ELECTRONIC SUPPLEMENTARY INFORMATION

N-Alkyl oxazolidines as stereocontrol elements in asymmetric Diels-Alder cycloadditions of 9-substituted anthracene derivatives

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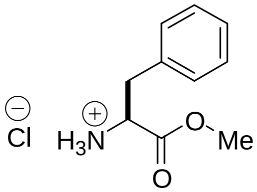
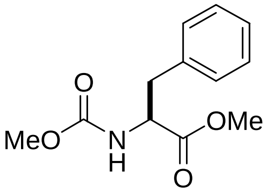
Preparation of L-Phenylalanine methyl ester hydrochloride **8**[2]



Thionyl chloride (6.0 cm^3, 82.1 mmol) was added *via* dropping funnel to a stirred suspension of L-phenylalanine (9.03 g, 54.7 mmol) in methanol (100 cm^3) at 0 °C. This was stirred for 24 h at room temperature and the solvent was removed. The crude product was recrystallised from EtOAc/EtOH (95:5) to give a white solid of the title compound (9.45 g, 97% yield), mp 150 – 154 °C (EtOAc/EtOH) (lit.[1] 159 – 161 °C); $[\alpha]_D$ –3.0 (*c* 1, H_2O) (lit.[2] –5.0; *c* 1, H_2O); δ_H (250 MHz; D_2O) 7.45 – 7.37 (3H, m, Ar-C*H*), 7.28 (2H, m, Ar-C*H*), 4.42 (1H, dd, *J* 5.2, 7.4, C*H*), 3.82 (3H, s, CH_3), 3.34 (1H, dd, *J* 14.6, 5.2, PhCH*H*), 3.21 (1H, dd, *J* 14.6, 7.4, PhC*H*H); δ_C (62.5 MHz; D_2O) 170.1 (*C*O), 133.7 (Ar-*C*), 129.4 (2 × Ar-*C*H), 129.3 (2 × Ar-*C*H), 128.2 (Ar-*C*H), 54.1 (*C*H), 53.6 (*C*H_2), 35.6 (*C*H_3). NMR data was in accordance with the literature.

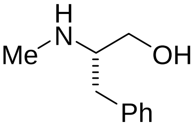
Preparation of N-*Methylformyl-L-phenylalanine methyl ester* **9**[3]



A solution of sodium hydrogen carbonate (8.53 g, 101.6 mmol in 100 cm^3 water) was added at 0 °C to a stirred solution of L-phenylalanine methyl ester hydrochloride **8** (10.8 g, 50.2 mmol) in distilled water (100 cm^3). Methyl chloroformate (4.4 cm^3, 55.7 mmol) was added dropwise. The reaction mixture was stirred for 24 h at room temperature, ethyl acetate (40 cm^3) was added and the organic layer was separated, washed with brine (3 × 20 cm^3), dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford a colourless oil of the target compound (10.7 g, 90% yield). This was used without further purification, $[\alpha]_D$ +57 (*c* 1, $CHCl_3$) (lit. was not reported); δ_H (250 MHz; $CDCl_3$) 7.12 – 7.08 (5H, m, Ar-C*H*), 5.29 (1H, d, *J* 7.9, N*H*), 4.63 (1H, m, C*H*), 3.69 (3H, s, CH_3), 3.62 (3H, s, CH_3), 3.15 – 3.00 (2H, m, PhCH_2); δ_C (62.5 MHz; $CDCl_3$) 172.2 (*C*O), 156.4 (*C*O), 135.9 (Ar-*C*), 129.2 (2 × Ar-

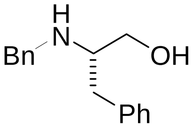
*C*H), 128.6 (2 × Ar-*C*), 127.1 (Ar-*C*H), 54.9 (*C*H), 52.2 (2 × O*C*H_3), 38.2 (Ph*C*H_2). NMR data was in accordance with the literature.

Preparation of N-*Methylphenylalaninol* **10**[2]



A solution of *N*-methylformyl-L-phenylalanine methyl ester **9** (5.02 g, 21.2 mmol) in dry THF (50cm^3) was added dropwise to a suspension of $LiAlH_4$ (3.22 g, 84.8 mmol) in dry THF (150 cm^3) at 50 °C. The reaction mixture was refluxed for 5 h, cooled gradually to 0 °C at which aqueous solution of NaOH (1 M, 20 cm^3) was added slowly. The resulting mixture was heated at reflux for a further 2 h, cooled to room temperature and filtered through a pad of Celite. The organic layer was separated, washed with brine (3 × 15 cm^3), dried over Na_2SO_4, filtered and removal of the solvent gave a white solid of the desired compound (3.13 g, 90% yield). No further purification was required, mp 68 – 70 °C (lit.[2] 68 °C); $[\alpha]_D$ +23 (*c* 1, $CHCl_3$) (lit.[2] +17.1; *c* 2, $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 7.33 – 7.16 (5H, m, Ar-C*H*), 3.64 (1H, dd, *J* 7.0, 2.5, CH*H*O), 3.34 (1H, dd, *J* 7.0, 2.5, C*H*HO), 2.83 – 2.68 (3H, m, PhC*H*$_2$, C*H*), 2.39 (3H, s, C*H*$_3$); δ_C (62.5 MHz; $CDCl_3$) 138.7 (Ar-*C*), 129.3 (Ar-*C*H), 129.2 (Ar-*C*H), 128.6 (2 × Ar-*C*H), 126.4 (Ar-*C*H), 62.1 (*C*H), 62.1 (*C*H_2OH), 37.5 (Ph*C*H_2), 33.8 (*C*H_3). NMR data was in accordance with the literature.

Preparation of N-*Benzyl-(*S*)-phenylalaninol* **11**[4]



Benzaldehyde (1.3 cm^3, 12.3 mmol) was added at room temperature to a stirred solution of (*S*)-phenylalaninol (1.85 g, 12.2 mmol) in dry methanol (20 cm^3). This was stirred for 1 h, cooled to 0 °C, $NaBH_4$ (0.70 g, 18.4 mmol) was added slowly, and the reaction mixture was stirred for a further 2 h at room temperature. The reaction was quenched with glacial acetic acid (10 cm^3) at 0 °C, the solvent was removed and the remaining white solid was dissolved in a mixture of H_2O/EtOAc (40 cm^3; 1:1 v/v). The organic layer was separated, washed with brine (3 × 15 cm^3), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the title compound as a white solid (2.92 g, 99% yield). This was used without further purification, mp 54 – 56 ºC (lit.[4] 67 – 68 °C, hexane); $[\alpha]_D$ –10 (*c* 1, $CHCl_3$) (lit.[5] –9.9; *c* 3.5, $CHCl_3$); δ_H (250 MHz; $CDCl_3$) 7.57 – 7.53 (2H, m, Ar-C*H*), 7.47 – 7.33 (3H, m, Ar-C*H*), 7.31 –

7.19 (3H, m, Ar-C*H*), 7.15 – 7.12 (2H, Ar-C*H*), 4.25 (1H, d, *J* 13.4, PhC*H*H), 4.05 (1H, d, *J* 13.4, PhCH*H*), 3.77 (1H, dd, *J* 12.9, 2.9, CH*H*O), 3.65 (1H, dd, *J* 12.9, 5.6, C*H*HO), 3.20 (2H, m, C*H* and PhCH*H*), 3.03 (1H, dd, *J* 14.4, 11.0, PhC*H*H); δ_C (62.5 MHz; $CDCl_3$) 135.9 (2 × Ar-*C*), 130.4 (2 × Ar-*C*H), 129.6 (2 × Ar-*C*H), 129.3 (Ar-*C*H), 129.2 (2 × Ar-*C*H), 128.9 (2 × Ar-*C*H), 127.2 (Ar-*C*H), 60.1 (*C*H), 59.6 ($\mathit{C}H_2O$), 49.1 (Ph$\mathit{C}H_2N$), 33.6 (Ph$\mathit{C}H_2$). NMR data was in accordance with the literature.

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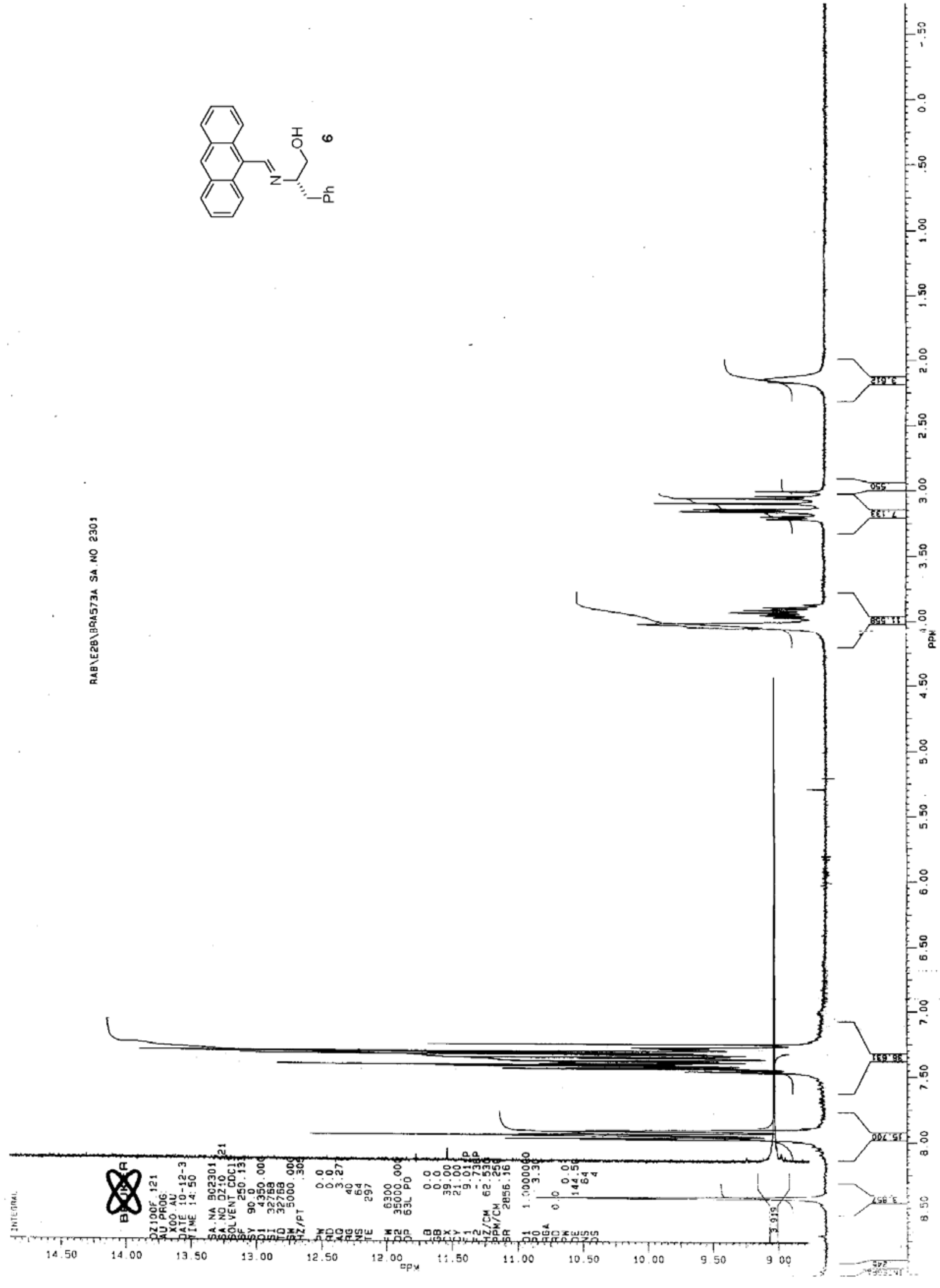

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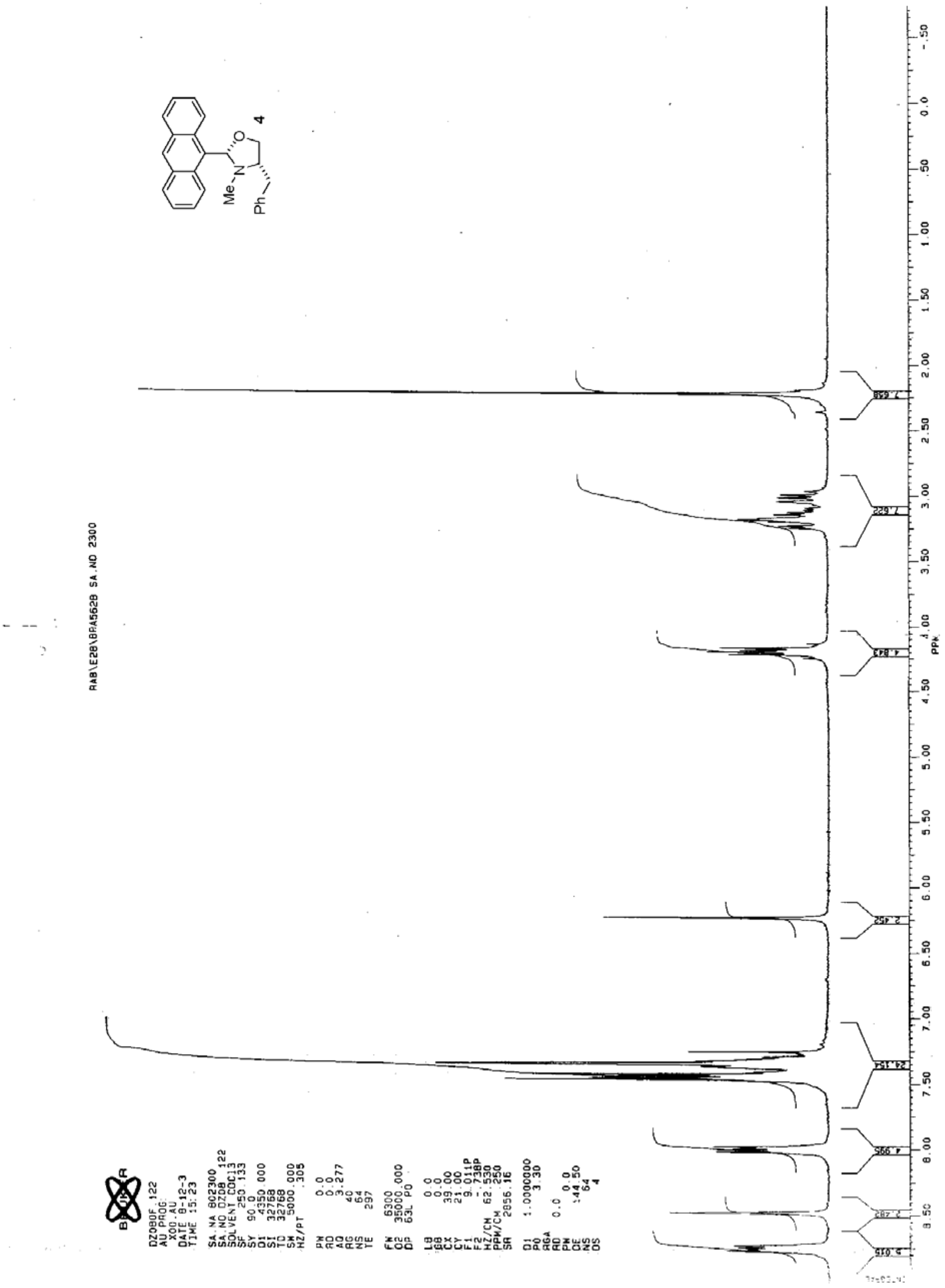

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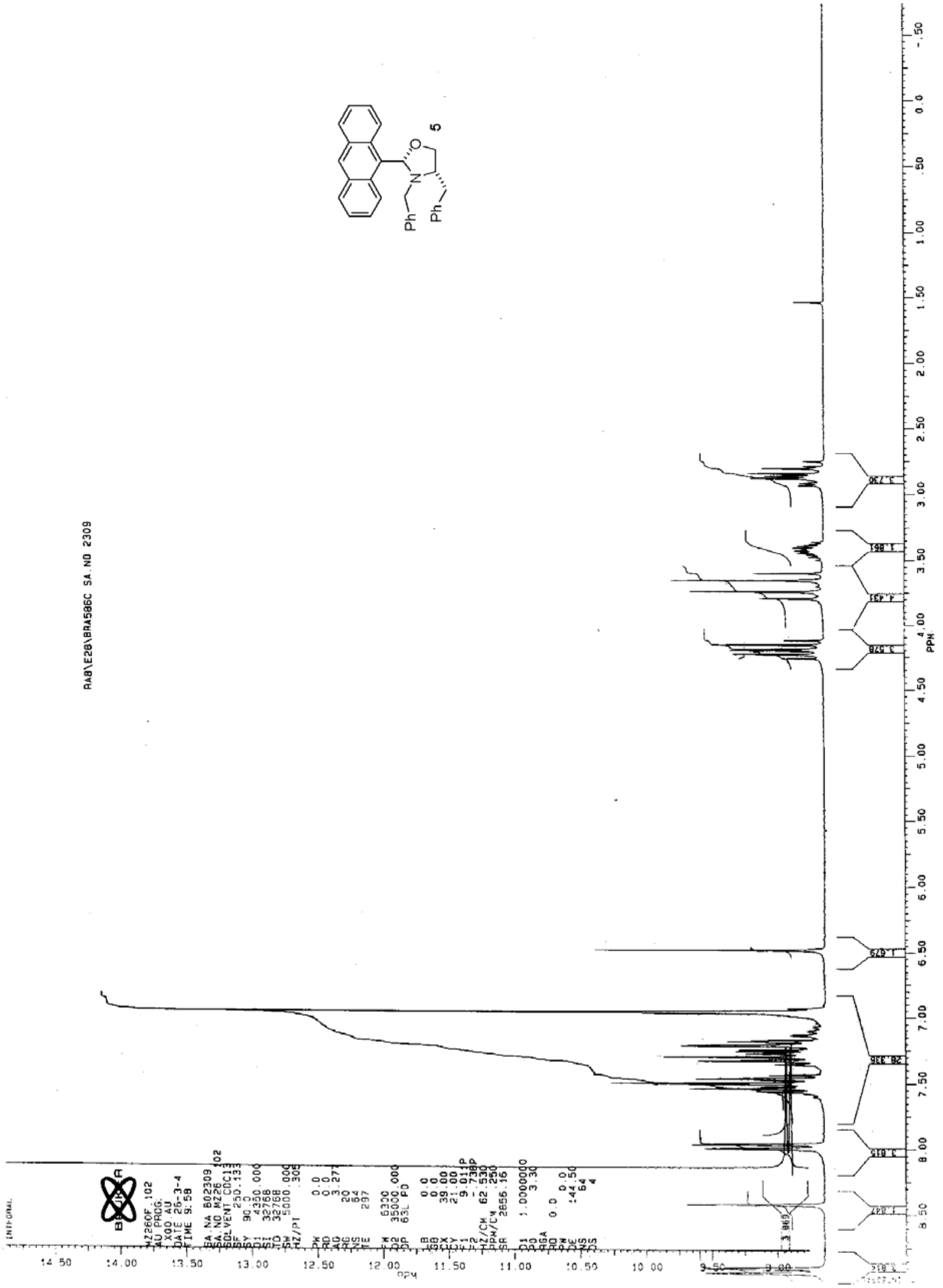
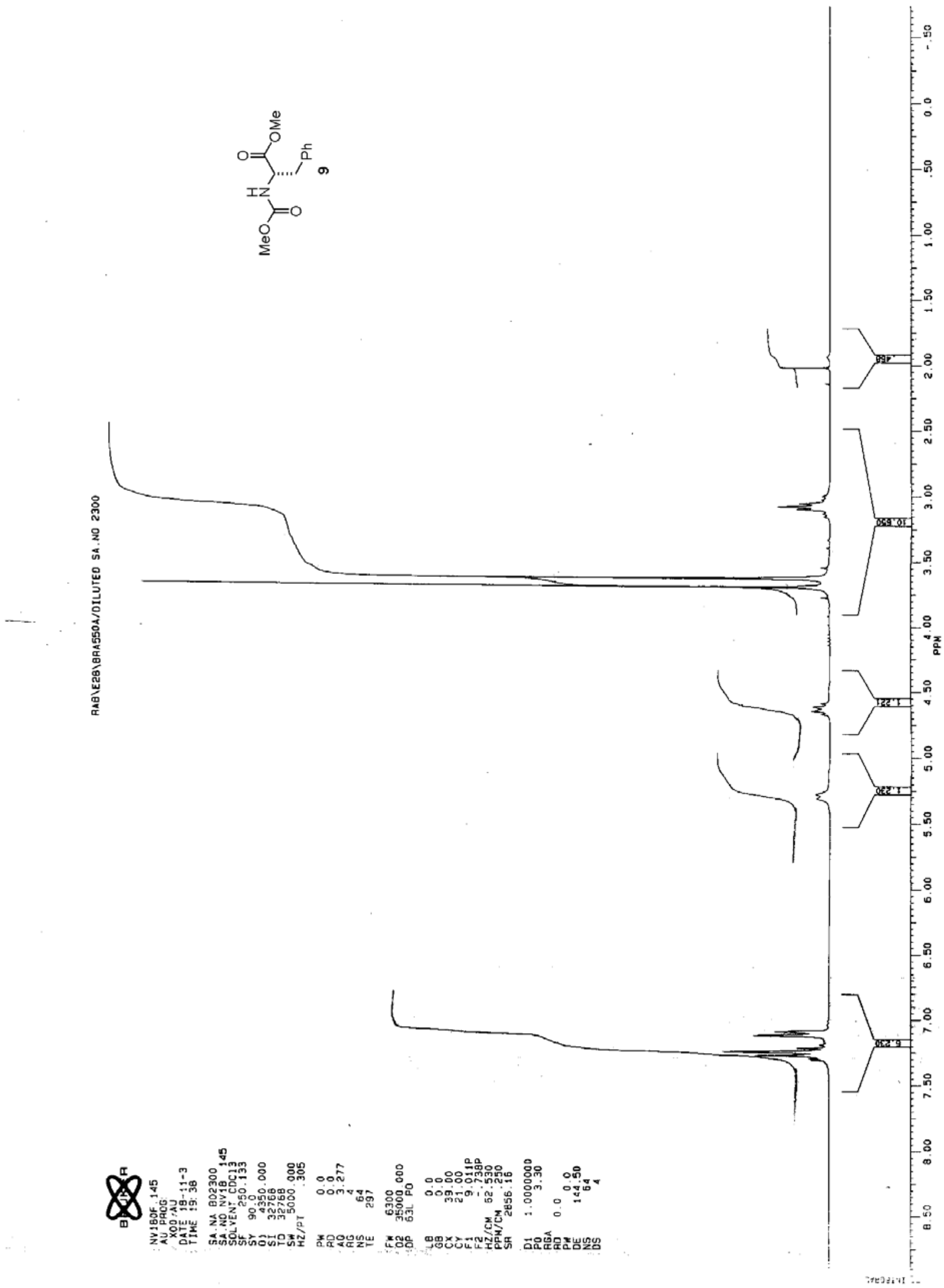


_N_-Methylformyl-(_S_)-phenylalanine Methyl Ester 9



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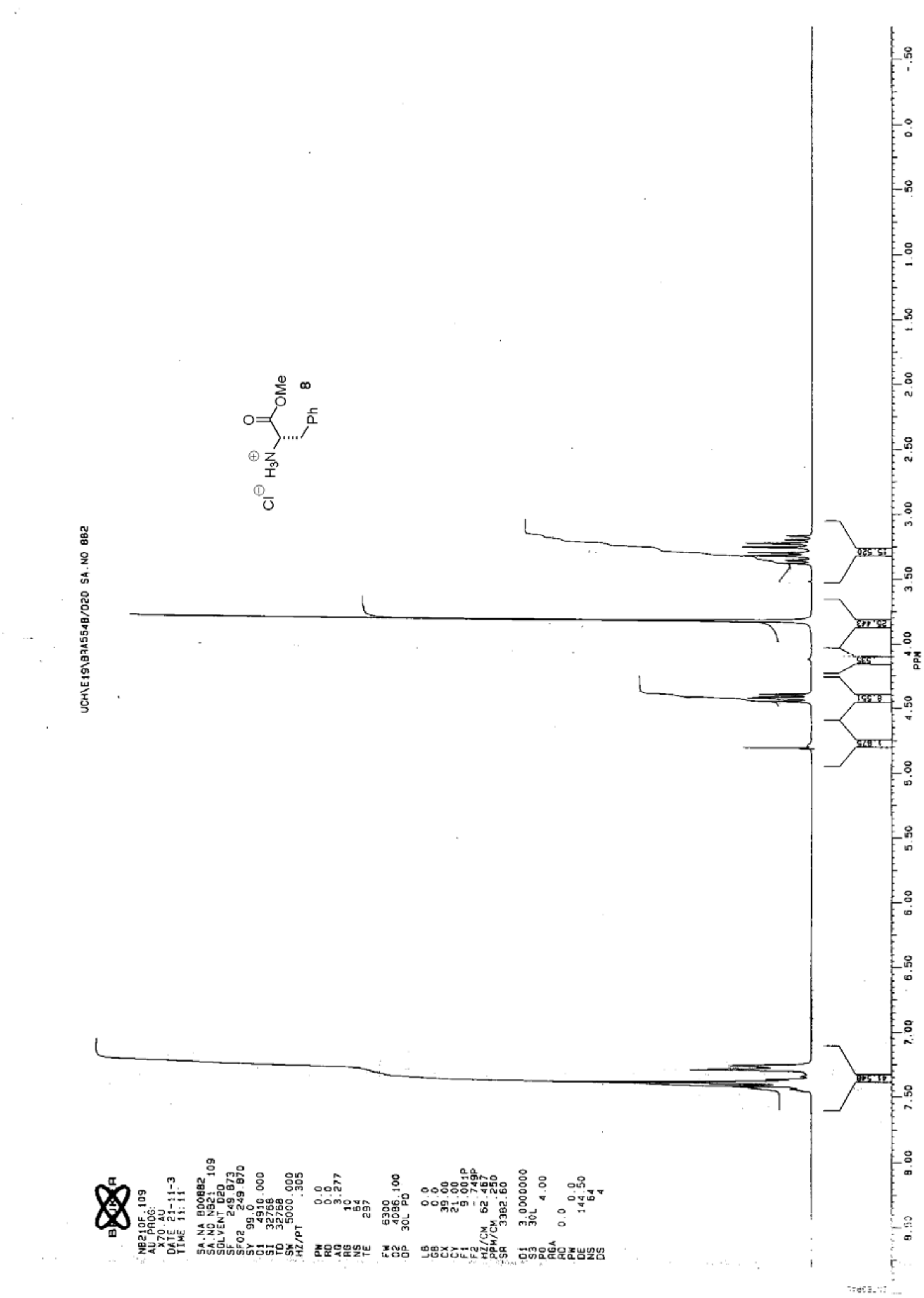

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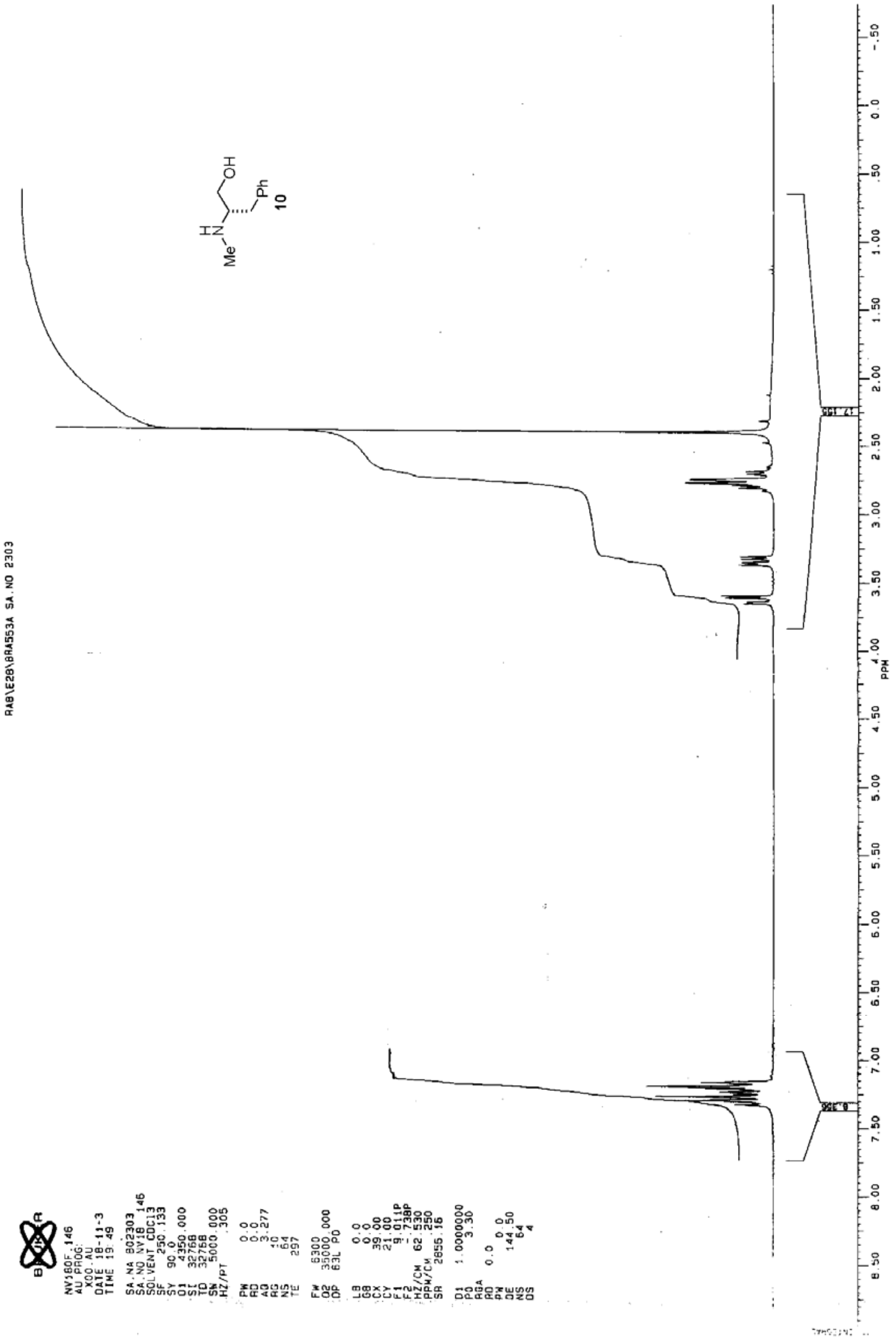

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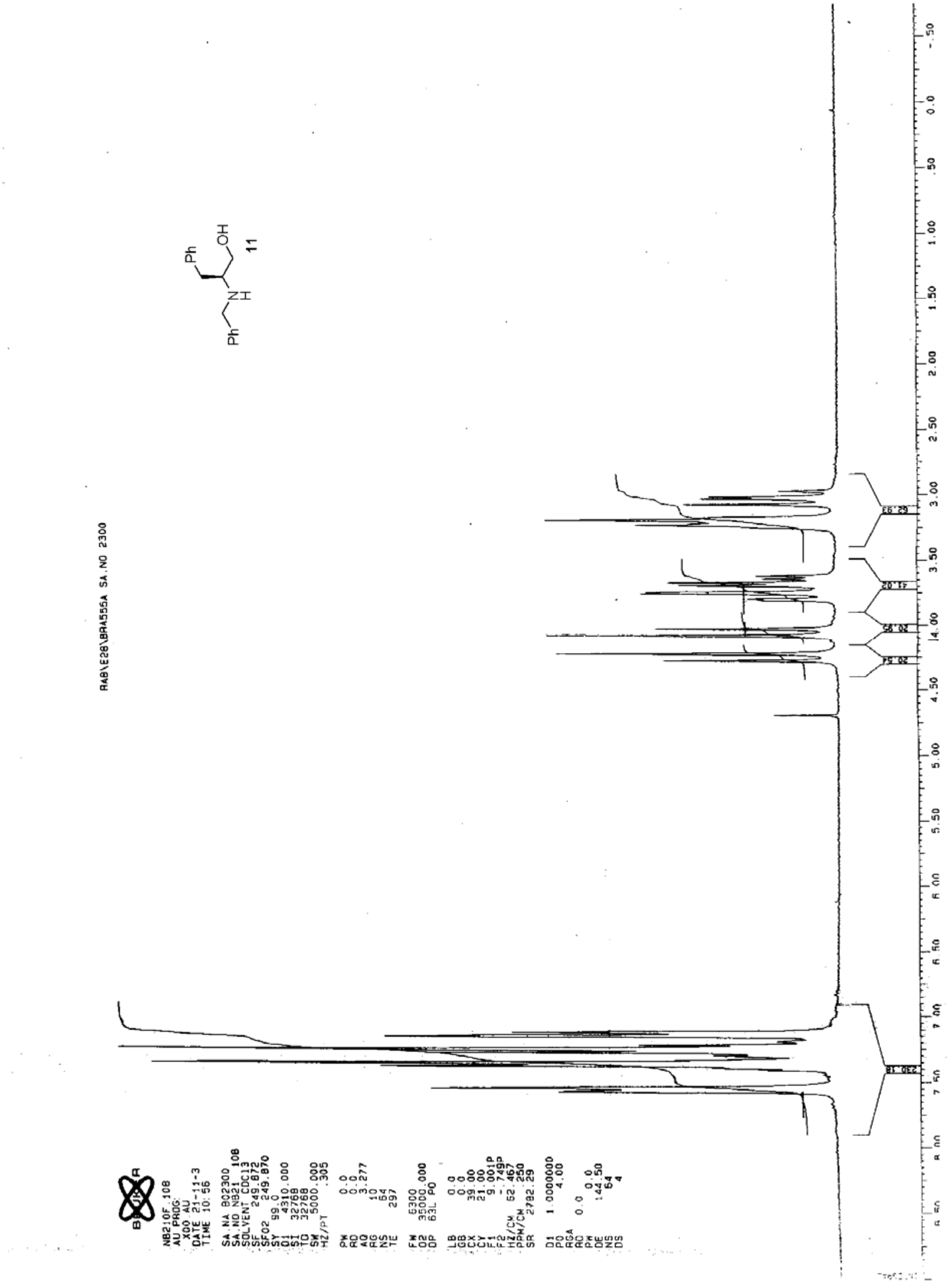

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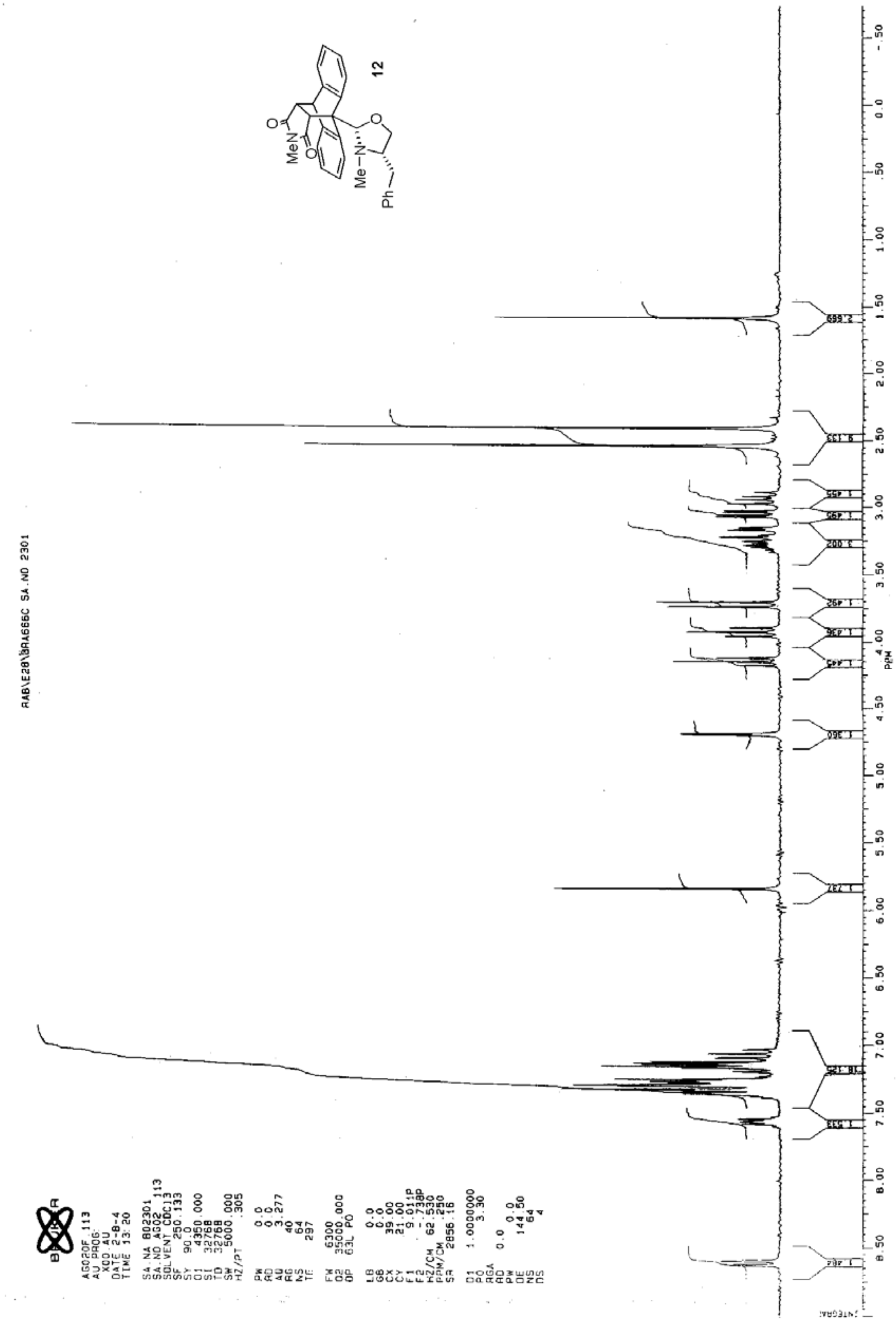

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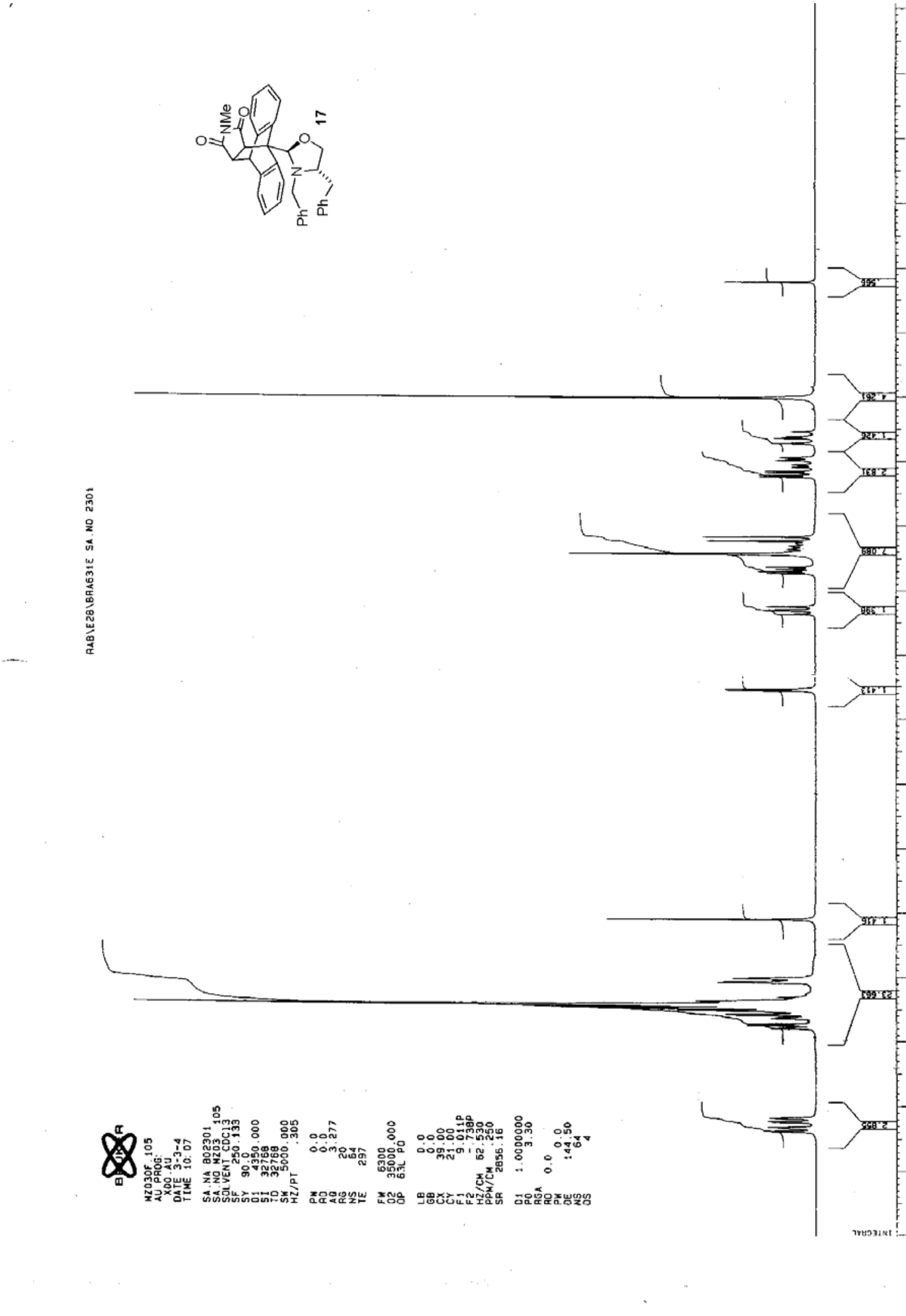

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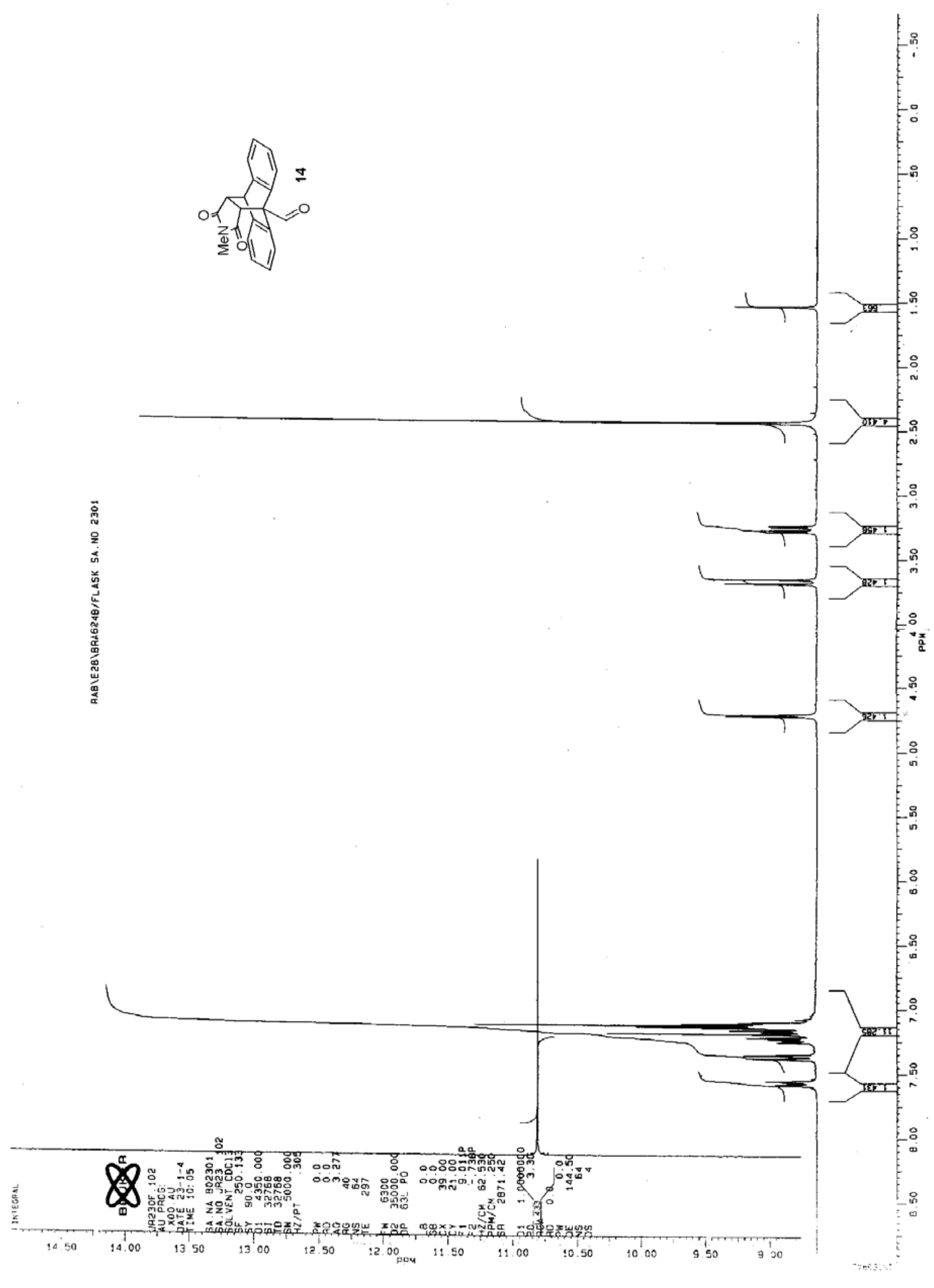
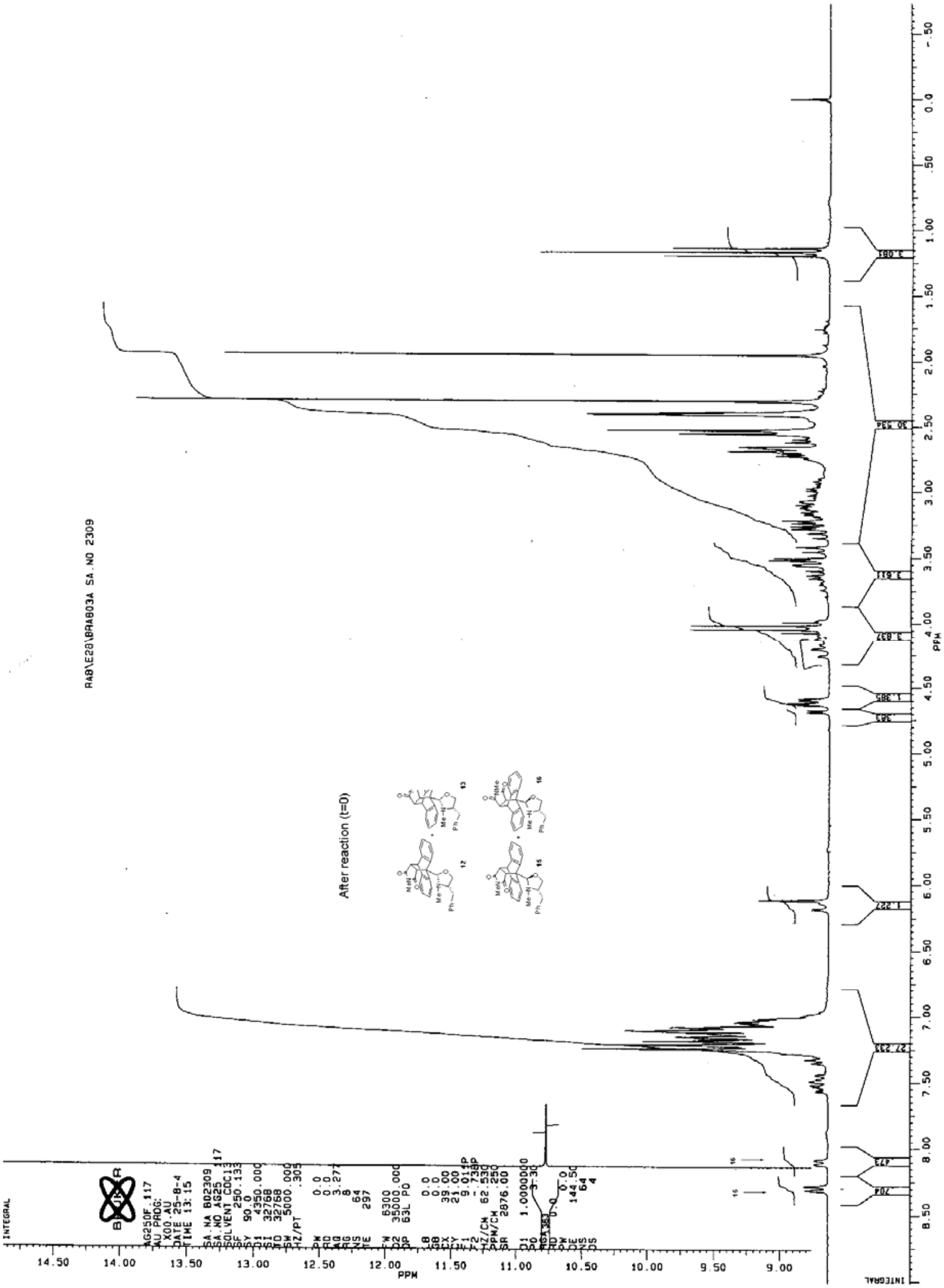
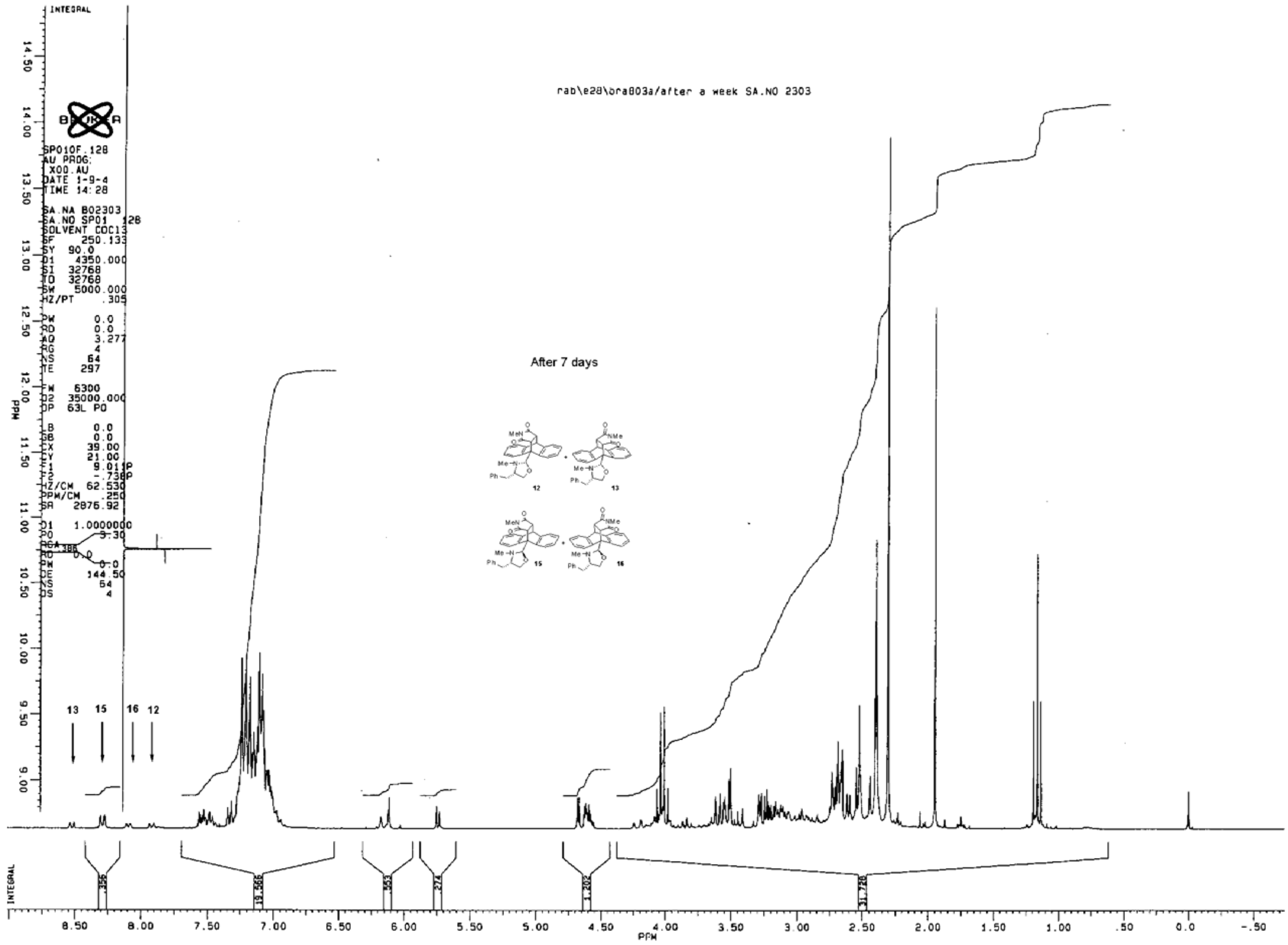


Copies of ^{1}H NMR spectra for oxazolidine interconversion (cf. Table 1)

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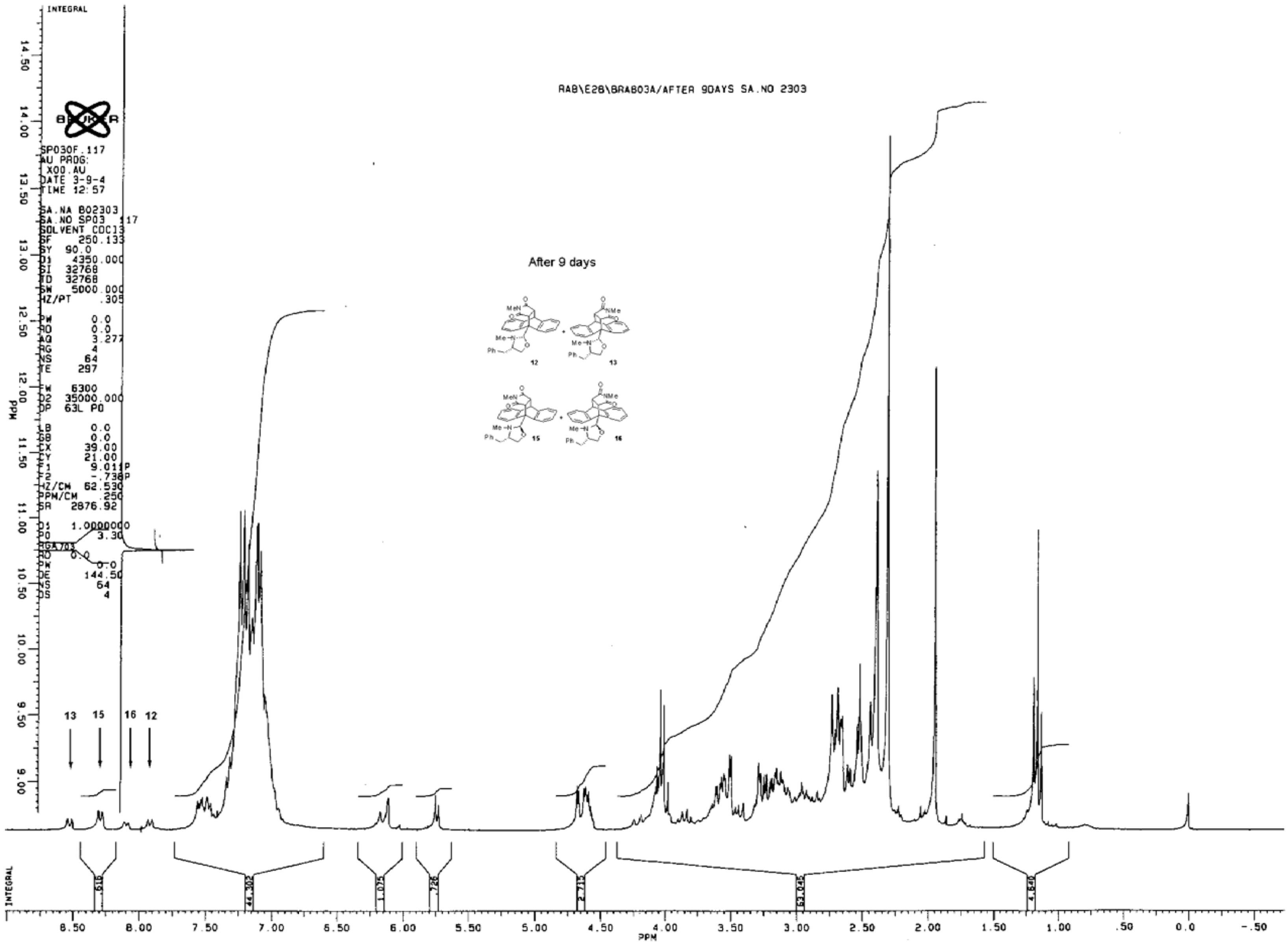
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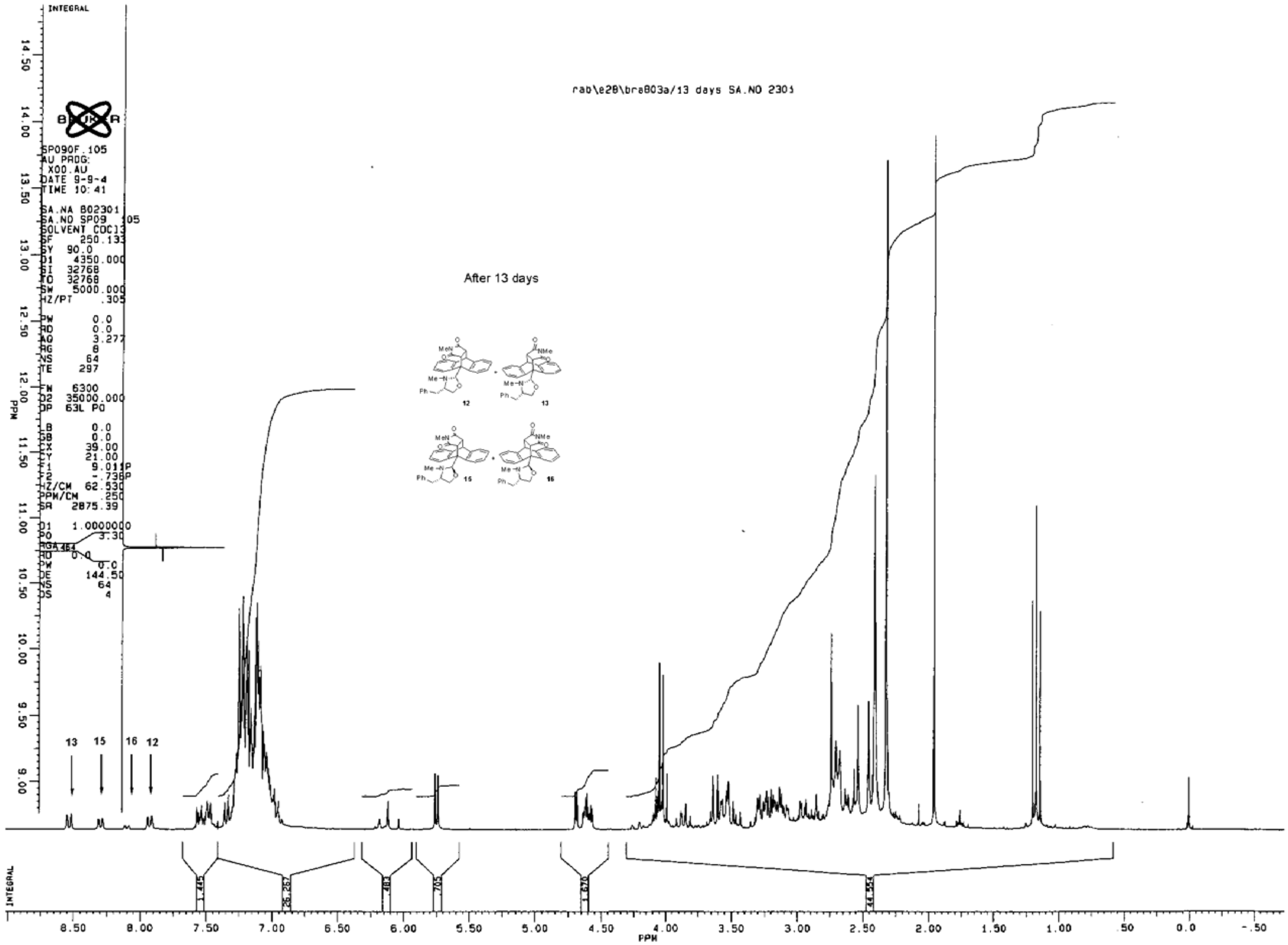

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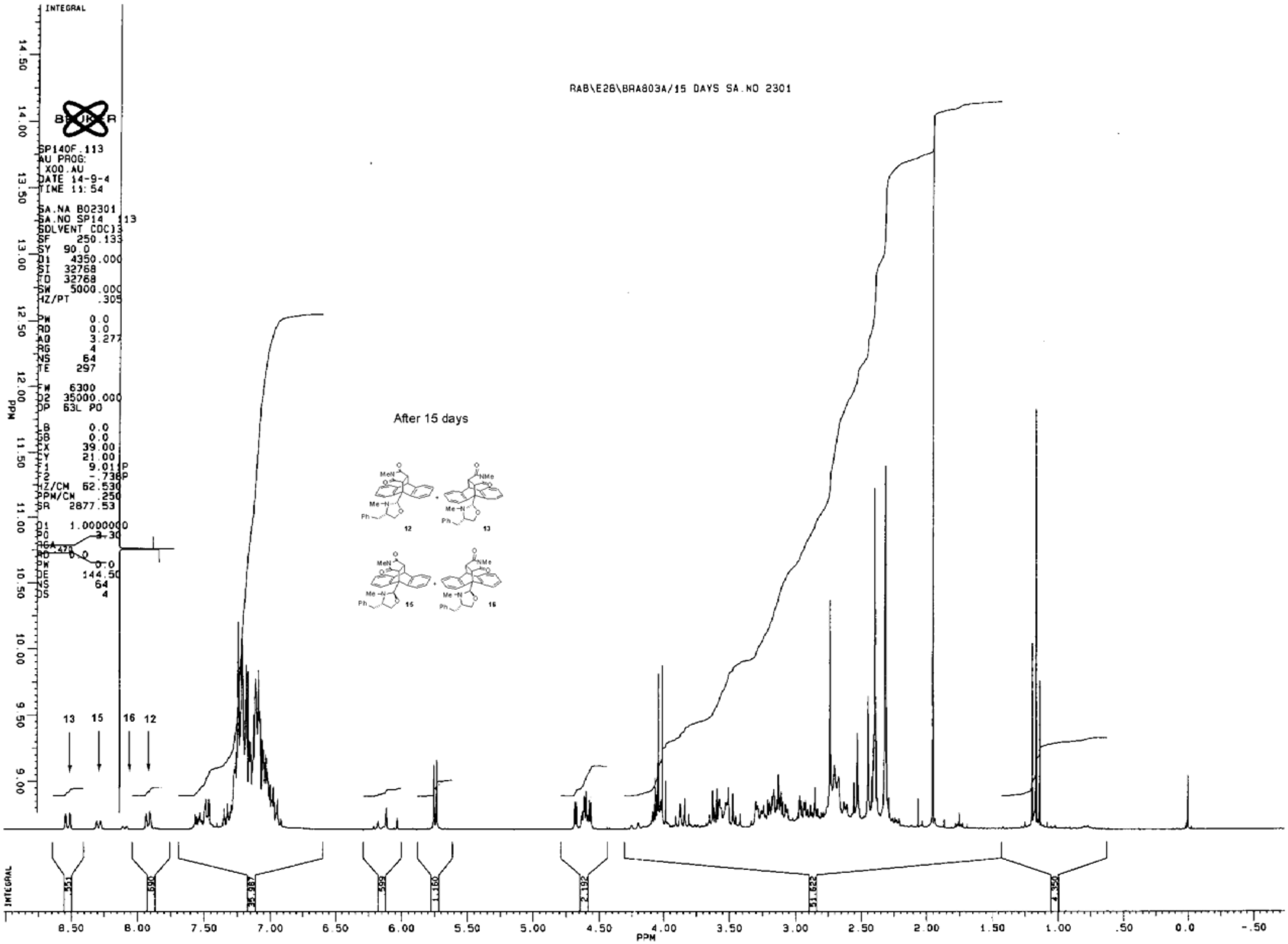
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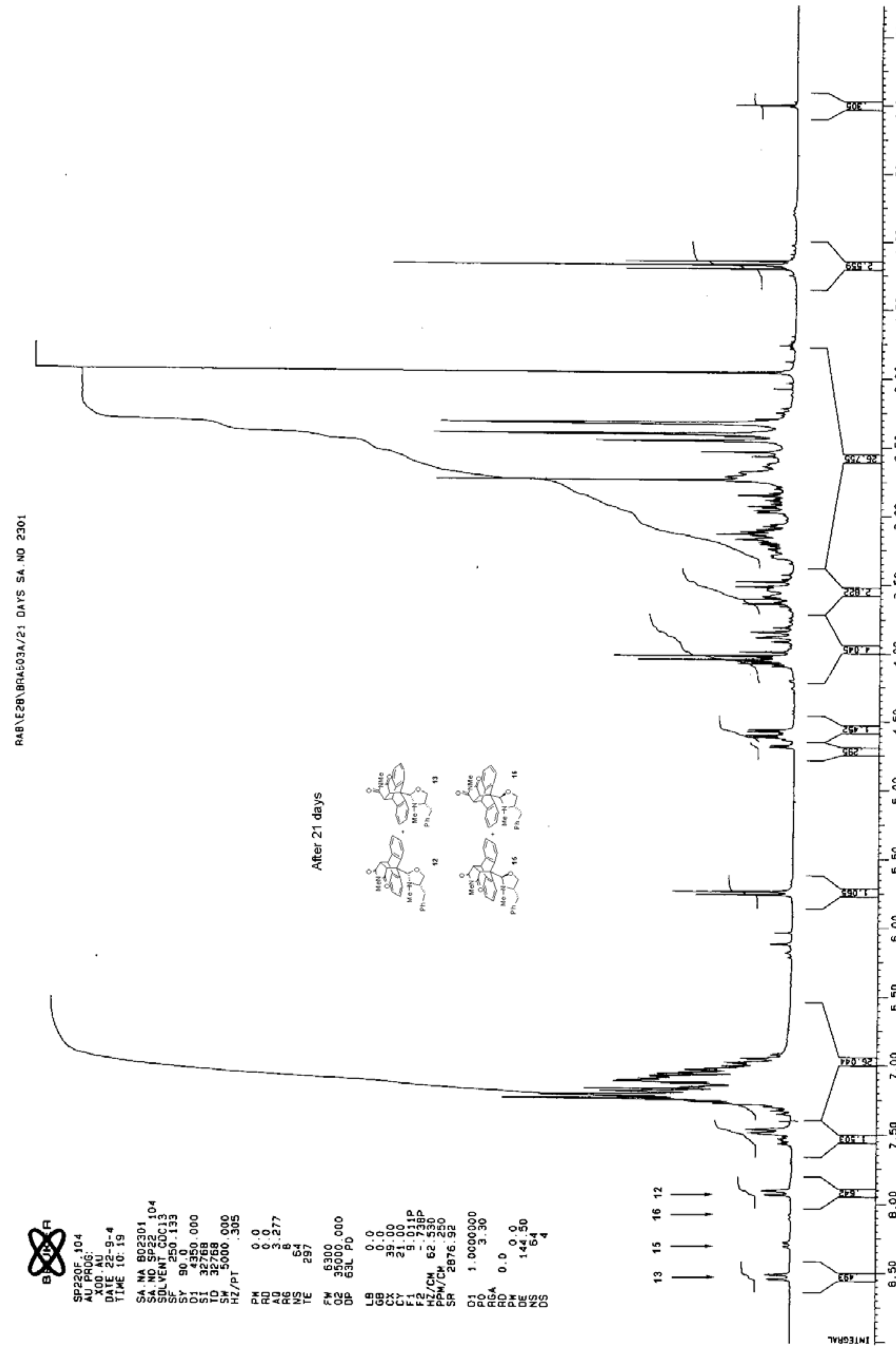
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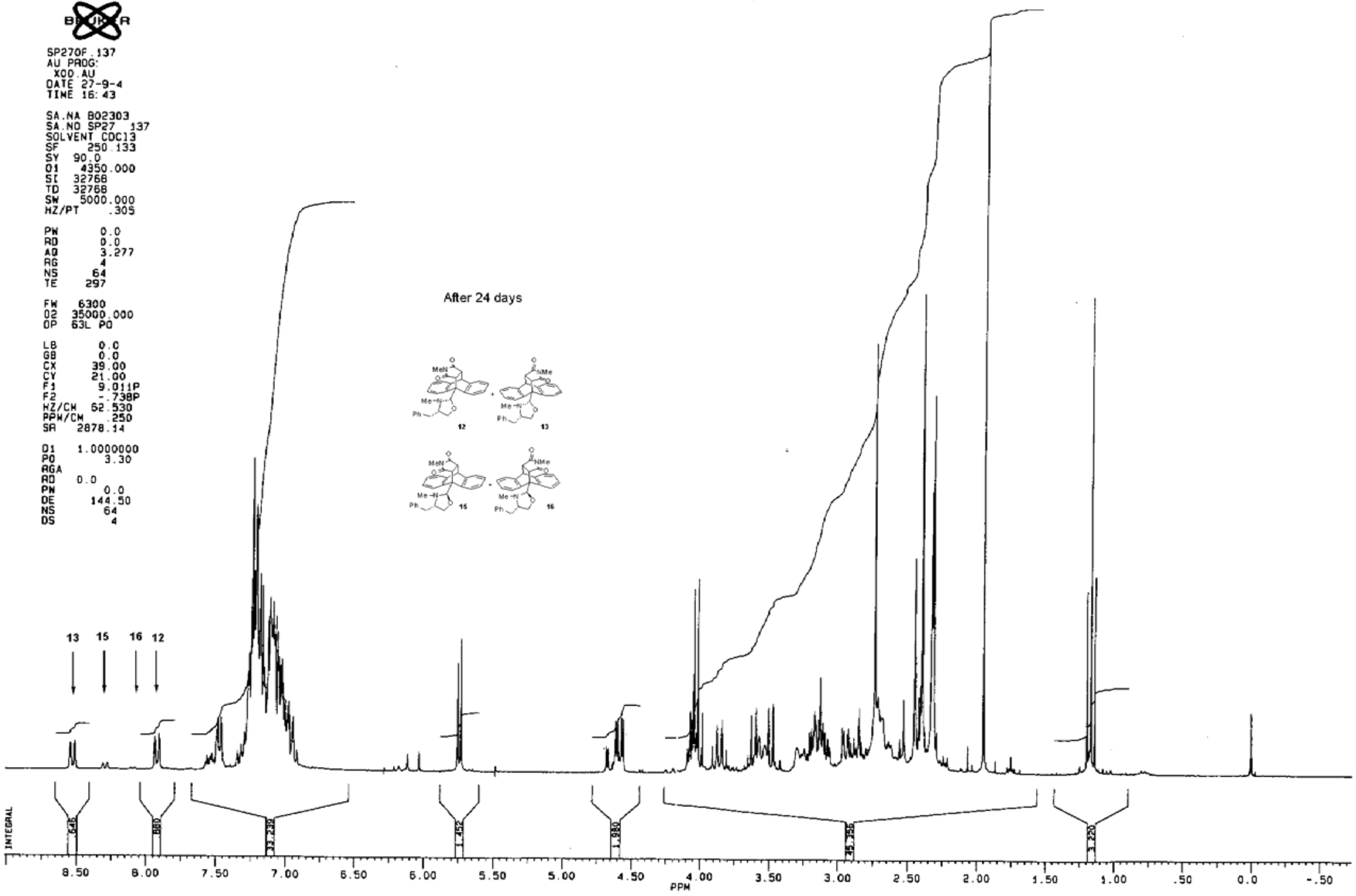

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RD       0.0
AQ       3.277
RG       4
NS      64
TE     297

FW   6300
O2  35000.000
OP  63L PO

LB       0.0
GB       0.0
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CY      21.00
F1       9.011P
F2       -.738P
HZ/CM  62.530
PPM/CM    .250
SR    2878.14

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DS         4
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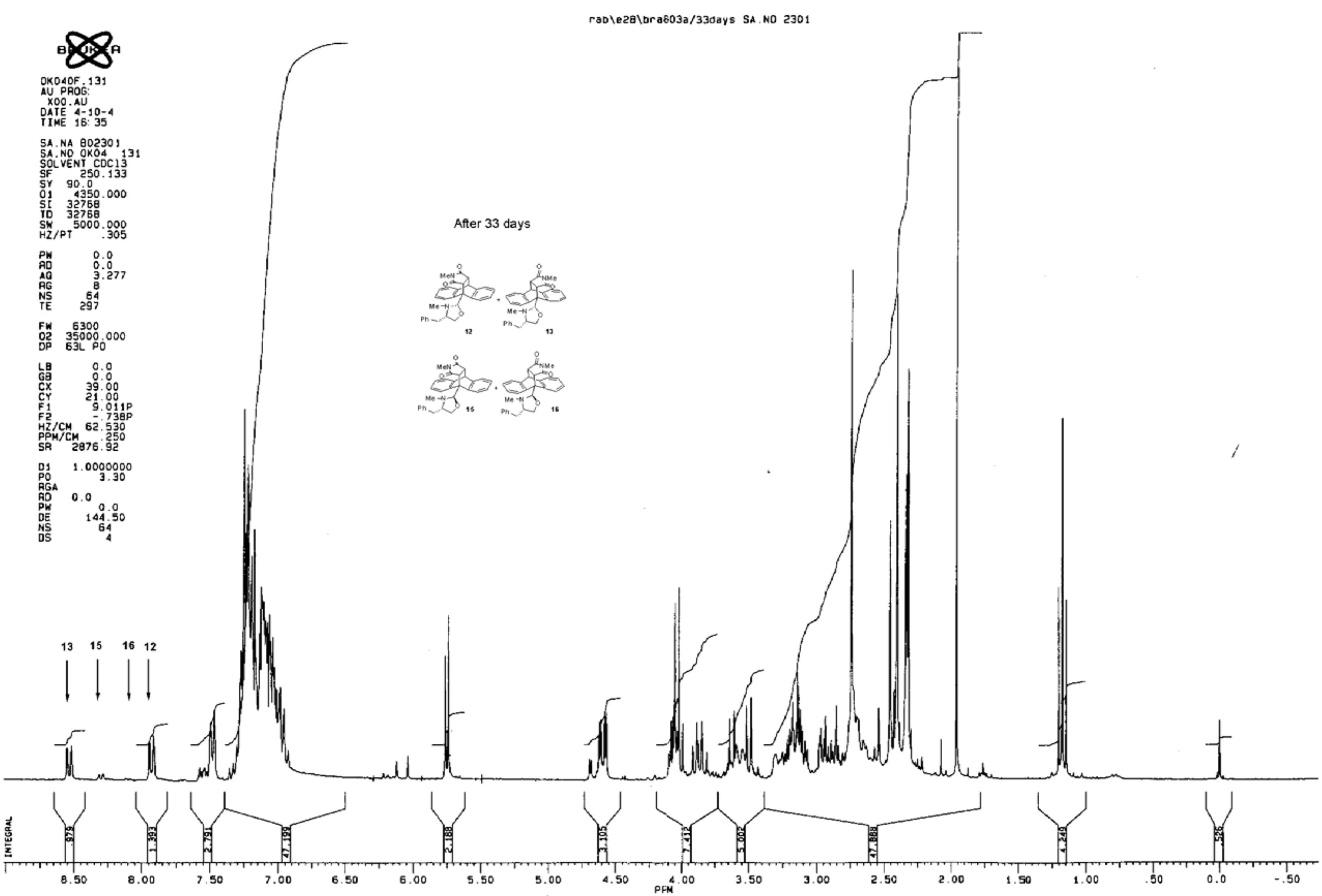
After 24 days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DS 4
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16
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PPM

X-Ray Crystallographic Information

(2*S*, 4*S*)-2-(9-Anthracenyl)-3-methyl-4-benzyl oxazolidine 4

Crystal data for $C_{25}H_{23}NO$; M = 353.44. Crystallises from dichloromethane/ pet ether as colourless blocks; crystal dimensions 0.43 x 0.25 x 0.14 mm^3. Monoclinic, *a* = 18.188(3), *b* = 7.0490 (10), *c* = 17.257(2) Å, β = 121.240(2)°, *U* = 1891.7(5) Å^3, *Z* = 4, D_c = 1.241 Mg/m^3, space group C2 , Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-K_α) = 0.075 mm^{-1}, F(000) = 752.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 3417 reflections (θ range 1.38 < 27.51°).

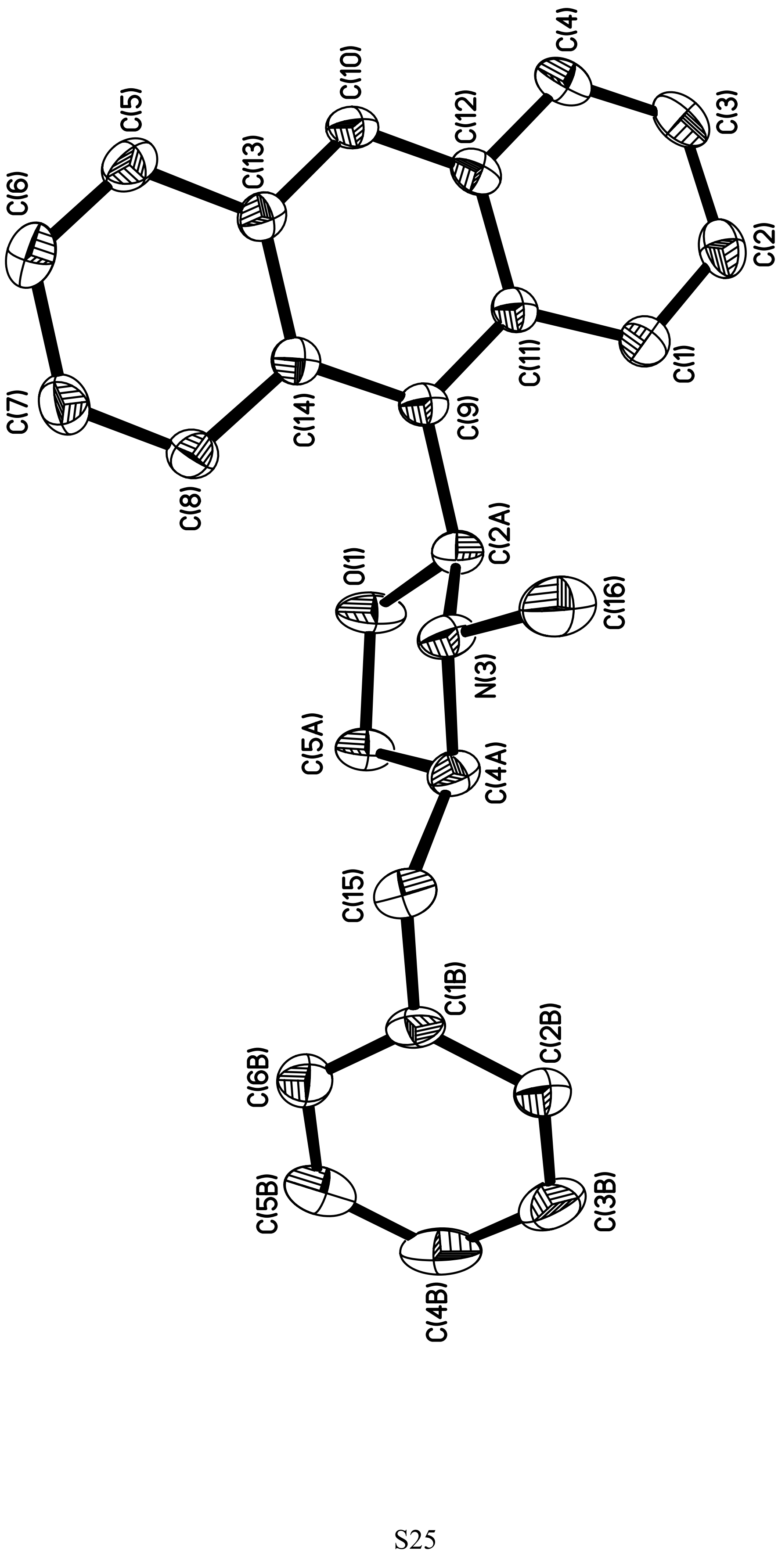
Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 10741 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.9685 and 0.9896) 1903 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by Patterson synthesis and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0370 (wR_2 = 0.0943, for all 2328 data, 246 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.190 and 0.199 e.Å^{-3}. A weighting scheme $w = 1/[\sigma^2(Fo^2) +(0.0487*P)^2+0.2084*P]$ where $P=(Fo^2+ 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL^6 as implemented on the Viglen Pentium computer.

Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s

hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.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C(5B)
C(3B)
C(4B)

(2*S*, 4*S*)-2-(9-Anthracenyl)-3,4-dibenzyl oxazolidine 5

Crystal data for $C_{31}H_{27}NO$; M = 429.54. Crystallises from dichloromethane/pet ether as colourless blocks; crystal dimensions 0.43 x 0.34 x 0.13 mm^3. Triclinic, *a* = 7.284(3), *b* = 9.462(3), *c* = 18.426(6) Å, α = 76.240(5)° β = 84.707(6)° γ = 68.069(5)° , *U* = 1144.2(7) $Å^3$, *Z* = 2, D_c = 1.247Mg/m^3, space group P1 (C_i^1 , No. 1) , Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-K_α) = 0.074 mm^{-1}, F(000) = 456.

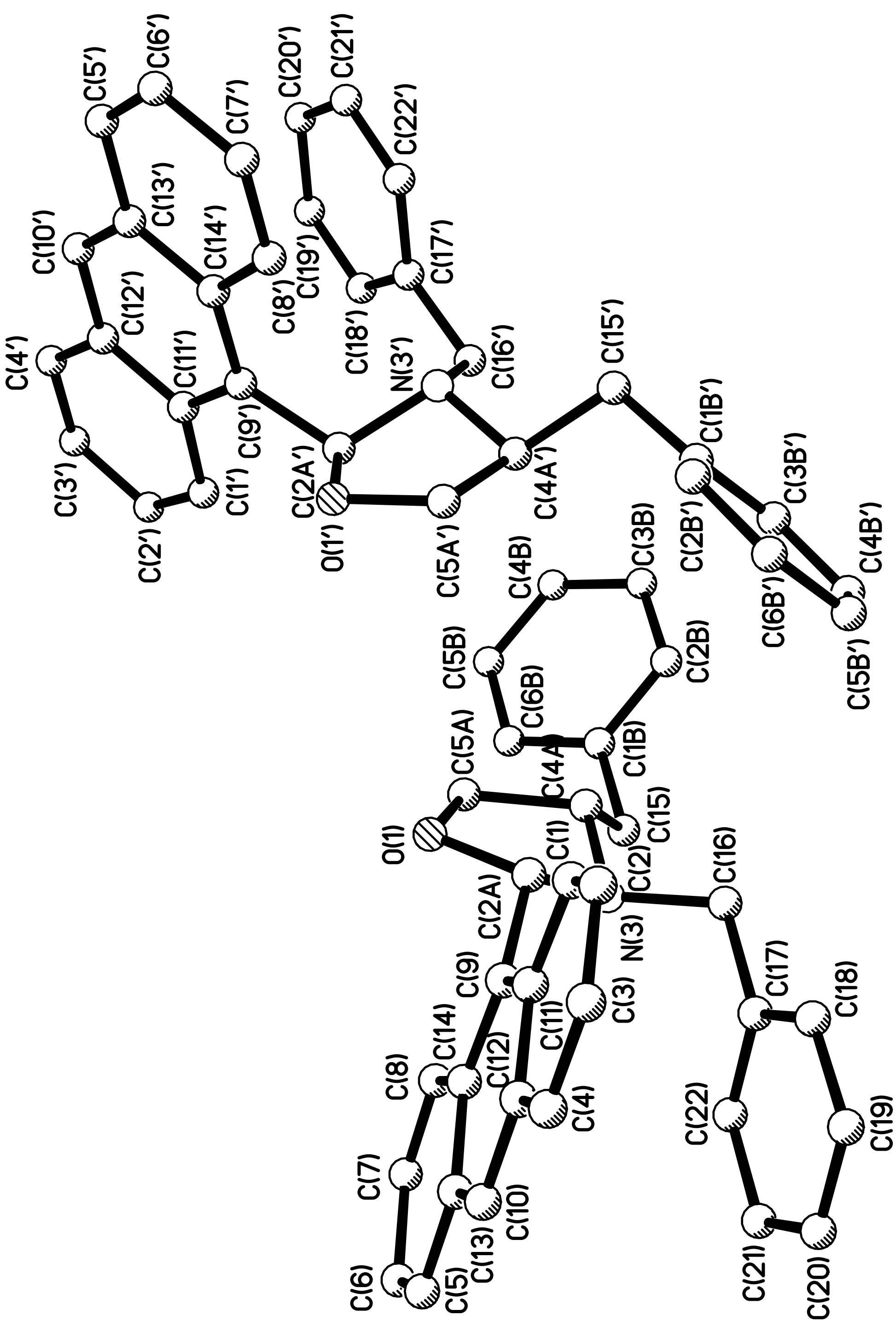
Data collected were measured on a Bruker Smart CCD area detector. Cell parameters were refined from the setting angles of 3918 reflections (θ range 2.28 < 27.58°).

Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega . Of the 12849 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.9687 and 0.9904) 3768 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Refinement converged at a final R= 0.0538(wR_2=0.1422, for all 5114 data, 595 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.244 and 0.351 e.$Å^{-3}$. A weighting scheme w = $1/[\sigma^2(Fo^2) + (0.0842*P)^2 + 0.00*P]$ where $P=(Fo^2 + 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[6] as implemented on the Pentium computer.

Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.



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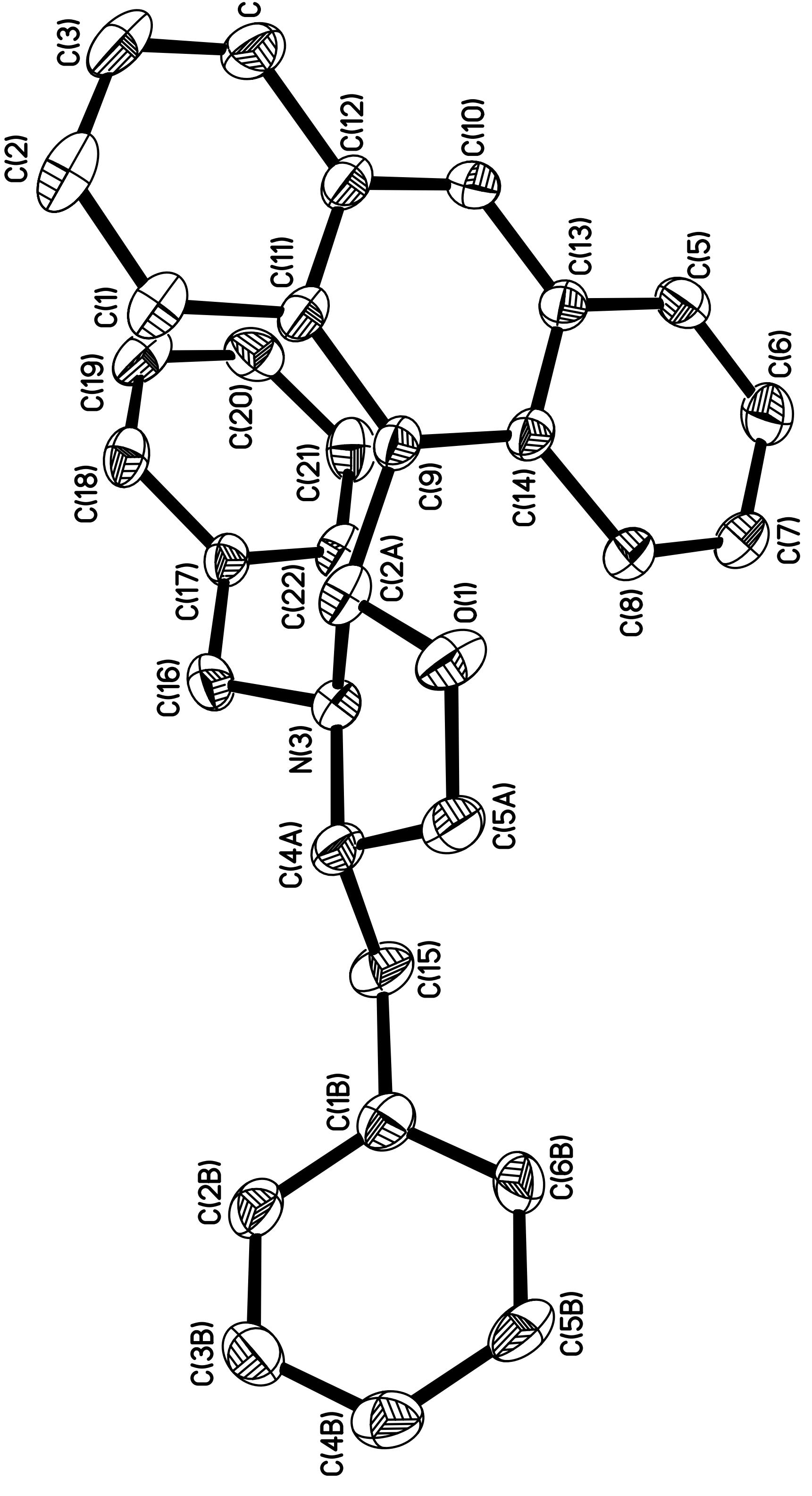
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(3a*R*, 9a*R*)-3a,4,9,9a-Tetrahydro-4-[(2*S*,4*S*)-5-benzyl-3-methyl-2-oxazolidinyl]-2-methyl-4,9[1',2']-benzeno-1H-benz[f]isoindole-1,3(2H)-dione 12

Crystal data for $C_{31}H_{30}Cl_2N_2O_3$; M = 549.47, crystallises from dichloromethane/pet ether as colourless blocks; crystal dimensions 0.49 x 0.49 x 0.26mm^3. Monoclinic, a = 7.6834(10), b = 10.5554(14), c = 16.299(2) Å, β = 93.517(3)° U = 1319.4(3) Å^3, Z = 2, D_c = 1.383 Mg/m^3, space group P2_1, Mo-K$_\alpha$ radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-K$_\alpha$) = 0.283 mm^{-1}, F(000) = 576.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 6694 reflections (θ range 2.30 < 27.62°),

Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega . Of the 11779 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections(minimum and maximum transmission coefficients 0.8737 and 0.9300) 2922 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$ The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2(1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R= 0.0309 (wR_2=0.0766, for all 3123 data, 346 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.296 and 0.264 e.Å^{-3}.

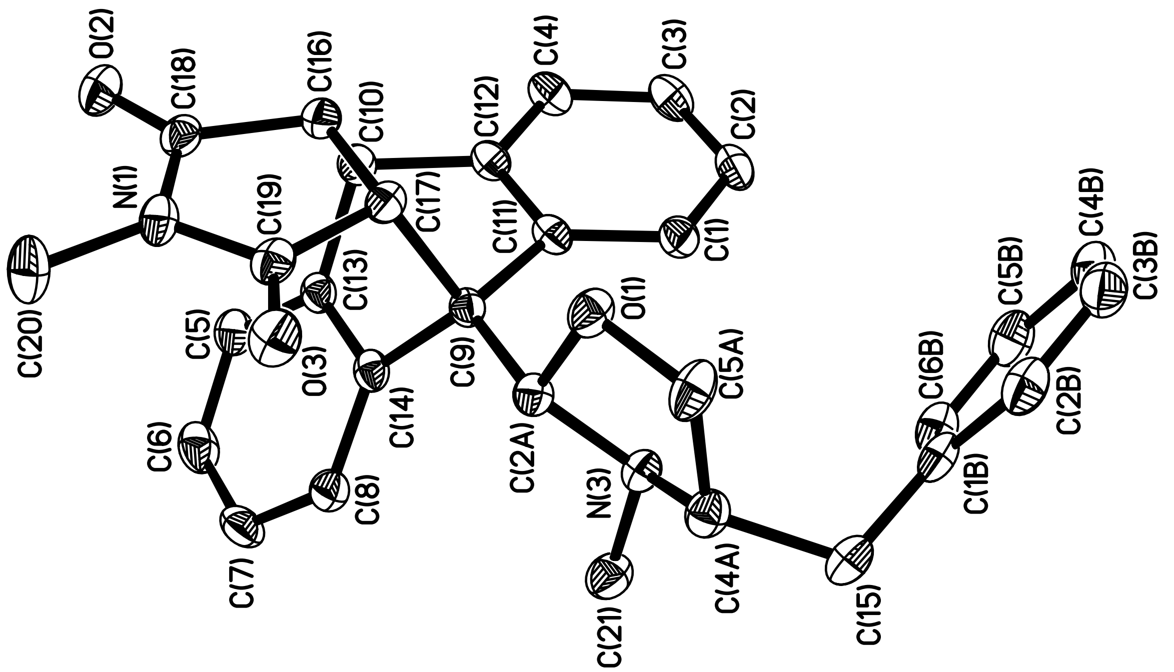
A weighting scheme $w = 1/[\sigma^2(Fo^2) + (0.0418*P)^2 + 0.3111*P]$ where $P = (Fo^2 + 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[6] as implemented on the Viglen Pentium computer.

Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s

hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.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C(15)

(3a*S*, 9a*S*)-3a,4,9,9a-Tetrahydro-4-[(2*R*,4*S*)-3,5-dibenzyl-2-oxazolidinyl]-2-methyl-4,9[1',2']-benzeno-1H-benz[f]isoindole-1,3(2H)-dione 17

Crystal data for $C_{36}H_{32}N_2O_3$; M =540.64, crystallises from dichloromethane/pet ether as colourless blocks; crystal dimensions 0.45 x 0.32 x 0.21mm^3. Monoclinic, *a* = 10.3383(14), *b* = 9.6773(13), *c* = 14.613(2) Å, β = 108.054(2)° *U* = 1390.0(3) Å^3, *Z* = 2, D_c = 1.292 Mg/m^3, space group $P2_1$, Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-K_α) = 0.082 mm^{-1}, F(000) = 572.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 4364 reflections (θ range 1.47 < 27.53°),

Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega . Of the 15882 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections(minimum and maximum transmission coefficients 0.9640 and 0.9830) 2690 independent reflections exceeded the significance level |F|/σ(|F|) > 4.0 The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2(1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R= 0.0386 (wR_2=0.0935, for all 3373 data, 370 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.193 and 0.194 e.Å^{-3}.

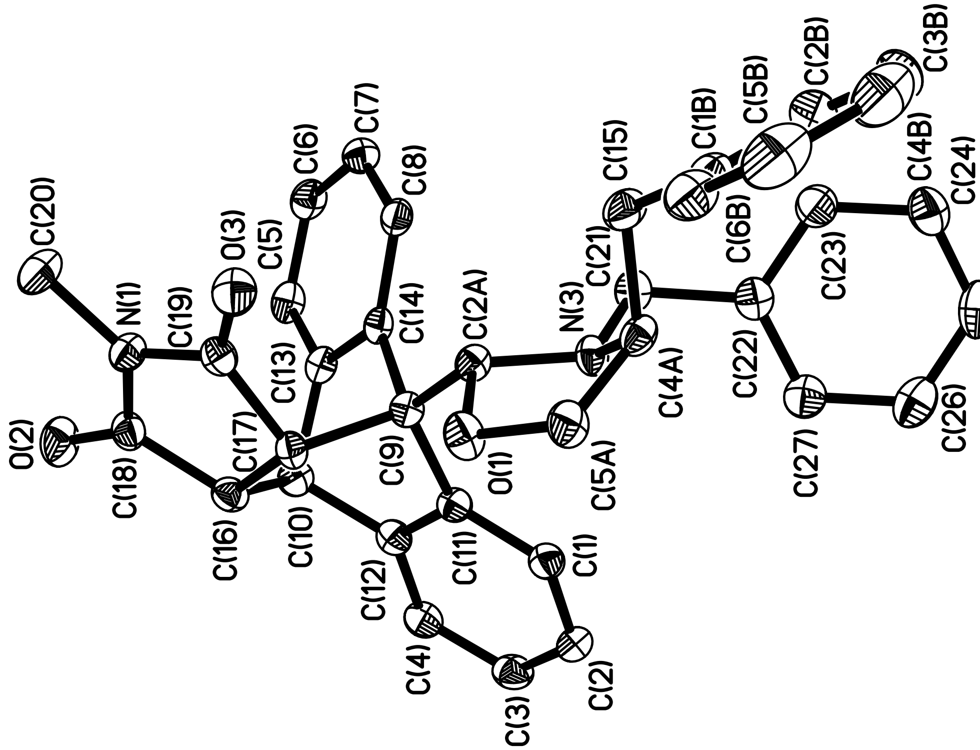
A weighting scheme $w = 1/[\sigma^2(Fo^2) +(0.0493*P)^2+0.00*P]$ where $P=(Fo^2+ 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[6] as implemented on the Viglen Pentium computer.

Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s

hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.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References

[1] Failli, A.; Nelson, V.; Immer, H.; Goetz, M. *Can. J. Chem.* **1973**, *51*, 2769.

[2] Karim, A.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G.; Siv, C. *J. Organomet. Chem.* **1986**, *317*, 93.

[3] Versleijen, J. P.; Sanders-Hovens, M. S.; Vanhommerig, S. A.; Vekemans, J. A.; Meijer, E. M. *Tetrahedron* **1993**, *49*, 7793.

[4] Hitchcock, S. R.; Nora, G. P.; Hedberg, C.; Casper, D. M.; Buchanan, L. S.; Squire, M. D.; West, D. X. *Tetrahedron* **2000**, *56*, 8799.

[5] Davoli, P.; Caselli, E.; Bucciarelli, M.; Forni, A.; Torre, G.; Prati, F. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1948.

[6] SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD.