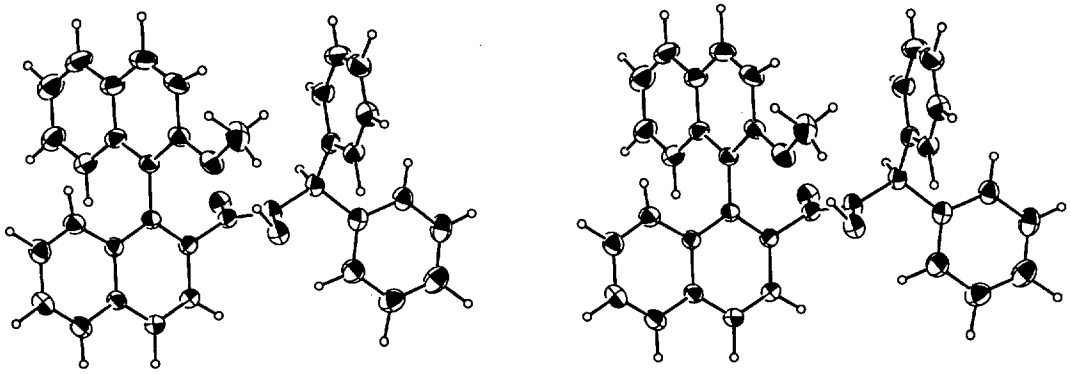


Figure 2. Stereoview of crystal structure of Ligand **1c.**