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**X-ray Structural Determination of 16a**. Single crystals were grown from an 80:20 % EtOAc:hexanes solution of the compound. A single crystal of approximate dimensions 0.18 x 0.20 x 0.22 $mm^3$ was mounted under Paratone-8277 on a glass fiber, and immediately placed in a cold nitrogen stream at -80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in $\omega$ and exposure times of 30 sec/frame using a detector-to-crystal distance of 5.094 cm (maximum $2\theta$ angle of 56.52°). The total data collection time was approximately 12 hours. Frames were integrated to a maximum $2\theta$ angle of 46.5° with the Siemens SAINT program to yield a total of 4233 reflections, of which 2695 were independent ($R_{int}$ = 2.07 %, $R_{sig}$ = 4.20 %)[1] and 2262 were above $2\sigma(I)$. Laue symmetry revealed a triclinic crystal system, and the final unit cell parameters (at -80 °C) were determined from the least-squares refinement of three dimensional centroids of 2700 reflections.[2] Data were corrected for absorption with the SADABS[3] program.

The space group was assigned as $P\bar{1}$ and the structure was solved by using direct methods and refined employing full-matrix least-squares on $F^2$ (Siemens, SHELXTL[4], version 5.04). For a Z value of 2, there is one molecule in the asymmetric unit. All of the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. The structure refined to a goodness of fit (GOF)[5] of 1.024 and final residuals[6] of $R_1 = 4.13$ % ($I > 2\sigma(I)$), $wR_2 = 9.60$ % ($I > 2\sigma(I)$).

[1] $R_{int} = \sum\left|F_o^2 - F_o^2(\text{mean})\right| / \sum\left[F_o^2\right]$; $R_{sigma} = \sum\left[\sigma(F_o^2)\right] / \sum\left[F_o^2\right]$

[2] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10x the listed value.

[3] The SADABS program is based on the method of Blessing; see Blessing, R.H. *Acta Crystallogr., Sect A* 1995, **51**, 33.

[4] *SHELXTL: Structure Analysis Program, version 5.04*; Siemens Industrial Automation Inc.: Madison, WI, 1995.

[5] $GOF = \left[\Sigma\left[w(F_o^2 - F_c^2)^2\right]/(n-p)\right]^{1/2}$, where n and p denote the number of data and parameters

[6] $R_1 = (\Sigma\|F_o| - |F_c\|)/\Sigma|F_o|$; $wR_2 = \left[\Sigma\left[w(F_o^2 - F_c^2)^2\right]/\Sigma\left[w(F_o^2)^2\right]\right]^{1/2}$

where $w = 1/\left[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P\right]$ and $P = \left[(Max;0, F_o^2) + 2 \cdot F_c^2\right]/3$

**Table IS. Summary of Crystallographic Data for 16a.**

| **Crystal Parameters** | **16a** |
|---|---|
| chemical formula | $C_{23}H_{21}NO_3S$ |
| formula weight | 391.47 |
| cryst syst | Triclinic |
| space group (No.) | $P\bar{1}$ (#2) |
| $Z$ | 2 |
| $a$, Å | 9.9188 (3) |
| $b$, Å | 10.0498 (2) |
| $c$, Å | 11.8120 (4) |
| $\alpha$, deg | 68.321 (2) |
| $\beta$, deg | 66.002 (2) |
| $\gamma$, deg | 72.636 (1) |
| vol., Å$^3$ | 984.23 (5) |
| $\rho_{calc}$, g cm$^{-3}$ | 1.321 |
| cryst dimens, mm | $0.22 \times 0.20 \times 0.18$ |
| temp, °C | -80 |
| **Measurement of Intensity Data** | |
| diffractometer | Siemens SMART |
| radiation, $\lambda$ | Mo, 0.71073 |
| 2$\theta$ range, deg | 4-46.5 |
| data collected | $-9 \leq h \leq 11$, $-6 \leq k \leq 11$, $-11 \leq l \leq 13$ |
| no. of data collected | 4233 |
| no. of unique data | 2695 |
| agreement between equiv data, % | 2.07 |
| no. of observed data | 2262 ($I > 2\sigma(I)$) |
| no. of params varied | 253 |
| $\mu$, cm$^{-1}$ | 1.88 |
| absorption correction | empirical (SADABS) |
| range of trans. Factors | 0.93-0.72 |
| $R_1(F_o)$, $wR_2(F_o^2)$, ($I > 2\sigma(I)$) % | 4.13, 9.60 |
| $R_1(F_o)$, $wR_2(F_o^2)$ %, all data | 5.26, 10.22 |
| goodness of fit | 1.024 |

Table IIS. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 2585(1) | 8383(1) | 7326(1) | 35(1) |
| O(1) | 5153(2) | 10584(2) | 6578(2) | 39(1) |
| O(2) | 2252(2) | 7102(2) | 7296(2) | 48(1) |
| O(3) | 1822(2) | 9790(2) | 6792(2) | 50(1) |
| N(1) | 6344(2) | 8128(2) | 7027(2) | 30(1) |
| C(1) | 5331(3) | 9304(3) | 6687(2) | 31(1) |
| C(2) | 4528(2) | 8357(2) | 6484(2) | 30(1) |
| C(3) | 5667(2) | 7043(2) | 6969(2) | 28(1) |
| C(4) | 6621(2) | 6149(2) | 6057(2) | 29(1) |
| C(5) | 6255(3) | 4841(3) | 6259(3) | 45(1) |
| C(6) | 7048(4) | 4039(3) | 5389(3) | 56(1) |
| C(7) | 8222(3) | 4527(3) | 4323(3) | 56(1) |
| C(8) | 8591(3) | 5824(4) | 4116(3) | 60(1) |
| C(9) | 7790(3) | 6644(3) | 4972(2) | 47(1) |
| C(10) | 2319(2) | 8198(2) | 8938(2) | 29(1) |
| C(11) | 2390(3) | 6820(3) | 9808(2) | 38(1) |
| C(12) | 2146(3) | 6700(3) | 11079(3) | 45(1) |
| C(13) | 1828(3) | 7925(3) | 11468(3) | 46(1) |
| C(14) | 1761(3) | 9289(3) | 10597(2) | 41(1) |
| C(15) | 2015(2) | 9434(3) | 9321(2) | 35(1) |
| C(16) | 7691(2) | 7935(3) | 7338(2) | 35(1) |
| C(18) | 7366(2) | 7624(2) | 8775(2) | 28(1) |
| C(19) | 5997(3) | 8124(3) | 9594(2) | 35(1) |
| C(20) | 5785(3) | 7907(3) | 10873(2) | 39(1) |
| C(21) | 6935(3) | 7164(3) | 11366(2) | 40(1) |
| C(22) | 8298(3) | 6650(3) | 10563(2) | 40(1) |
| C(23) | 8523(3) | 6883(3) | 9275(2) | 35(1) |
| C(17) | 8465(3) | 9238(3) | 6551(2) | 52(1) |

Table IIIS. Bond lengths [A] and angles [deg] for 1.

| | |
|---|---|
| S(1)-O(3) | 1.436(2) |
| S(1)-O(2) | 1.437(2) |
| S(1)-C(10) | 1.757(2) |
| S(1)-C(2) | 1.770(2) |
| O(1)-C(1) | 1.210(3) |
| N(1)-C(1) | 1.355(3) |
| N(1)-C(16) | 1.466(3) |
| N(1)-C(3) | 1.475(3) |
| C(1)-C(2) | 1.541(3) |
| C(2)-C(3) | 1.558(3) |
| C(3)-C(4) | 1.498(3) |
| C(4)-C(5) | 1.378(3) |
| C(4)-C(9) | 1.378(3) |
| C(5)-C(6) | 1.379(4) |
| C(6)-C(7) | 1.370(4) |
| C(7)-C(8) | 1.367(4) |
| C(8)-C(9) | 1.381(4) |
| C(10)-C(15) | 1.386(3) |
| C(10)-C(11) | 1.388(3) |
| C(11)-C(12) | 1.384(4) |
| C(12)-C(13) | 1.377(4) |
| C(13)-C(14) | 1.379(4) |
| C(14)-C(15) | 1.381(3) |
| C(16)-C(17) | 1.513(3) |
| C(16)-C(18) | 1.518(3) |
| C(18)-C(19) | 1.384(3) |
| C(18)-C(23) | 1.392(3) |
| C(19)-C(20) | 1.378(3) |
| C(20)-C(21) | 1.381(3) |
| C(21)-C(22) | 1.377(4) |
| C(22)-C(23) | 1.383(3) |
| | |
| O(3)-S(1)-O(2) | 119.57(11) |
| O(3)-S(1)-C(10) | 108.86(11) |
| O(2)-S(1)-C(10) | 107.87(11) |
| O(3)-S(1)-C(2) | 107.22(11) |
| O(2)-S(1)-C(2) | 106.59(11) |
| C(10)-S(1)-C(2) | 105.94(10) |
| C(1)-N(1)-C(16) | 133.6(2) |
| C(1)-N(1)-C(3) | 96.5(2) |
| C(16)-N(1)-C(3) | 129.9(2) |
| O(1)-C(1)-N(1) | 133.9(2) |
| O(1)-C(1)-C(2) | 135.0(2) |
| N(1)-C(1)-C(2) | 91.1(2) |
| C(1)-C(2)-C(3) | 86.0(2) |
| C(1)-C(2)-S(1) | 119.1(2) |
| C(3)-C(2)-S(1) | 119.2(2) |
| N(1)-C(3)-C(4) | 117.4(2) |
| N(1)-C(3)-C(2) | 86.2(2) |
| C(4)-C(3)-C(2) | 116.0(2) |
| C(5)-C(4)-C(9) | 119.1(2) |
| C(5)-C(4)-C(3) | 119.0(2) |
| C(9)-C(4)-C(3) | 121.7(2) |
| C(4)-C(5)-C(6) | 120.5(3) |
| C(7)-C(6)-C(5) | 120.2(3) |
| C(6)-C(7)-C(8) | 119.6(3) |
| C(7)-C(8)-C(9) | 120.5(3) |
| C(4)-C(9)-C(8) | 120.1(3) |
| C(15)-C(10)-C(11) | 121.3(2) |
| C(15)-C(10)-S(1) | 119.2(2) |
| C(11)-C(10)-S(1) | 119.5(2) |
| C(12)-C(11)-C(10) | 118.5(2) |

| | |
|---|---|
| C(13)-C(12)-C(11) | 120.4(3) |
| C(12)-C(13)-C(14) | 120.6(2) |
| C(13)-C(14)-C(15) | 119.9(2) |
| C(14)-C(15)-C(10) | 119.2(2) |
| N(1)-C(16)-C(17) | 110.1(2) |
| N(1)-C(16)-C(18) | 112.7(2) |
| C(17)-C(16)-C(18) | 111.8(2) |
| C(19)-C(18)-C(23) | 118.4(2) |
| C(19)-C(18)-C(16) | 122.8(2) |
| C(23)-C(18)-C(16) | 118.6(2) |
| C(20)-C(19)-C(18) | 120.9(2) |
| C(19)-C(20)-C(21) | 120.4(2) |
| C(22)-C(21)-C(20) | 119.3(2) |
| C(21)-C(22)-C(23) | 120.6(2) |
| C(22)-C(23)-C(18) | 120.4(2) |

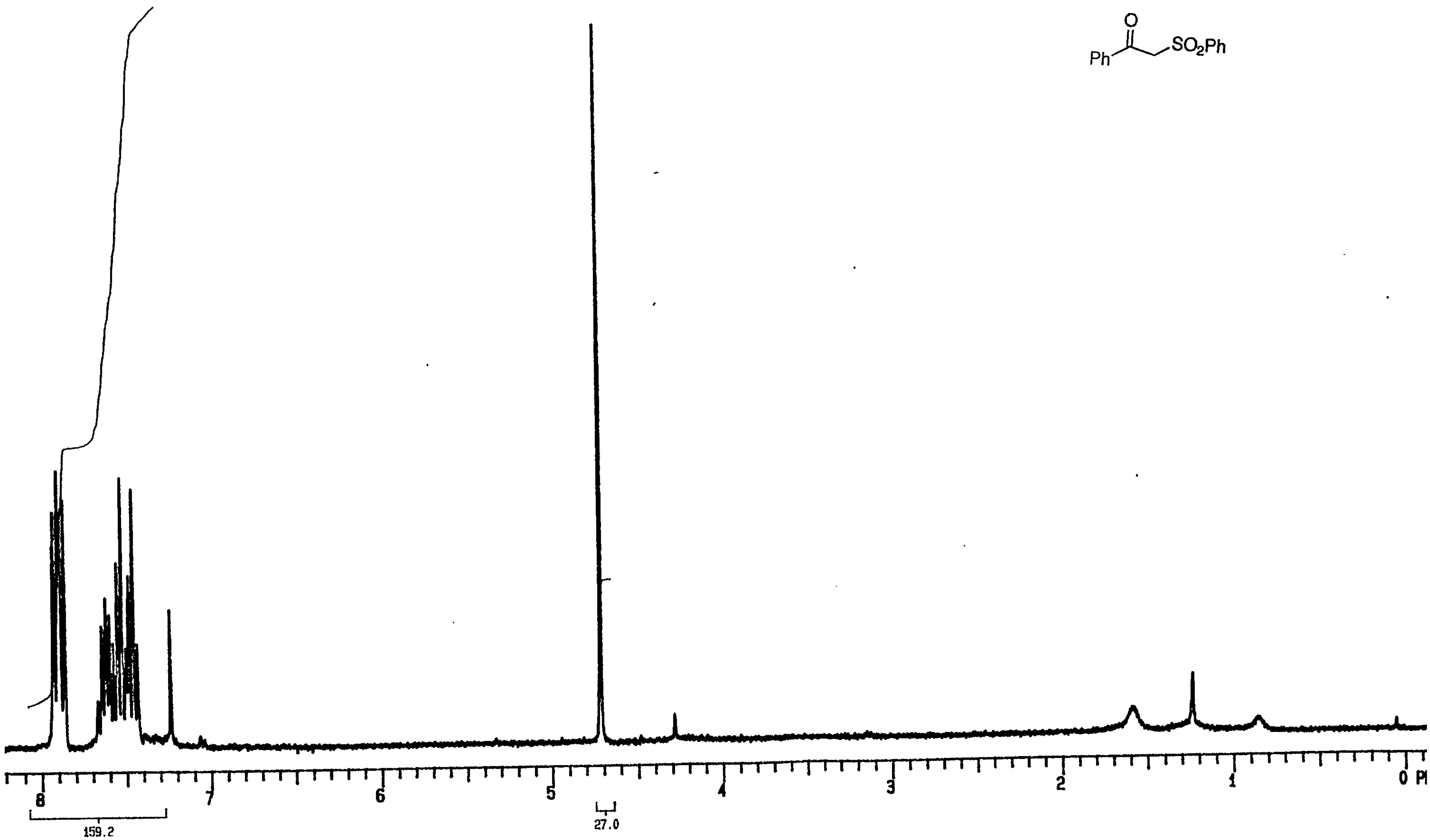
Symmetry transformations used to generate equivalent atoms:

Table IVS. Anisotropic displacement parameters (A^2 x 10^3) for 1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| S(1) | 29(1) | 47(1) | 38(1) | -16(1) | -17(1) | -7(1) |
| O(1) | 49(1) | 37(1) | 36(1) | -1(1) | -15(1) | -12(1) |
| O(2) | 40(1) | 65(1) | 57(1) | -31(1) | -14(1) | -20(1) |
| O(3) | 44(1) | 59(1) | 52(1) | -14(1) | -32(1) | 7(1) |
| N(1) | 28(1) | 38(1) | 31(1) | -11(1) | -13(1) | -9(1) |
| C(1) | 33(1) | 41(2) | 21(1) | -9(1) | -8(1) | -11(1) |
| C(2) | 31(1) | 38(1) | 24(1) | -8(1) | -12(1) | -9(1) |
| C(3) | 26(1) | 33(1) | 26(1) | -4(1) | -1(1) | -10(1) |
| C(4) | 28(1) | 35(1) | 26(1) | -7(1) | -13(1) | -8(1) |
| C(5) | 51(2) | 42(2) | 42(2) | -9(1) | -12(1) | -18(1) |
| C(6) | 70(2) | 43(2) | 69(2) | -26(2) | -30(2) | -6(2) |
| C(7) | 47(2) | 77(2) | 61(2) | -47(2) | -22(2) | 5(2) |
| C(8) | 48(2) | 96(3) | 49(2) | -42(2) | 3(1) | -28(2) |
| C(9) | 47(2) | 59(2) | 41(2) | -20(1) | -4(1) | -24(1) |
| C(10) | 20(1) | 36(1) | 36(1) | -11(1) | -1(1) | -9(1) |
| C(11) | 32(1) | 42(2) | 41(2) | -14(1) | -7(1) | -13(1) |
| C(12) | 42(2) | 48(2) | 40(2) | -4(1) | -11(1) | -16(1) |
| C(13) | 34(1) | 69(2) | 36(2) | -18(2) | -6(1) | -16(1) |
| C(14) | 34(1) | 52(2) | 45(2) | -24(1) | -11(1) | -8(1) |
| C(15) | 28(1) | 39(2) | 42(2) | -12(1) | -14(1) | -7(1) |
| C(16) | 25(1) | 52(2) | 35(1) | -16(1) | -12(1) | -7(1) |
| C(18) | 28(1) | 30(1) | 32(1) | -9(1) | -12(1) | -1(1) |
| C(19) | 26(1) | 50(2) | 34(1) | -13(1) | -14(1) | -6(1) |
| C(20) | 31(1) | 57(2) | 32(1) | -14(1) | -9(1) | -13(1) |
| C(21) | 48(2) | 47(2) | 30(1) | -2(1) | -18(1) | -19(1) |
| C(22) | 41(2) | 39(2) | 46(2) | -4(1) | -28(1) | -6(1) |
| C(23) | 28(1) | 35(1) | 47(2) | -14(1) | -17(1) | -2(1) |
| C(17) | 48(2) | 81(2) | 36(2) | -2(1) | -17(1) | -37(2) |

Table VS. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 4748(2) | 8537(2) | 5540(2) | 36 |
| H(3A) | 5175(2) | 6423(2) | 7851(2) | 34 |
| H(5A) | 5450(3) | 4490(3) | 7003(3) | 54 |
| H(6A) | 6779(4) | 3145(3) | 5531(3) | 68 |
| H(7A) | 8777(3) | 3967(3) | 3730(3) | 67 |
| H(8A) | 9406(3) | 6164(4) | 3376(3) | 72 |
| H(9A) | 8045(3) | 7551(3) | 4814(2) | 57 |
| H(11A) | 2601(3) | 5978(3) | 9537(2) | 45 |
| H(12A) | 2198(3) | 5766(3) | 11687(3) | 54 |
| H(13A) | 1654(3) | 7830(3) | 12345(3) | 55 |
| H(14A) | 1540(3) | 10129(3) | 10874(2) | 49 |
| H(15A) | 1982(2) | 10370(3) | 8714(2) | 42 |
| H(16A) | 8394(2) | 7071(3) | 7073(2) | 43 |
| H(19A) | 5193(3) | 8625(3) | 9270(2) | 42 |
| H(20A) | 4843(3) | 8270(3) | 11419(2) | 47 |
| H(21A) | 6786(3) | 7010(3) | 12248(2) | 48 |
| H(22A) | 9091(3) | 6130(3) | 10898(2) | 48 |
| H(23A) | 9473(3) | 6535(3) | 8729(2) | 42 |
| H(17A) | 8655(3) | 9405(3) | 5631(2) | 78 |
| H(17B) | 9418(3) | 9054(3) | 6695(2) | 78 |
| H(17C) | 7822(3) | 10098(3) | 6815(2) | 78 |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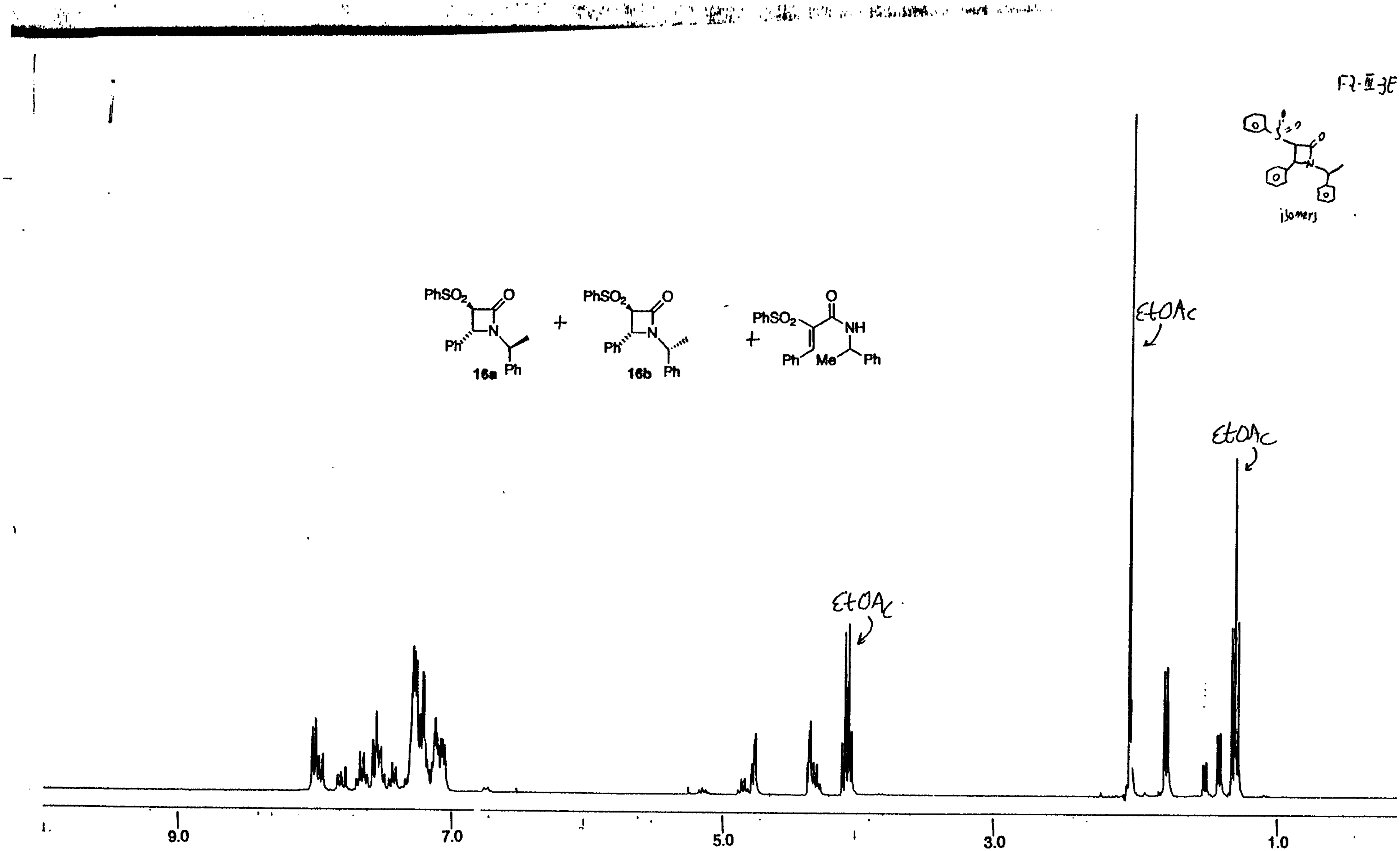
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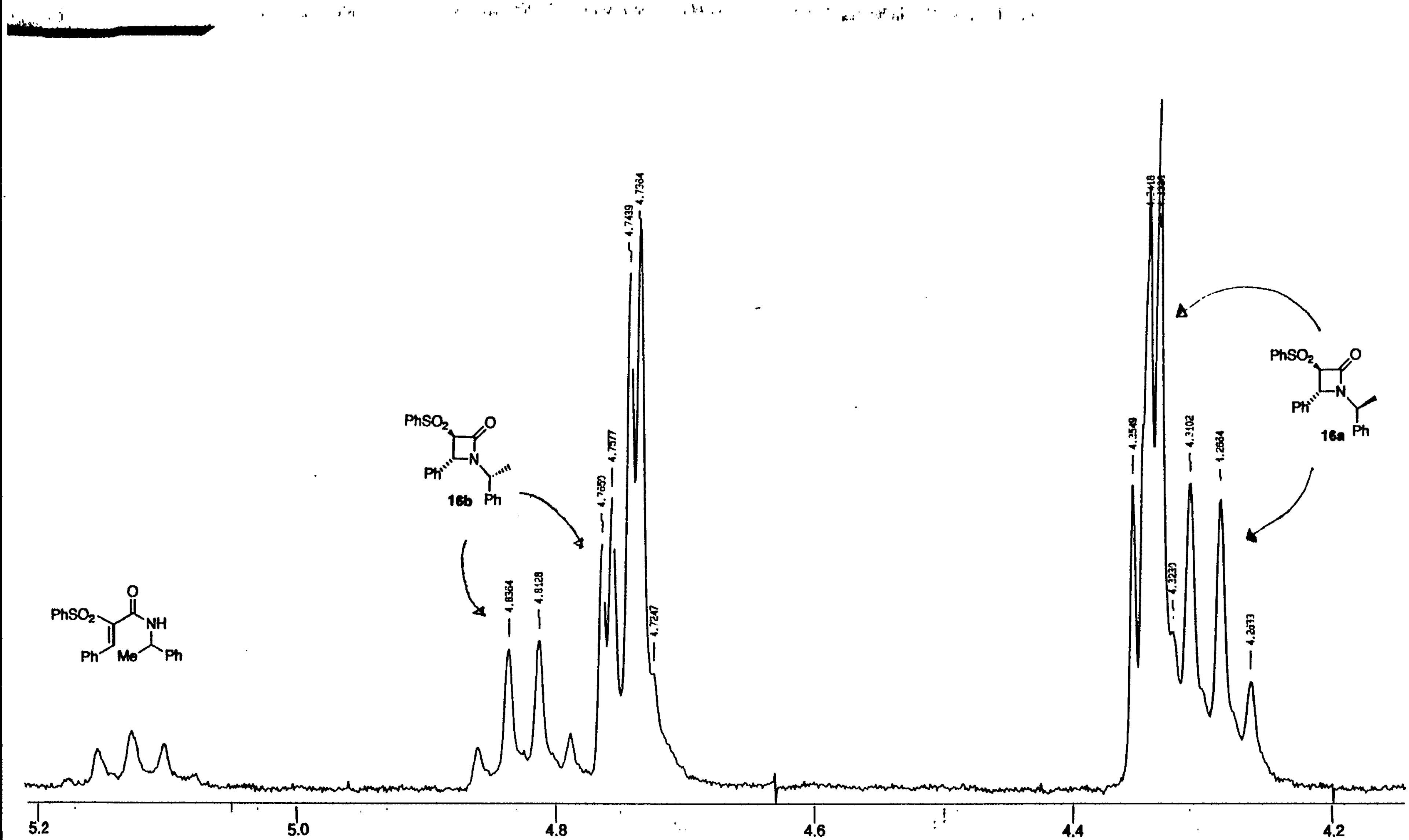
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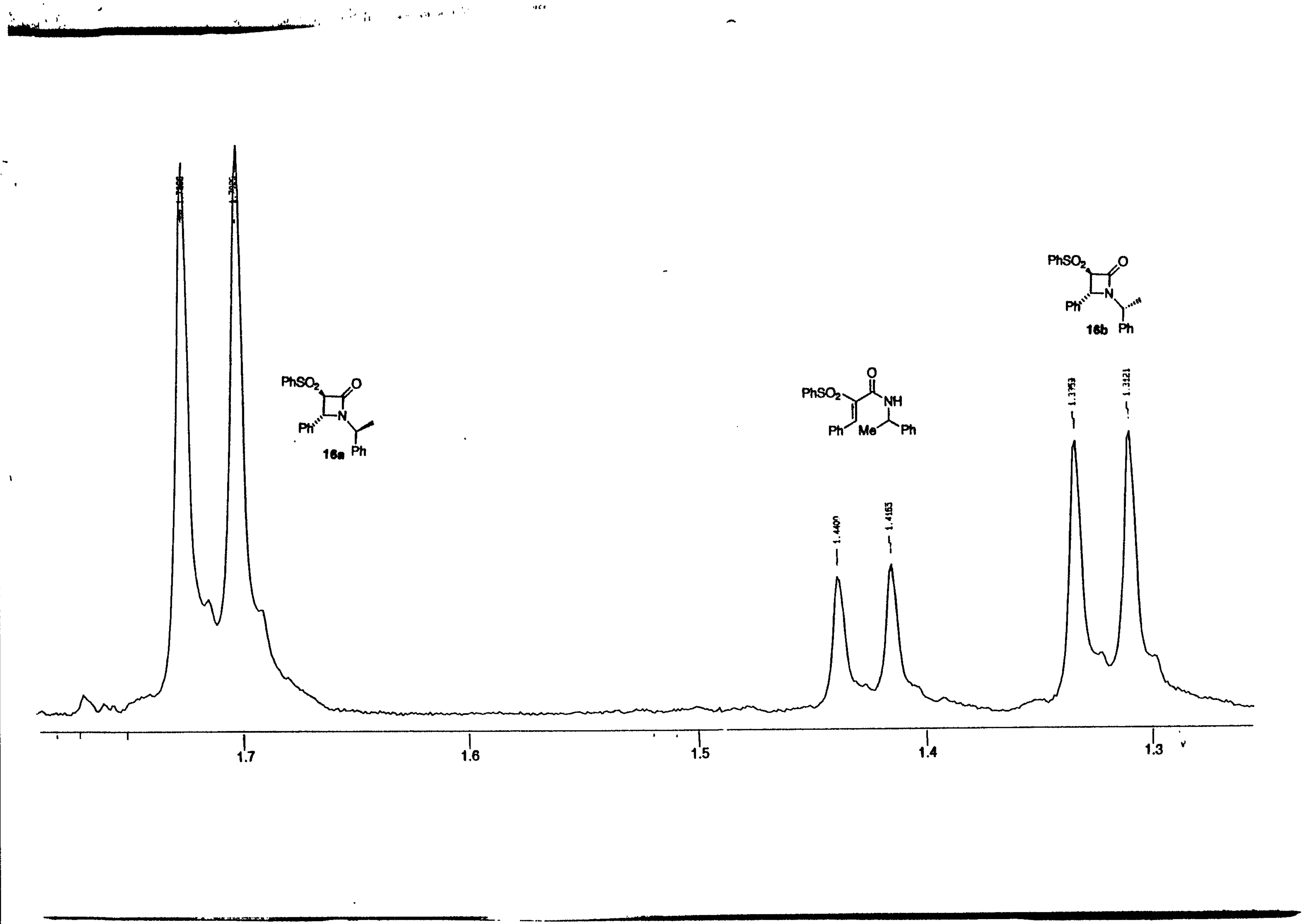

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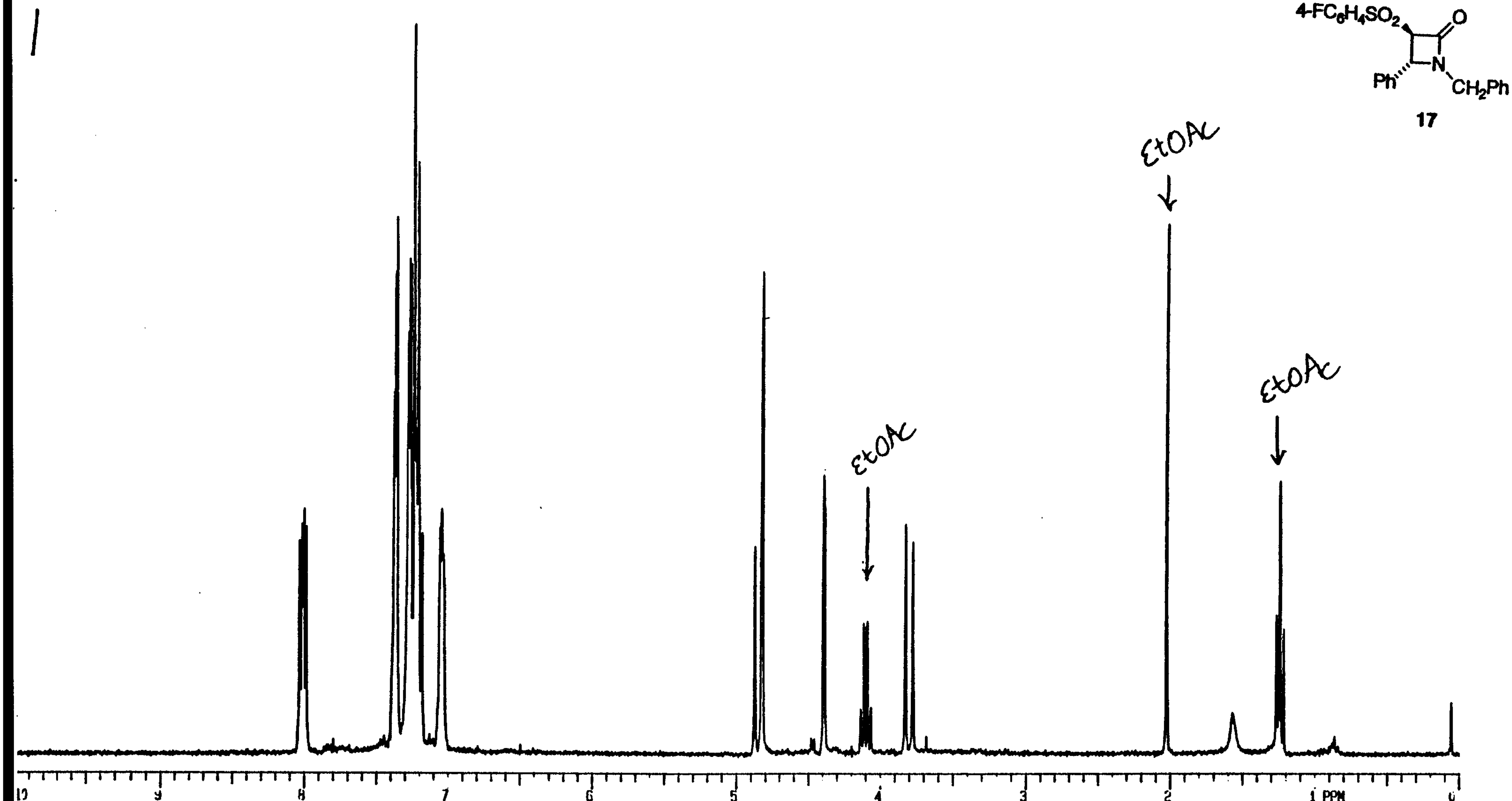
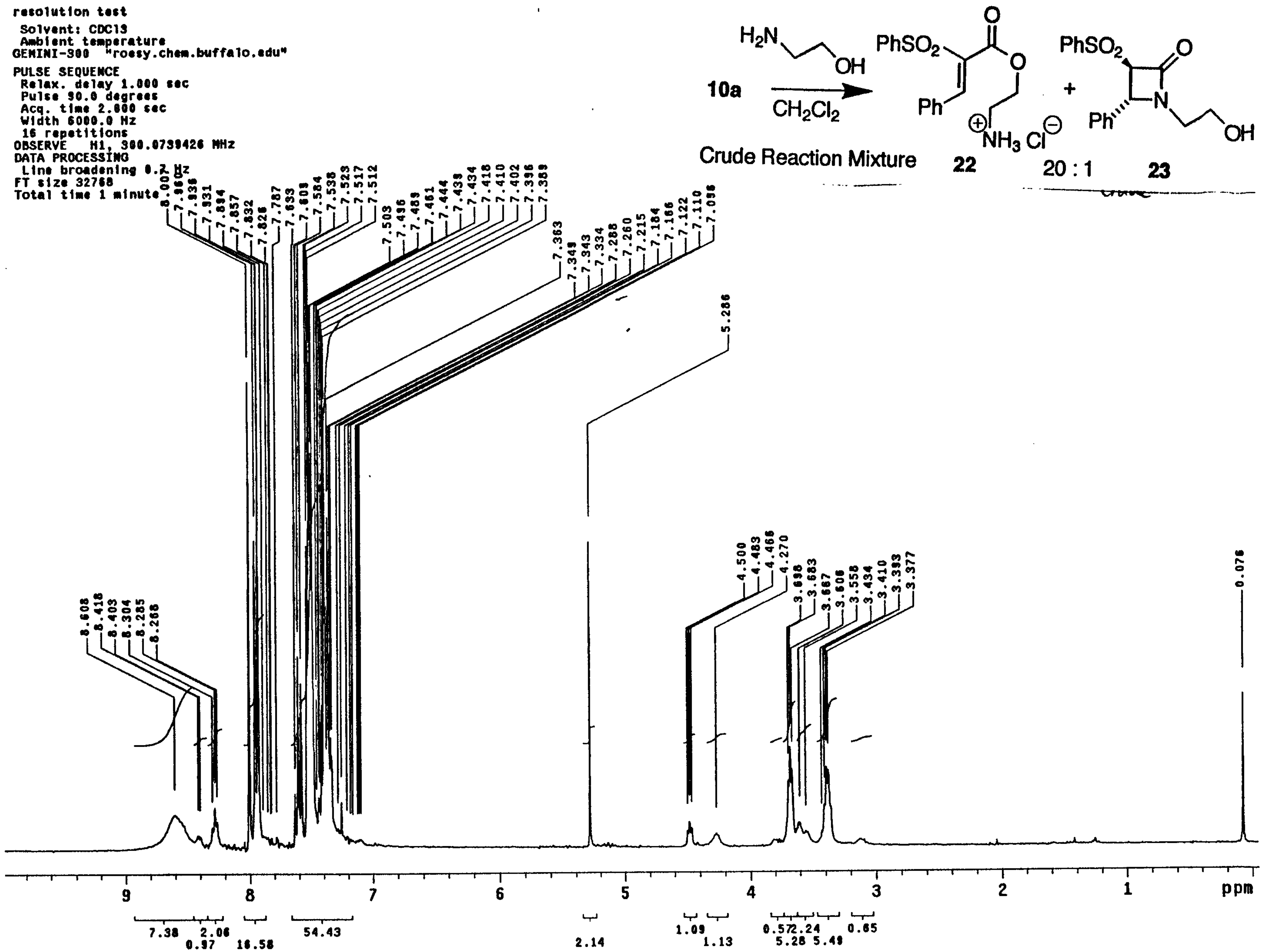
1.3



17



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Width 6000.0 Hz
16 repetitions
OBSERVE H1, 300.0739426 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 minute
10a
$CH_2Cl_2$
Crude Reaction Mixture
22
20 : 1
23
ppm

```
resolution test
 Solvent: CDCl3
 Ambient temperature
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PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 2.000 sec
 Width 6000.0 Hz
 16 repetitions
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Total time 1 minute
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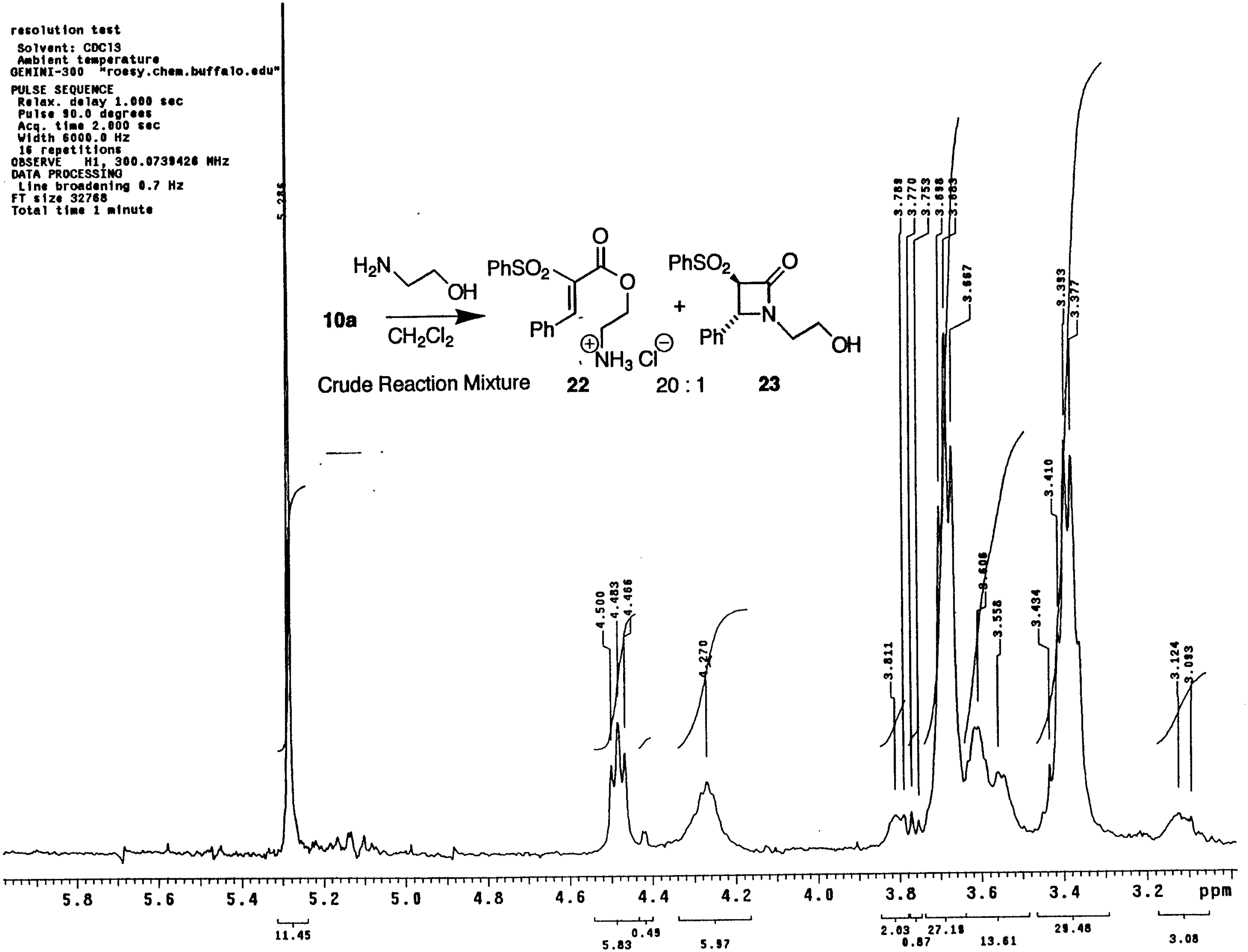

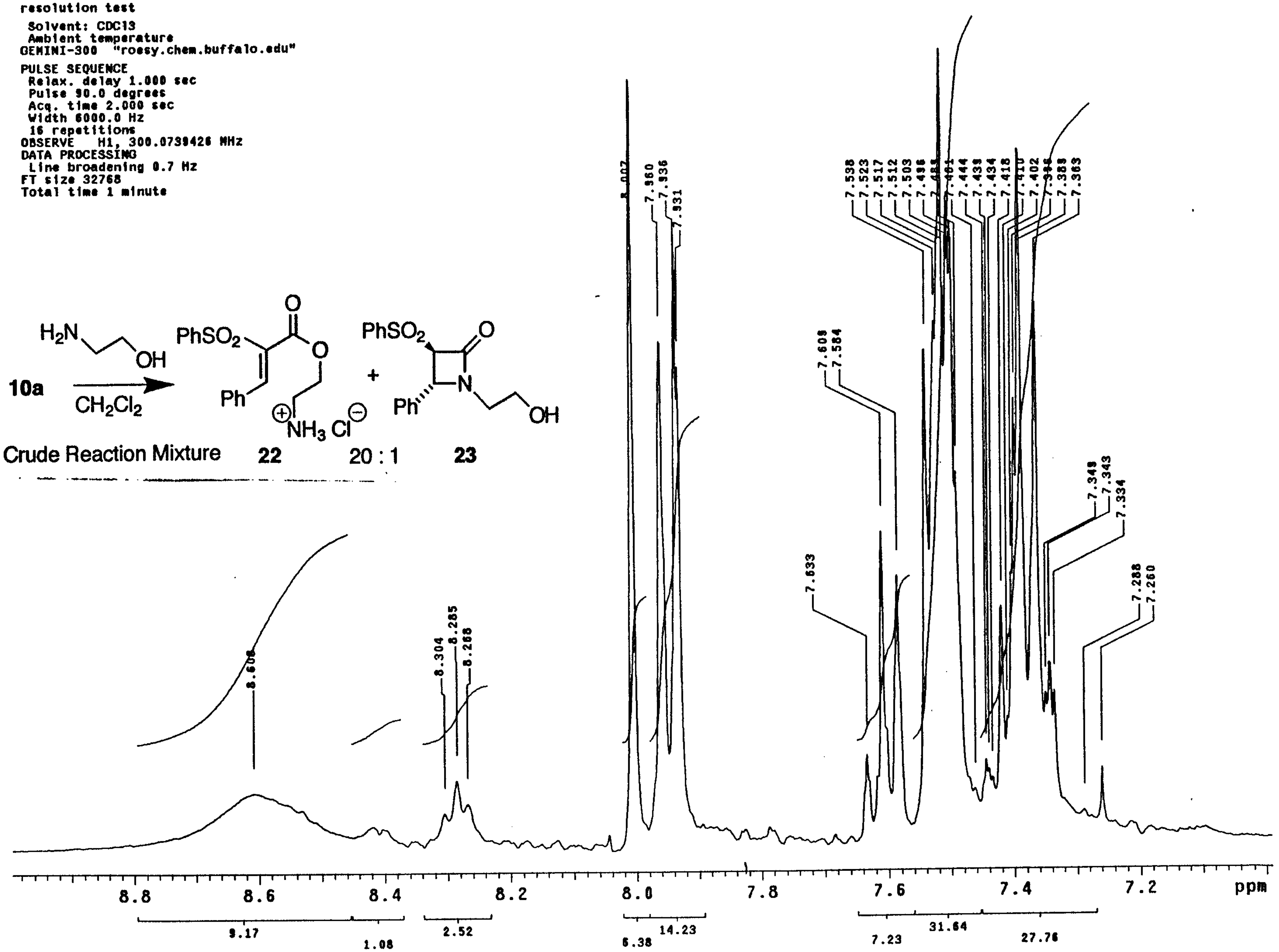

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Solvent: CDCl3
Ambient temperature
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Pulse 90.0 degrees
Acq. time 2.000 sec
Width 6000.0 Hz
16 repetitions
OBSERVE H1, 300.0739426 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 32768
Total time 1 minute
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OH
$CH_2Cl_2$
$PhSO_2$
Ph
$NH_3$ Cl
+
OH
Crude Reaction Mixture
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20 : 1
23
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7.388
7.383
7.363
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8.8
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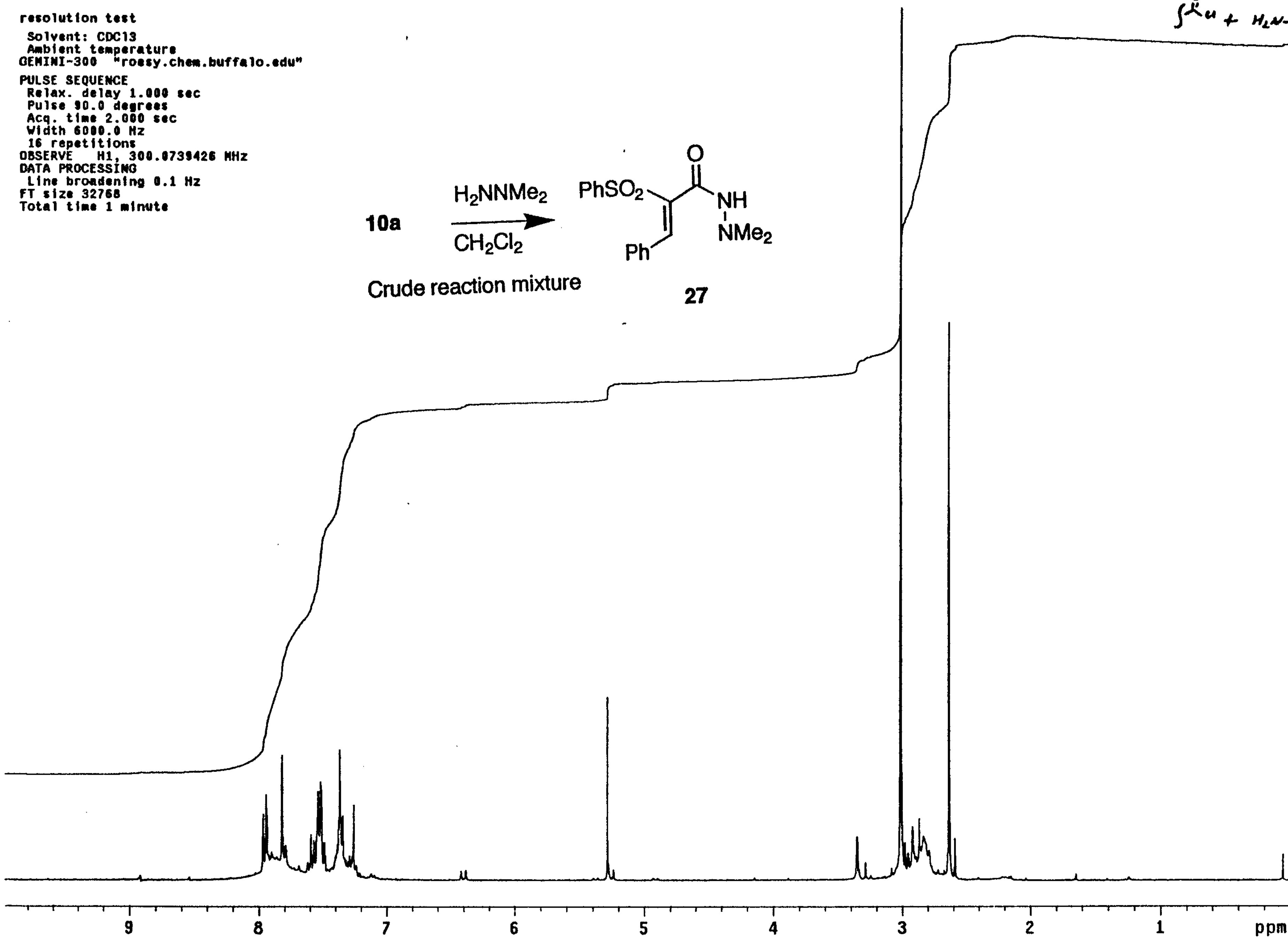
27.76

FZ-III-75 crude



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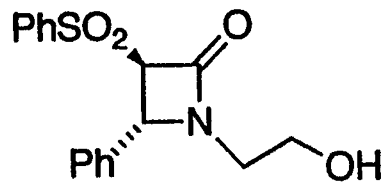
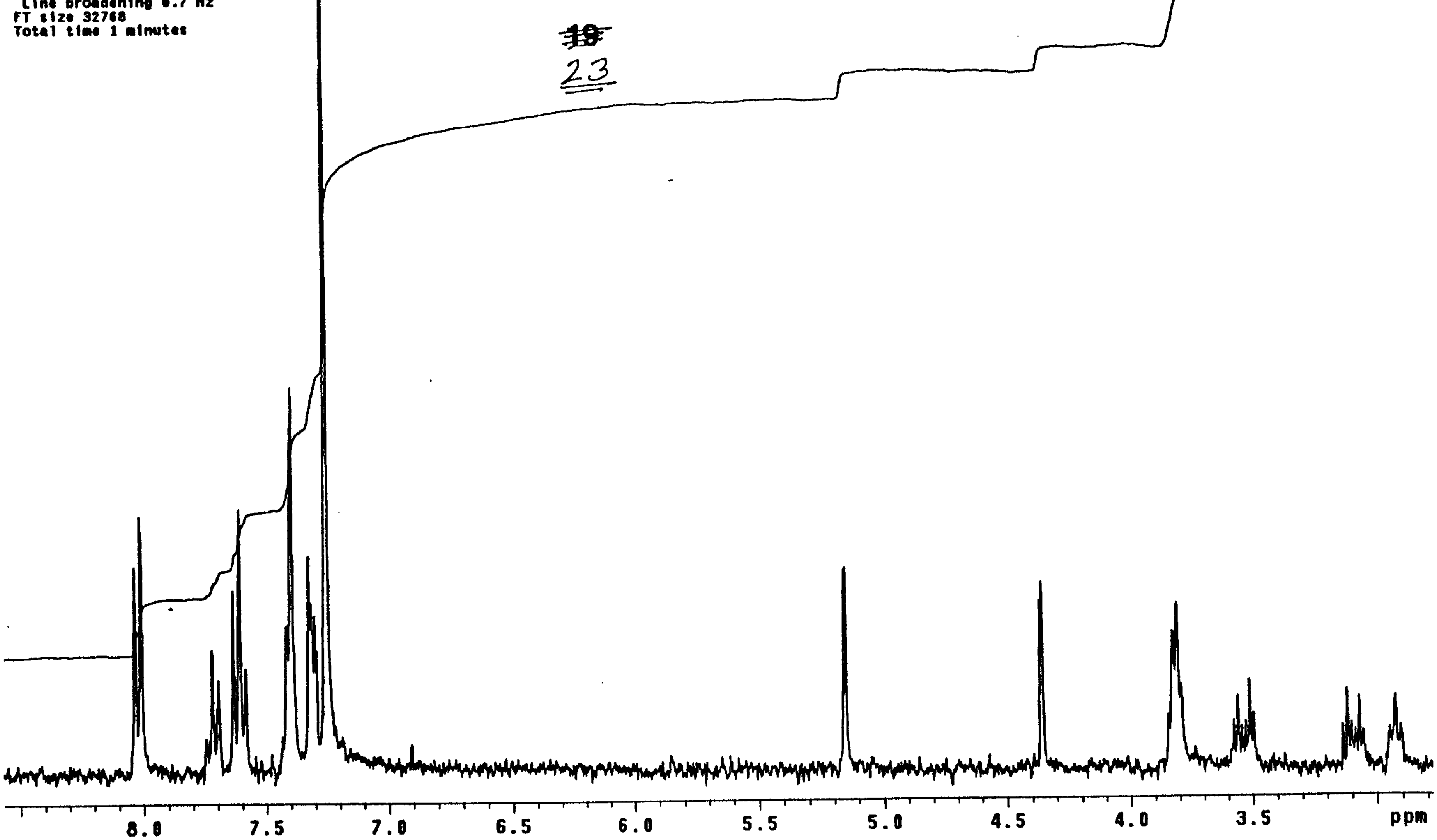
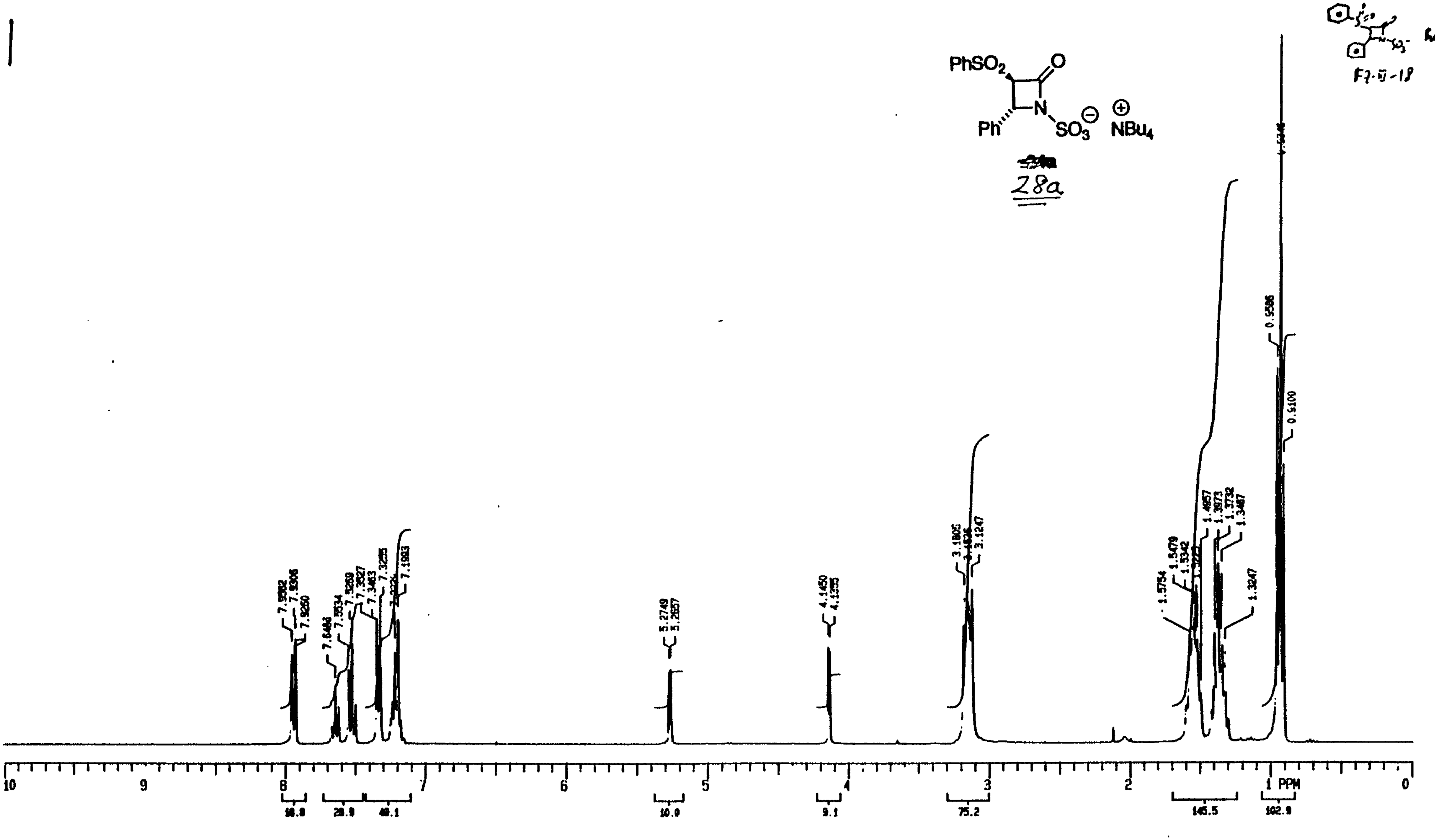
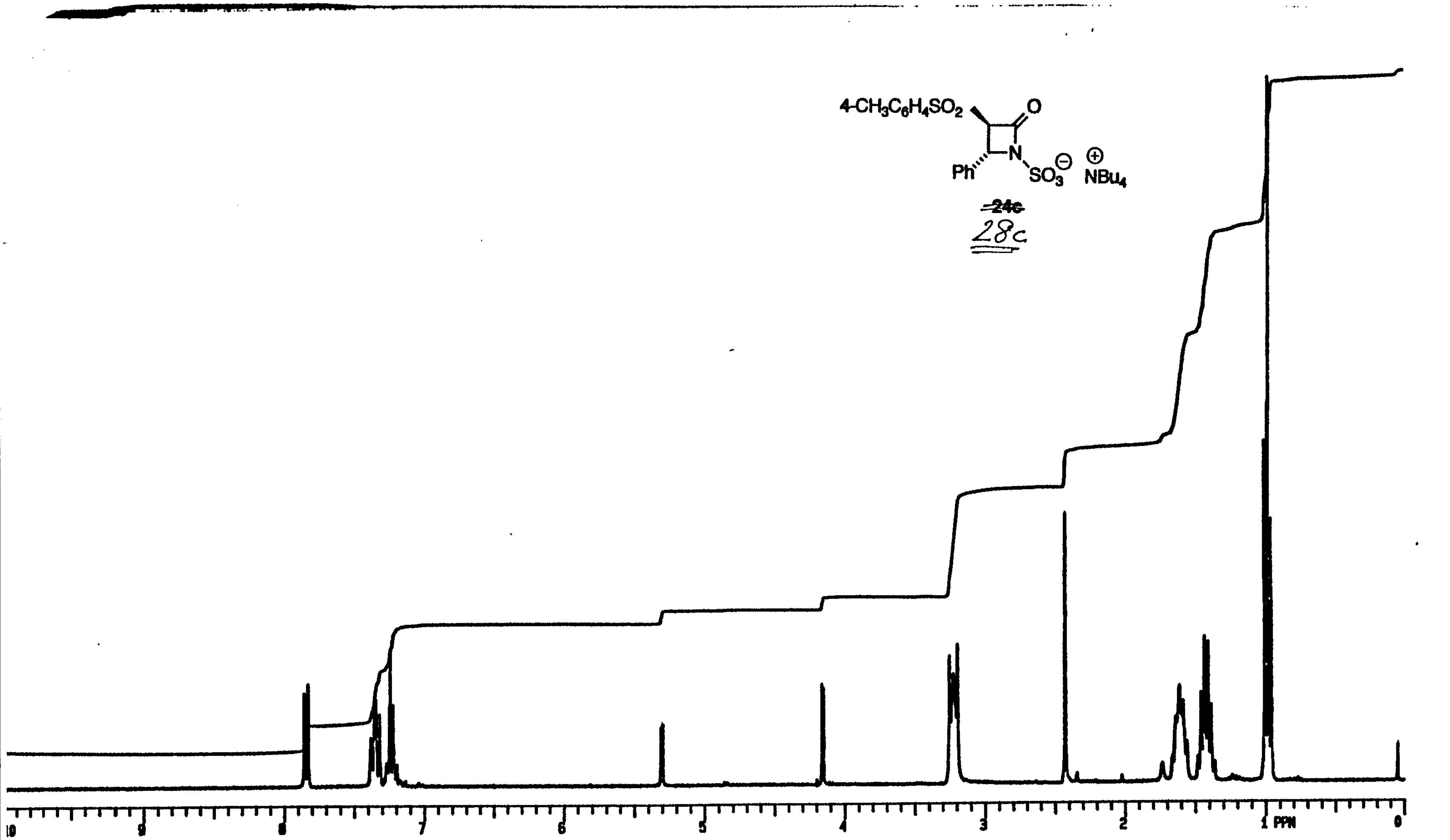
GEMINI-300 "roesy.chem.buffalo.edu"
PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 2.000 sec
Width 6000.0 Hz
16 repetitions
OBSERVE H1, 300.0739426 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 32768
Total time 1 minutes



~~19~~
23




PhSO2
O
N
Ph
SO3
NBu4
28a
PPM
10
9
8
7
6
5
4
3
2
1
0


4-CH3C6H4SO2
O
N
Ph
SO3
NBu4
~~24c~~
28c
10
9
8
7
6
5
4
3
2
1 PPM
0