

# An Investigation of the Scope and Regiochemistry of Alkynylboronate Cycloadditions with Sydnone

Duncan L. Browne,<sup>†</sup> Jerome F. Vivat,<sup>†</sup> Andrew Plant,<sup>‡</sup> Enrique Gomez-Bengoa,<sup>\*,‡</sup> Joseph P. A.  
Harrity<sup>\*,†</sup>

<sup>‡</sup>*Departamento de Química Orgánica I, Facultad de Química, Universidad del País Vasco, San Sebastián, Spain, †Department of  
Chemistry, University of Sheffield, Sheffield, S3 7HF, U. K.,*

<sup>‡</sup>*Research Chemistry, Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire, RG42 6EY, U.K. and Syngenta  
Crop Protection AG, Schaffhauserstrasse, 4332 Stein, Switzerland.*

## SUPPORTING INFORMATION: REGIOCHEMISTRY

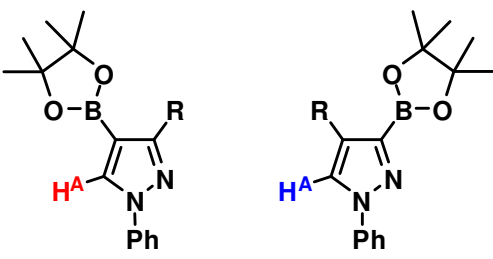
### On the Assignment of Regiochemistry

Regiochemical assignment of <b>10a</b> by nOe	RC1
Regiochemical assignment of <b>10b</b> by nOe	RC4
Regiochemical assignment of <b>13</b> by nOe	RC5
Regiochemical assignment of <b>13</b> by nOe	RC6
Regiochemical assignment of <b>21</b> by nOe	RC8
Regiochemical assignment of <b>22</b> by nOe	RC10
Regiochemical assignment of <b>23</b> by nOe	RC11
Regiochemical assignment of <b>25</b> by nOe	RC13
Regiochemical assignment of <b>27</b> by nOe	RC16
Regiochemical assignment of <b>29</b> by nOe	RC18
Regiochemical assignment of <b>31a/b</b> by nOe	RC21
Regiochemical assignment of <b>35</b> by nOe	RC23
Regiochemical assignment of <b>36</b> by nOe	RC25

## On the Assignment of Regiochemistry

**Evidence for the assigned regioselectivity in Table 1:** the isomeric identity of compound **11** was assigned by X-ray crystallography (CCDC 656450). The regiochemistry of compounds **10a** and **10b** was assigned by nOe studies. The regioselectivity of **8a/b** and **9a/b** were assigned by correlation of their C-5 proton shift (SI Table 1). The regiochemistry of benzyl protected pyrazole **13** was assigned by nOe studies and the isomeric identity of **12** was assigned by correlation with these observed regiochemistries.

SI Table 1

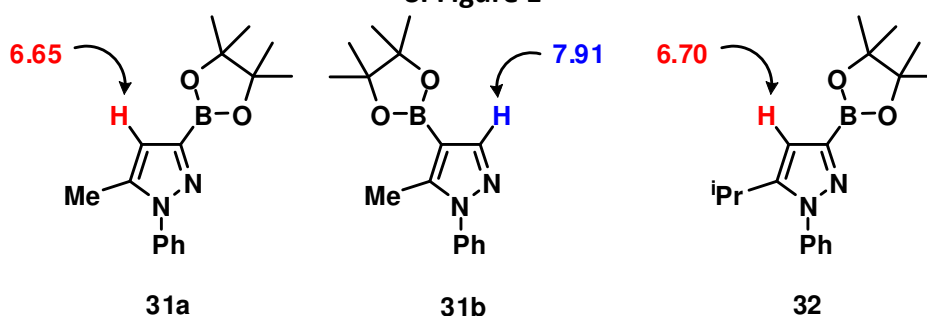


R	$H^A$ $\delta$ shift (PPM)	$H^A$ $\delta$ shift (PPM)
Ph	8.32	-
TMS	8.30	7.82
$^n$ Bu	8.05	7.65
H	8.17 & 7.91 (d, J = 0.5)	7.84 & 6.77 (d, J = 2.5)

**Evidence for the assigned regioselectivity in Table 2:** Regiochemistry for a range of tetra-substituted pyrazoles was assigned by nOe, **21**, **22**, **23**, **25**, **27** and **29**. The remainder have been assigned based on the assumption of an analogous regiochemical insertion pattern.

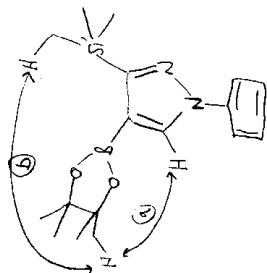
Molecules **31a/b** can be assigned on the basis of their diagnostic pyrazole-H shift, nOe analysis of the mixture confirms our assignment. The *iso*-propyl analogue **32** is assigned by chemical shift analogy (SI figure 1).

SI Figure 1

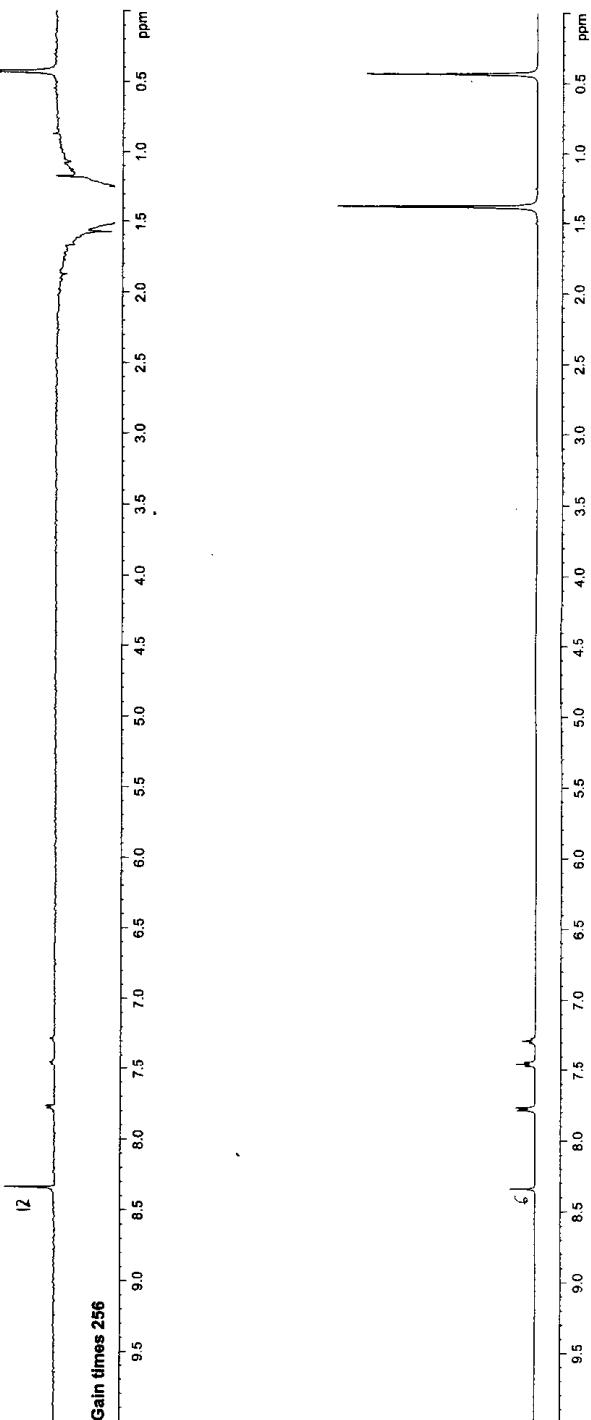


**Evidence for the assigned regioselectivity in Table 3:** The isomeric identity of the 5,5 bicyclic pyrazole boronic ester **35** has been confirmed by nOe, so too has that of the 6,5 bicycle **36**. The 6,5 bicyclic system **37** is assigned based on the assumption of an analogous regiochemical insertion pattern. Tri-substituted bicycle **38** is assigned based on chemical shift (6.40 ppm, cf. SI figure 1).

The regiochemistry of 5-iodo-4-boronic ester pyrazoles **43** and **44** was assigned based on the assumption of an analogous regiochemical insertion pattern to other tetrasubstituted pyrazoles. Nonetheless, this was ultimately confirmed in the case of pyrazole **44** by means of a chemical transformation to pyrazole **45** which gave a diagnostic C-5 H-signal at 8.41 ppm (cf SI table 1).

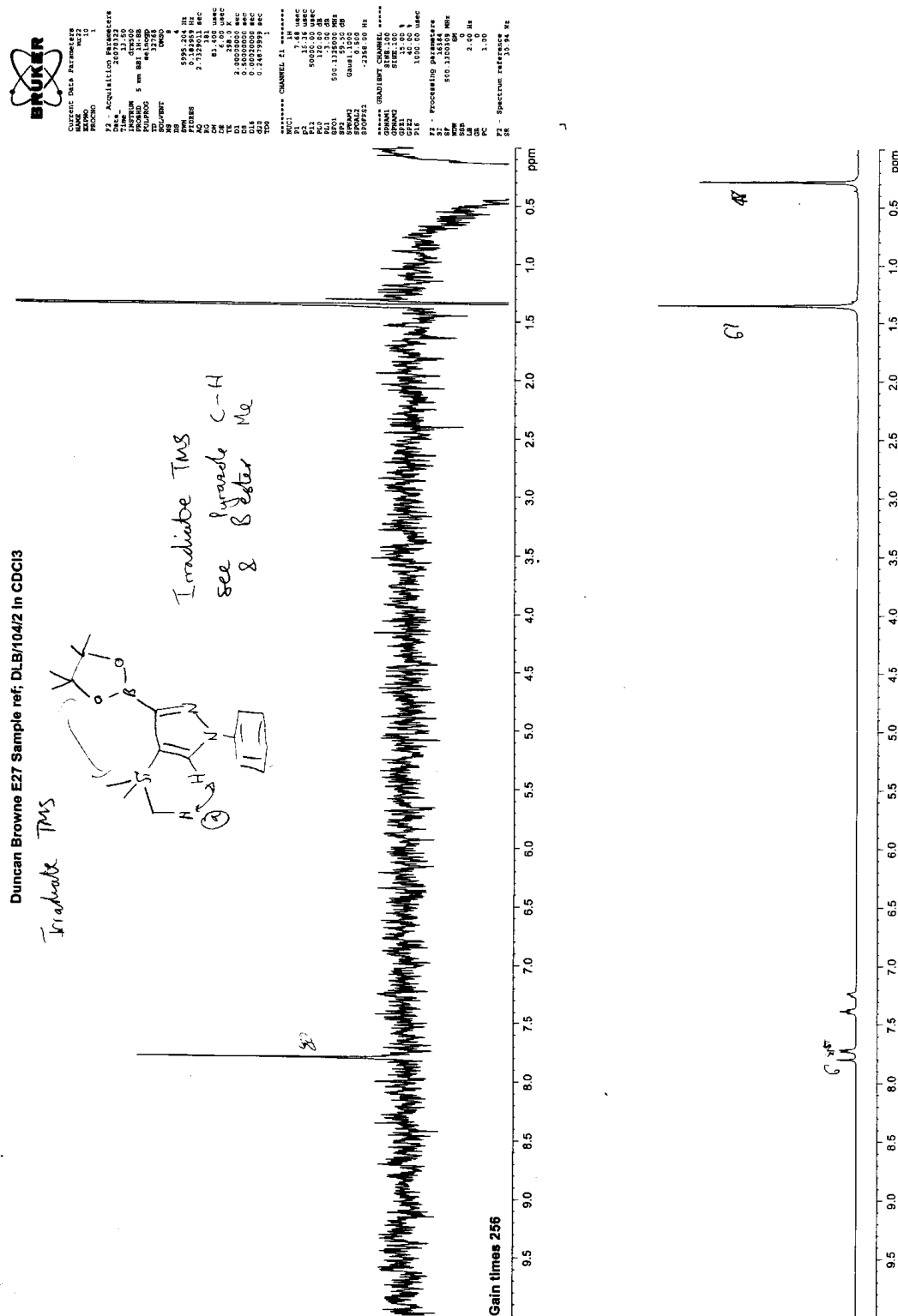
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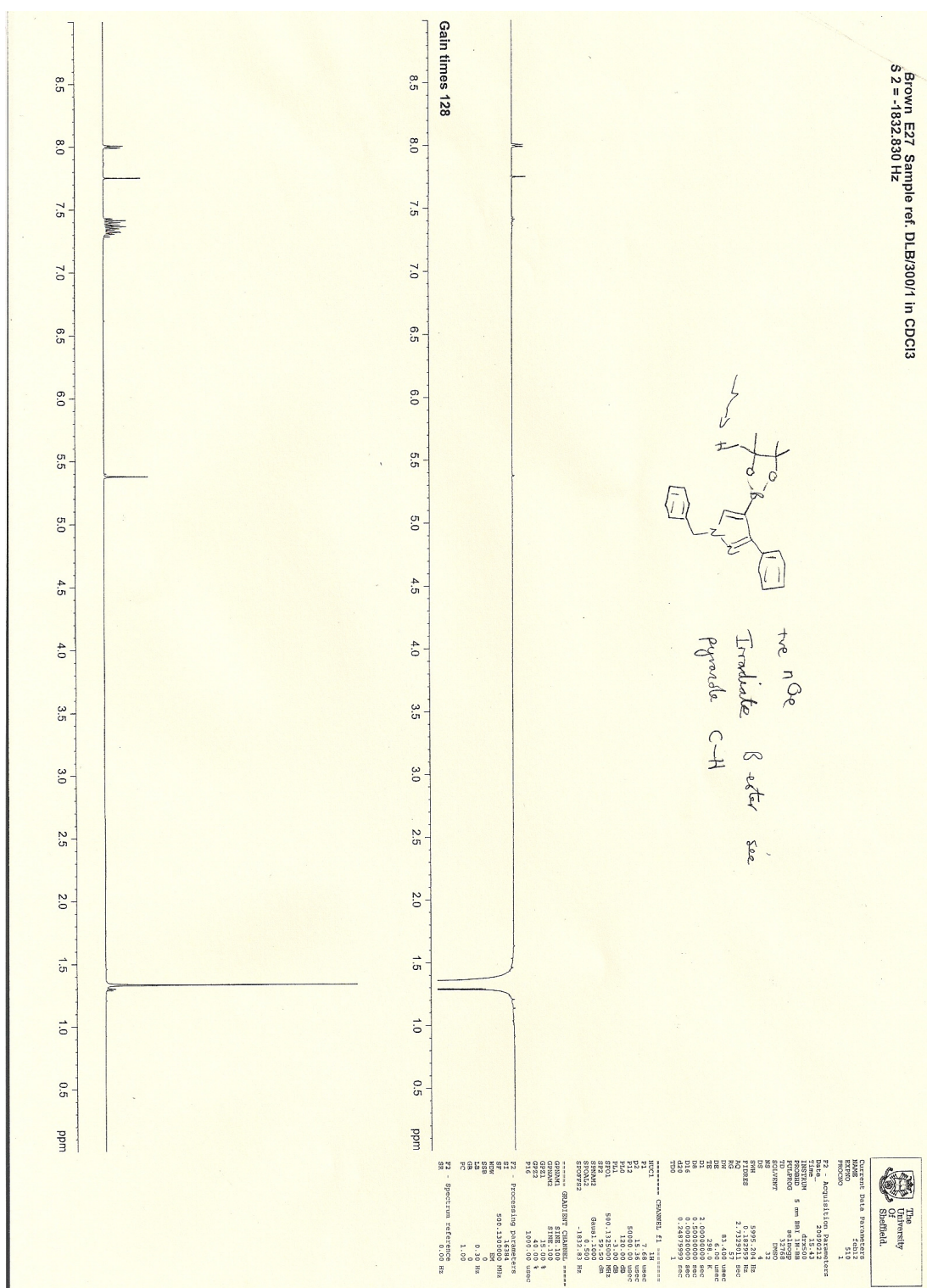
Irradiate before  $\mu$ ,  
see TMS & pyrazole  
C-4

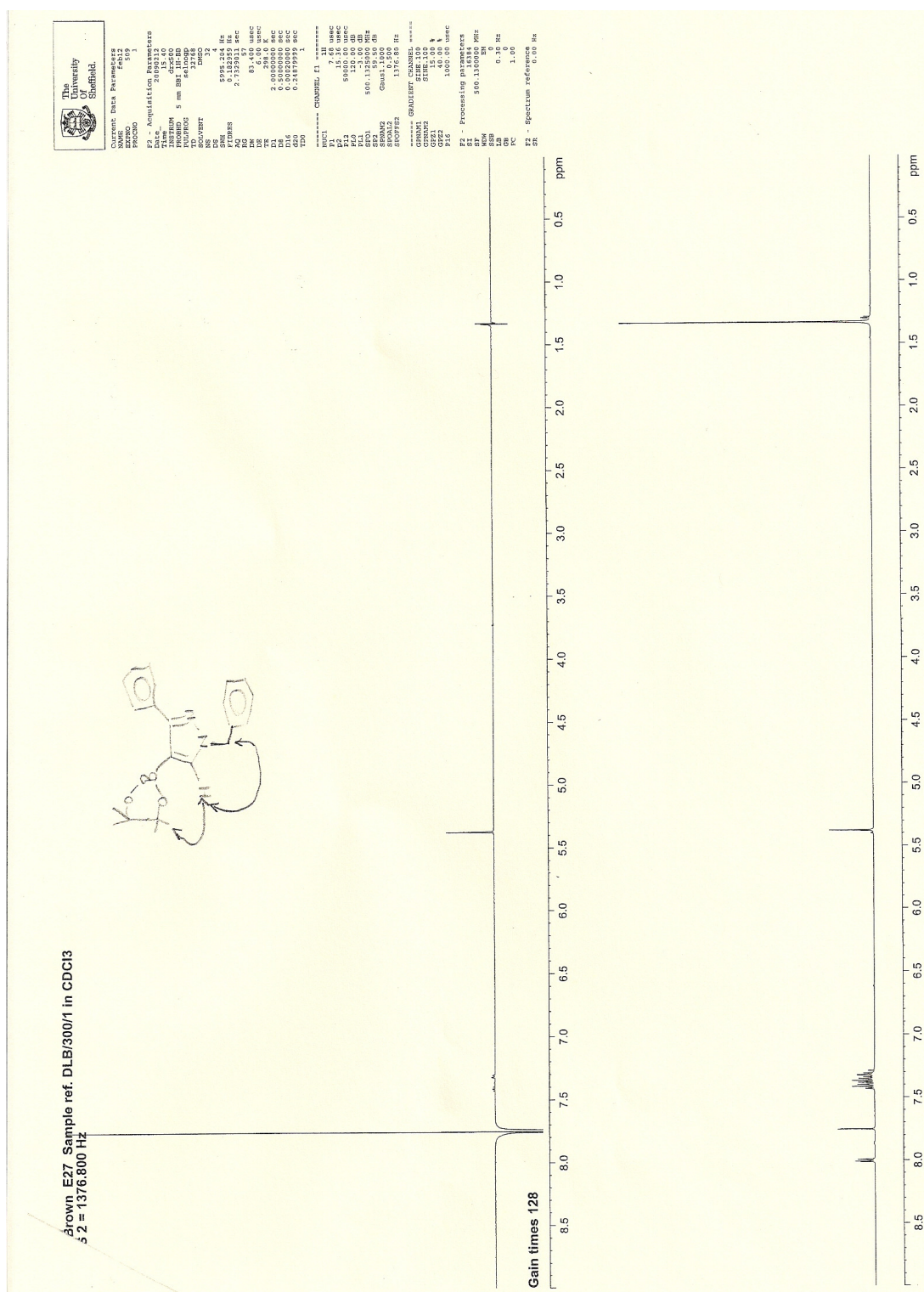




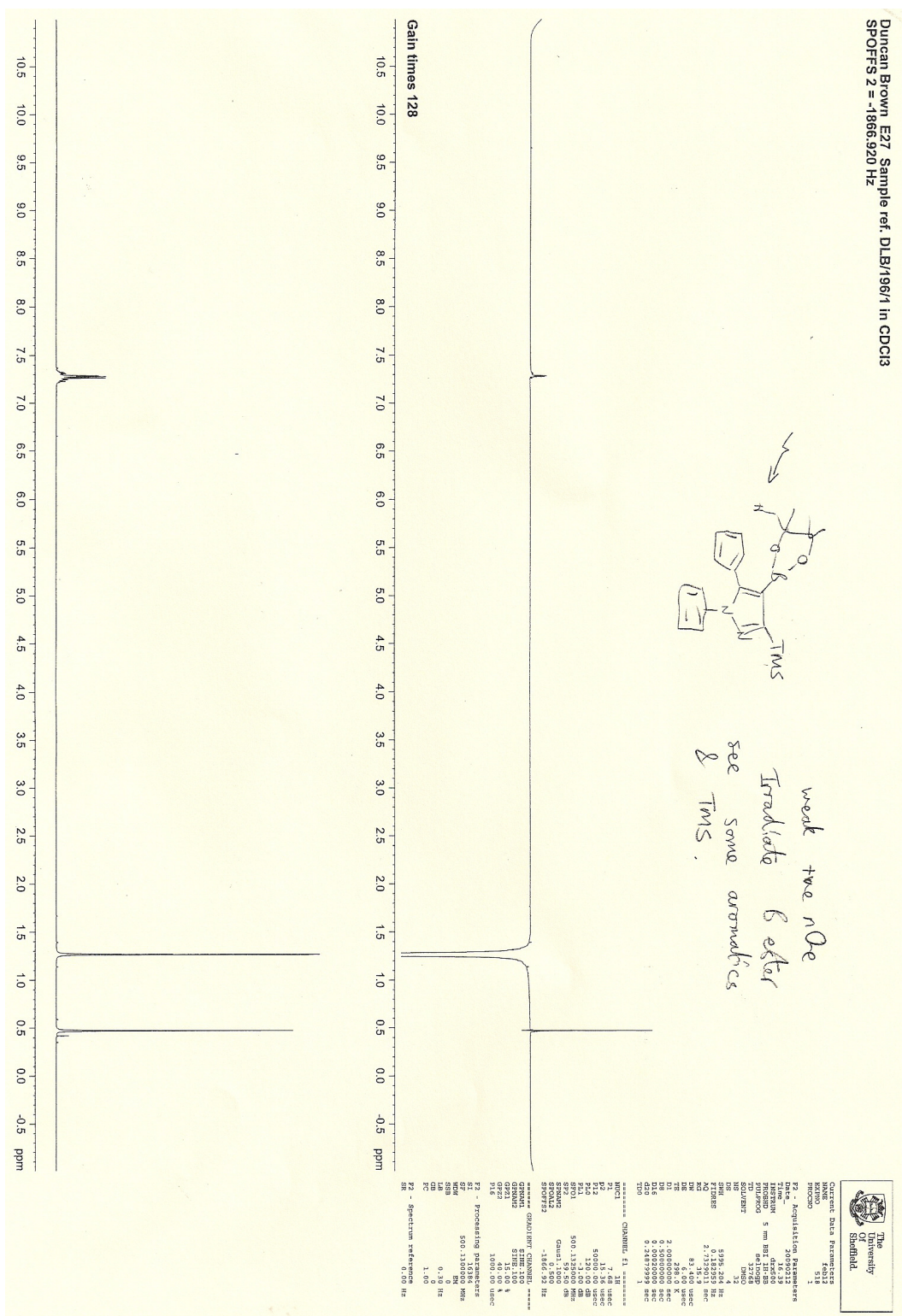
Regiochemical assignment of **10b** by nOe.

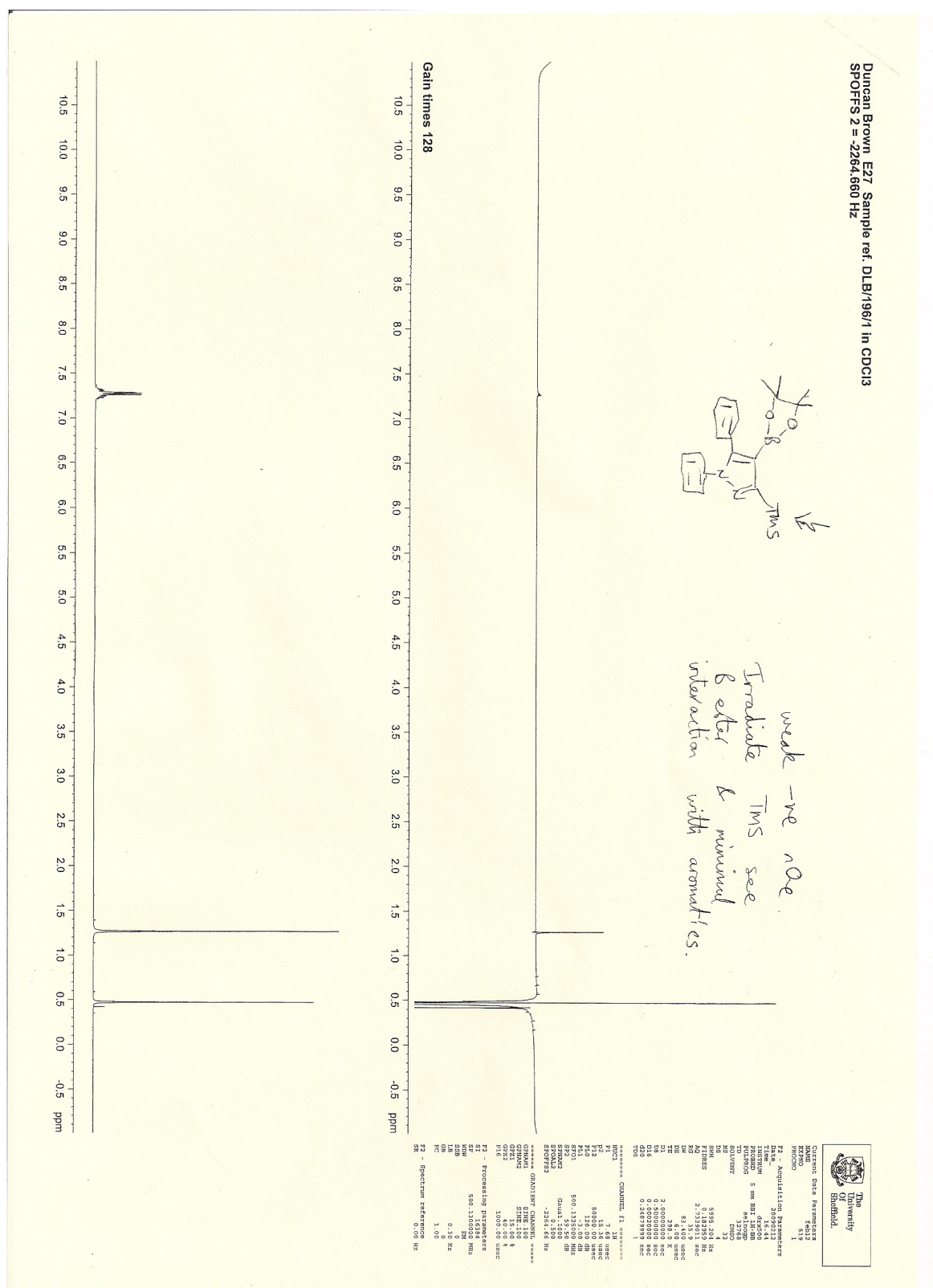


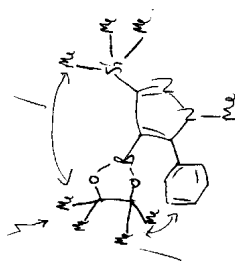
Regiochemical assignment of **13** by nOe

Regiochemical assignment of **13** by nOe

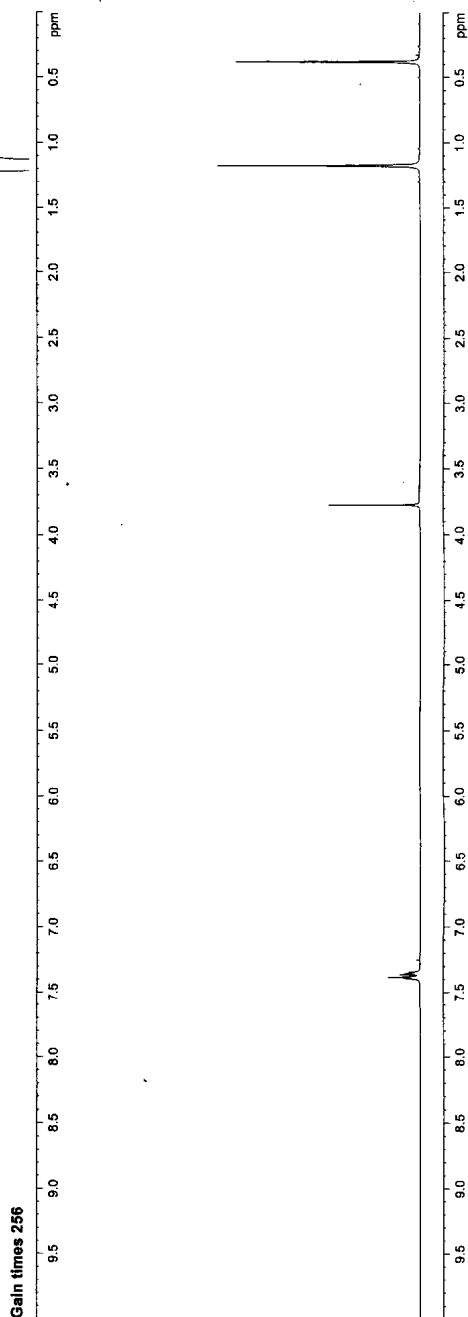
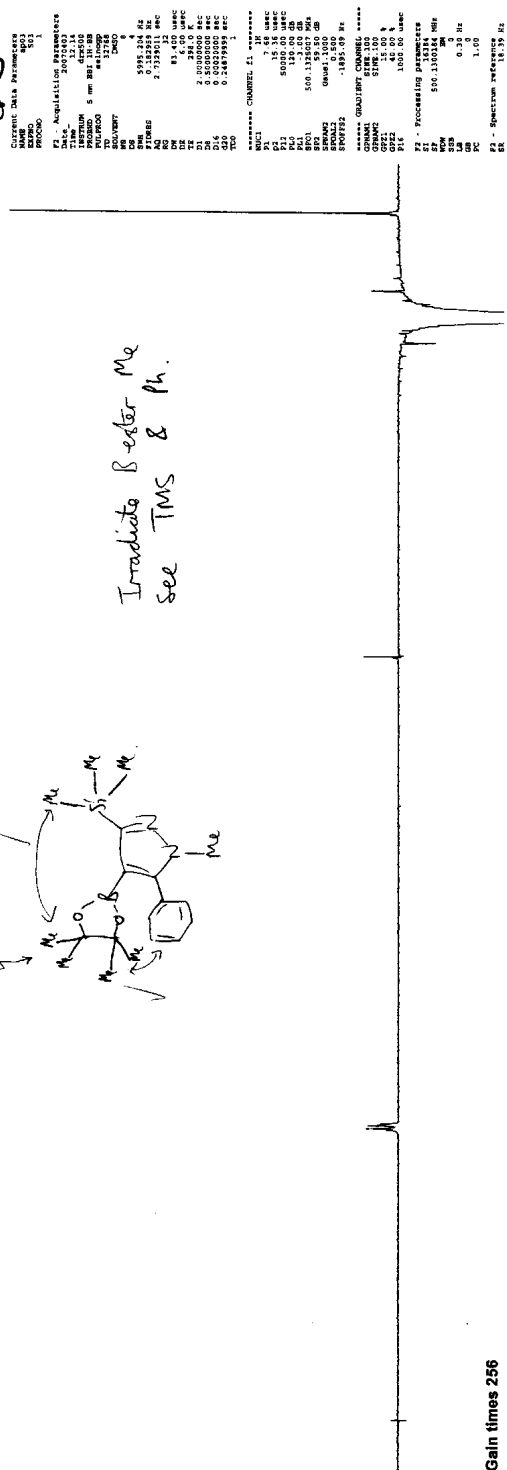


Regiochemical assignment of **21** by nOe

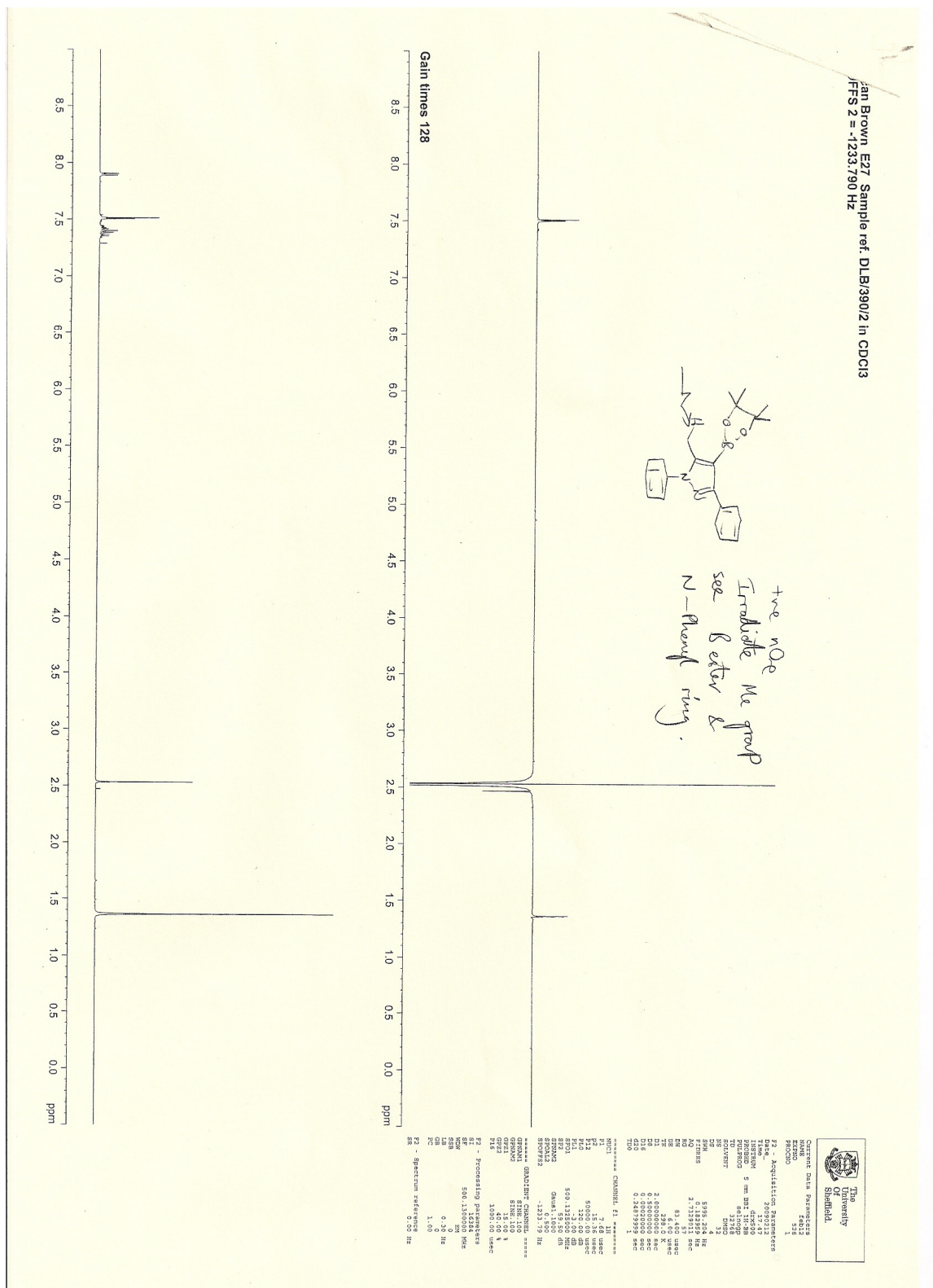
Regiochemical assignment of **21** by nOe

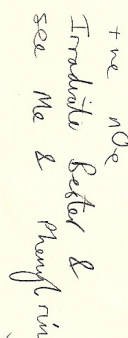


Irradiate Bester Me  
see TMS & Ph.



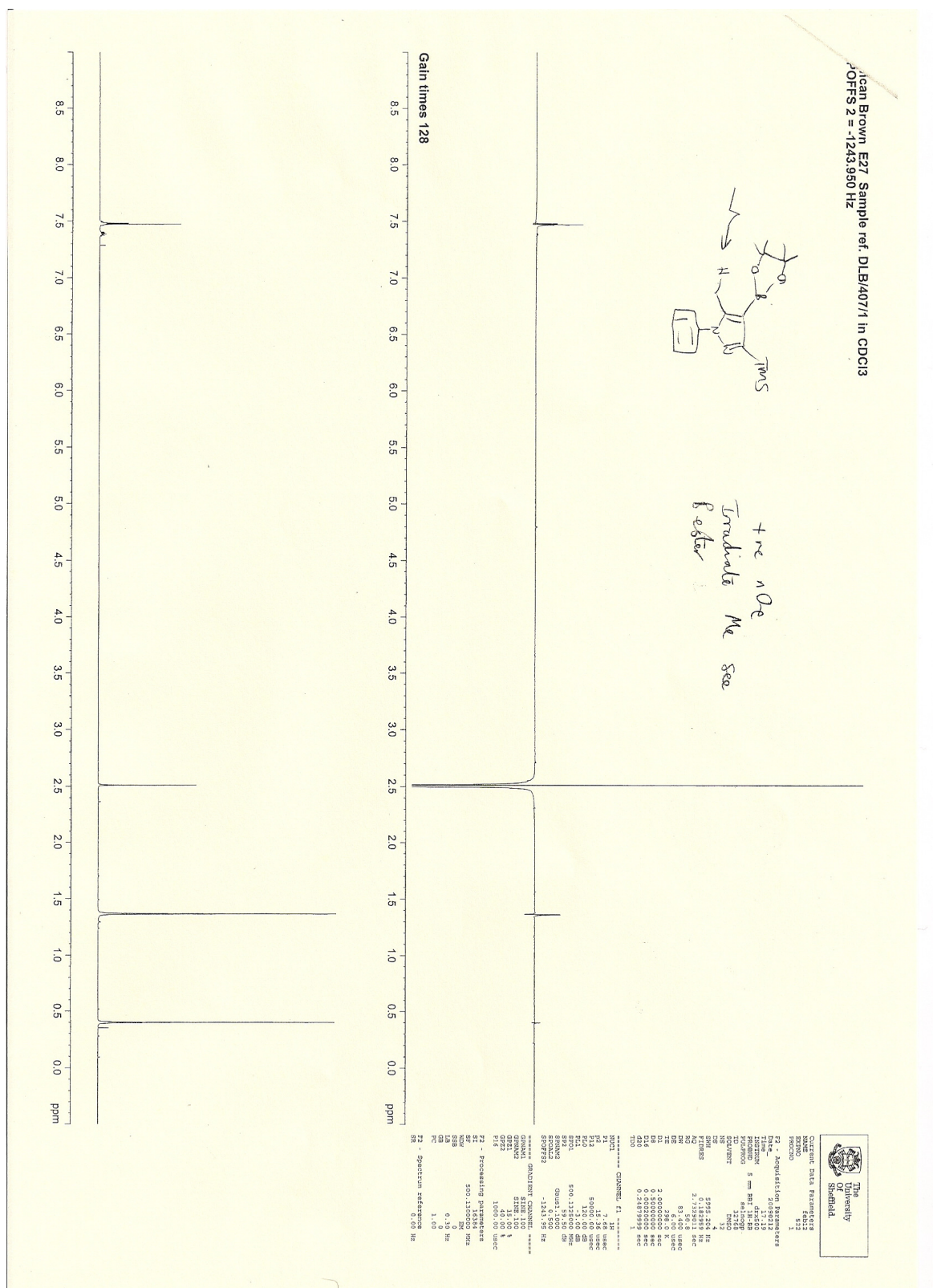


Regiochemical assignment of **23** by nOe

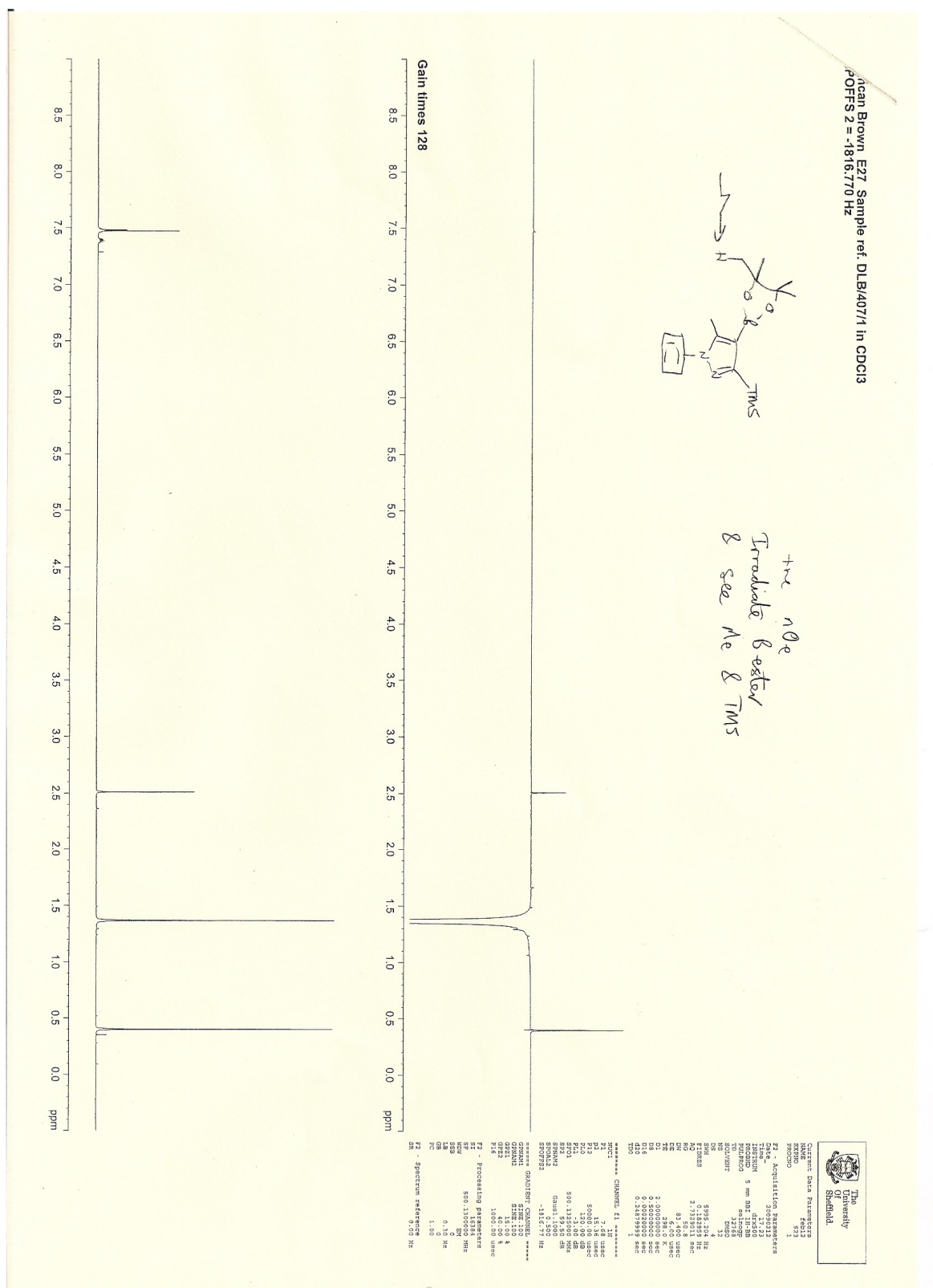




Regiochemical assignment of **25** by nOe



Regiochemical assignment of **25** by nOe

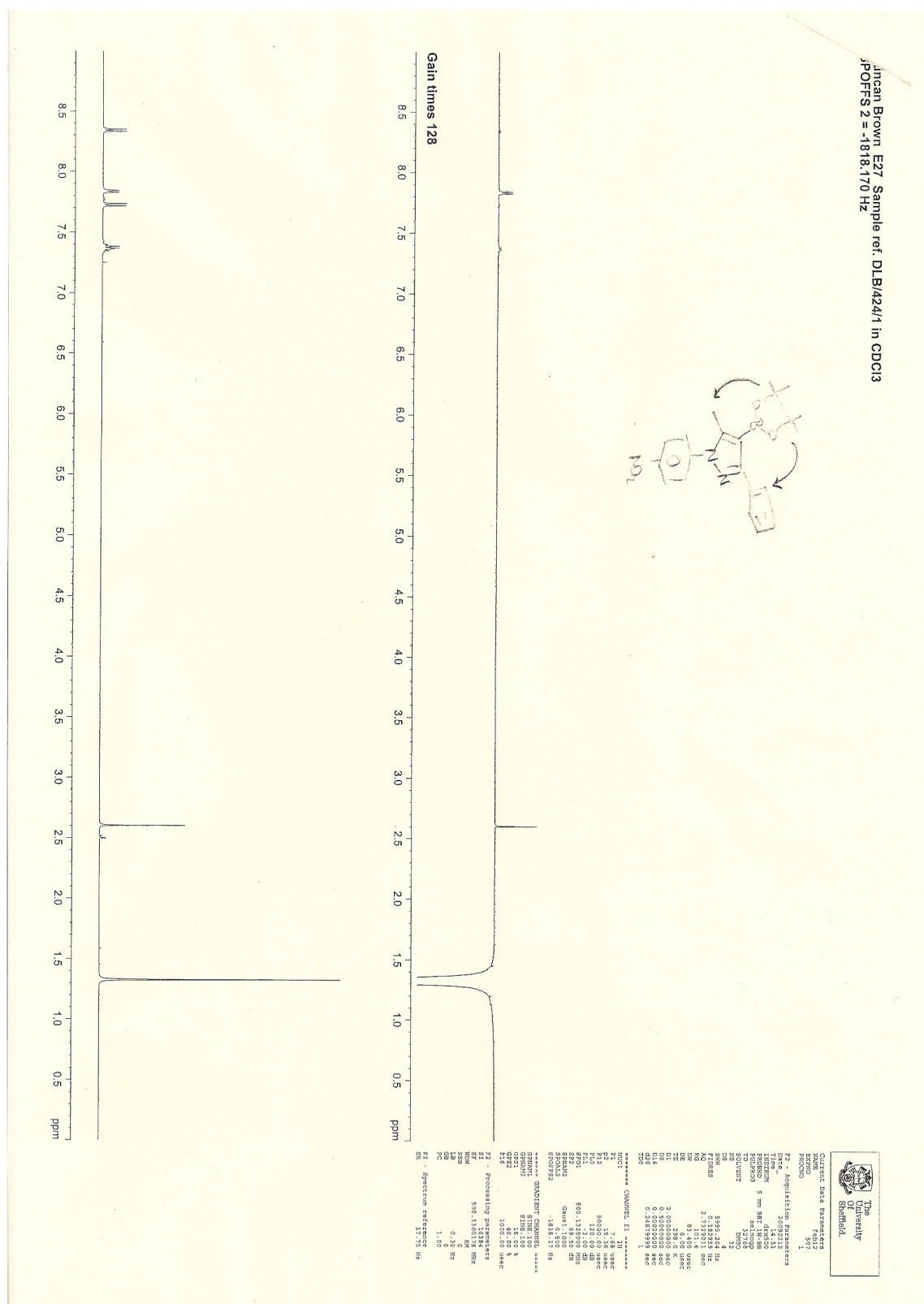


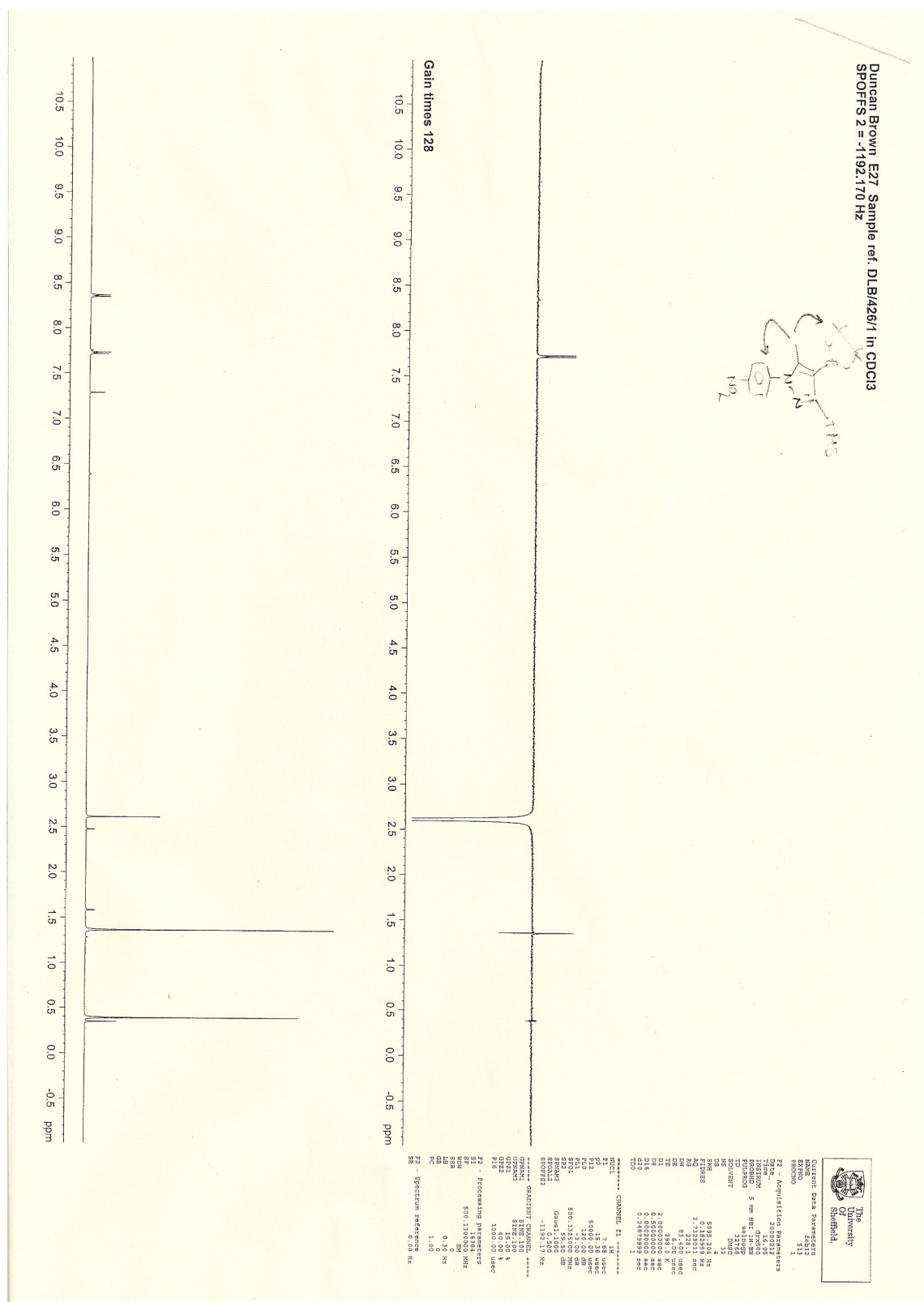




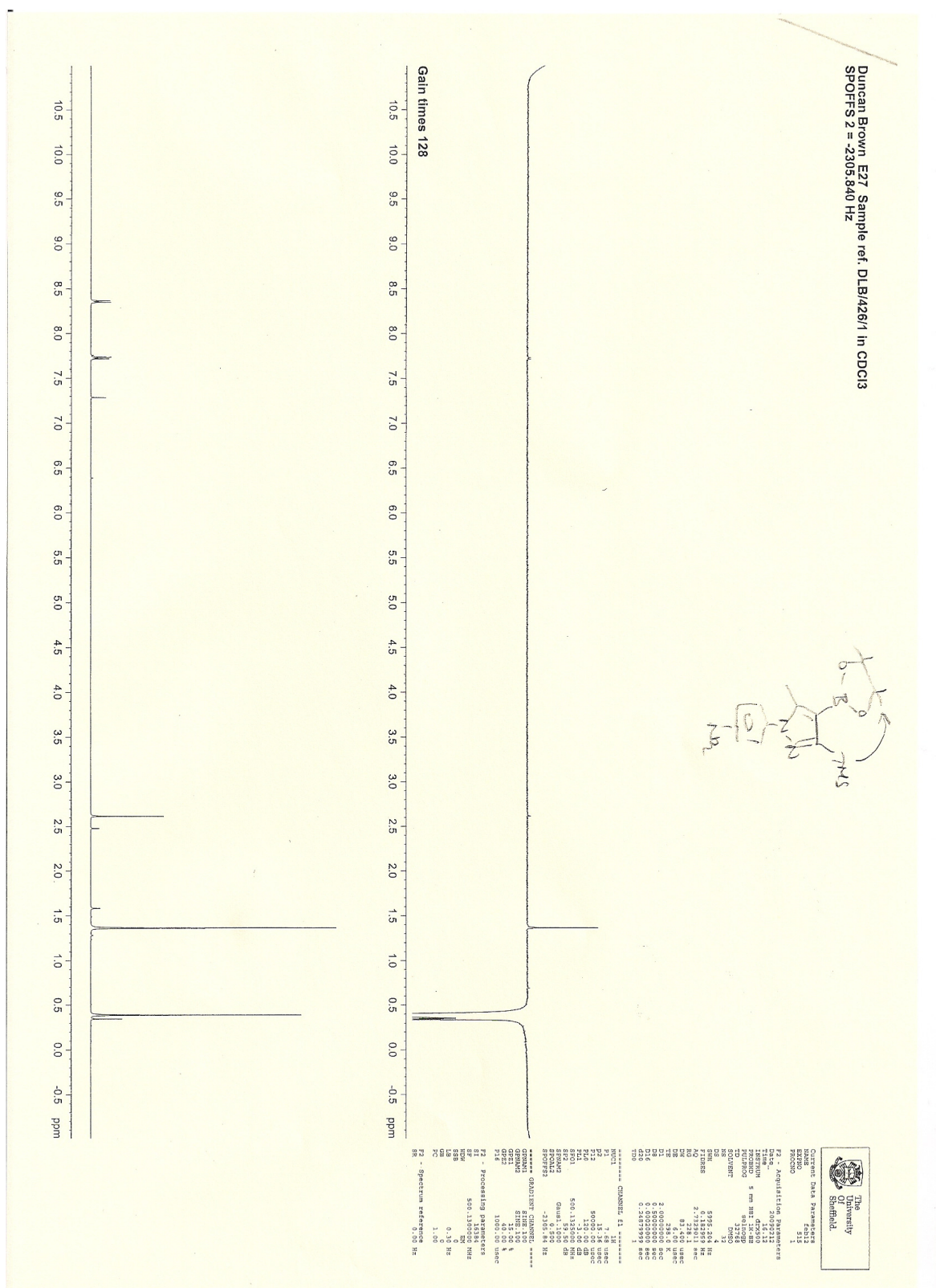


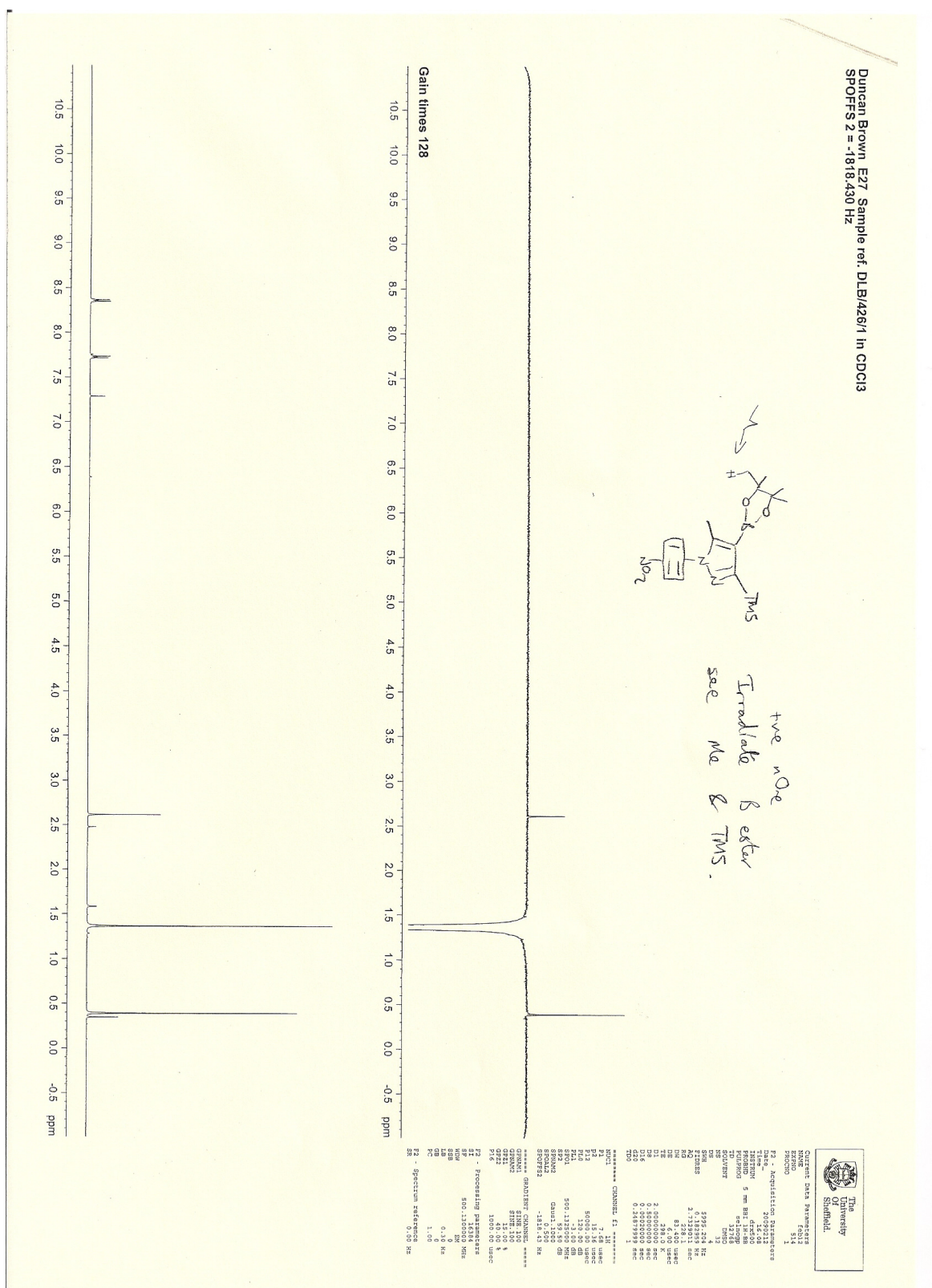


Regiochemical assignment of **27** by nOe

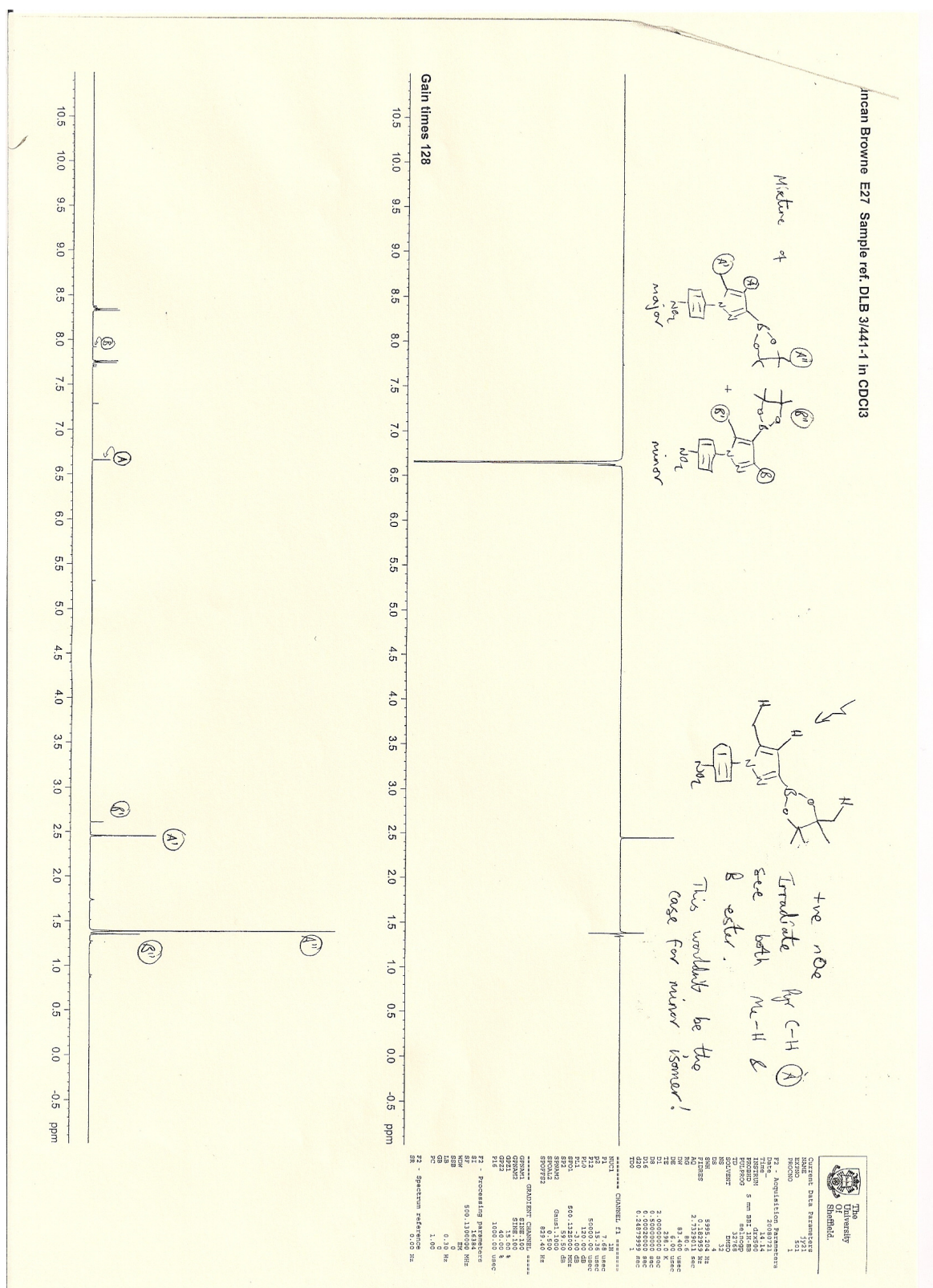




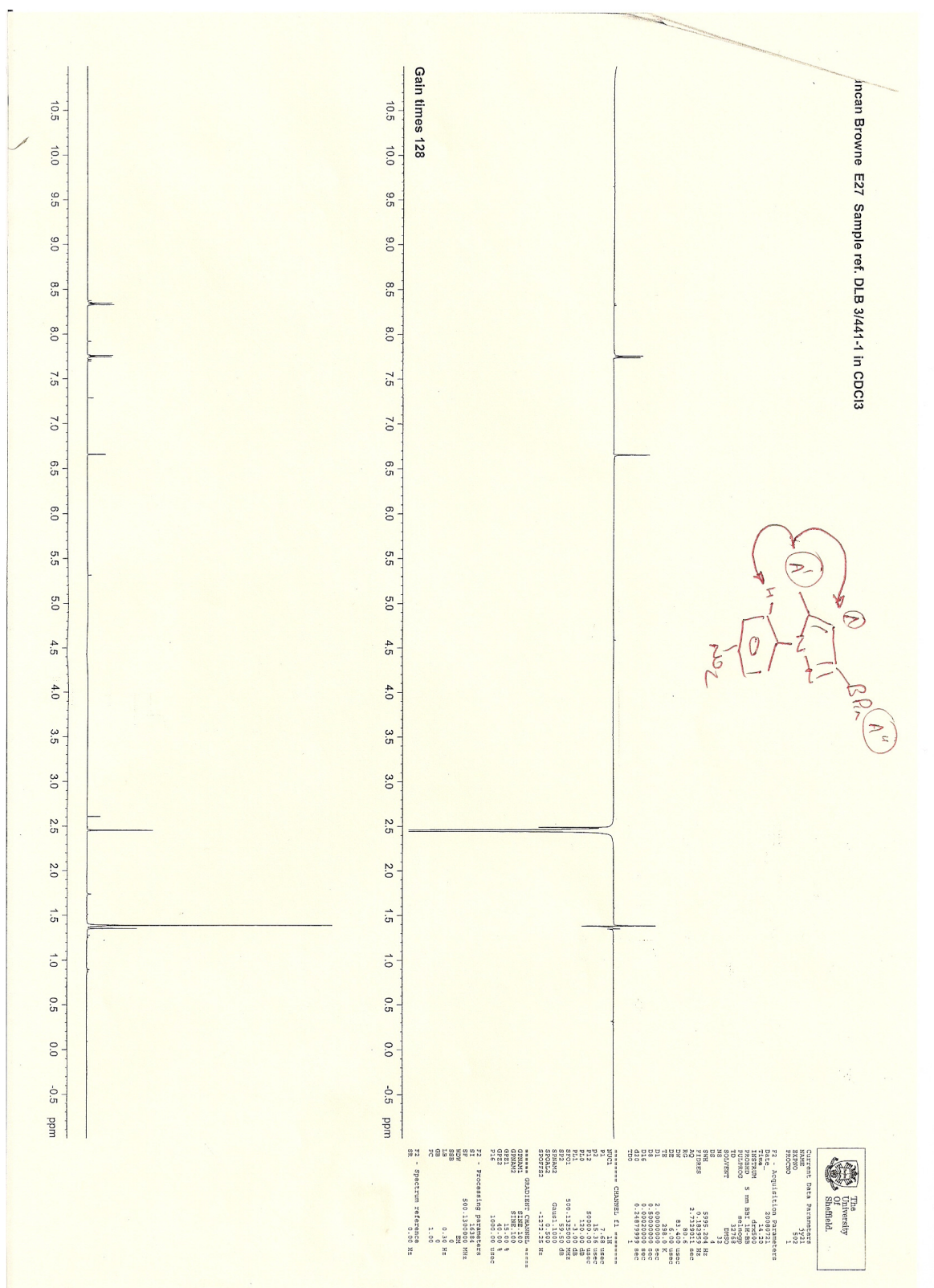


Regiochemical assignment of **29** by nOe

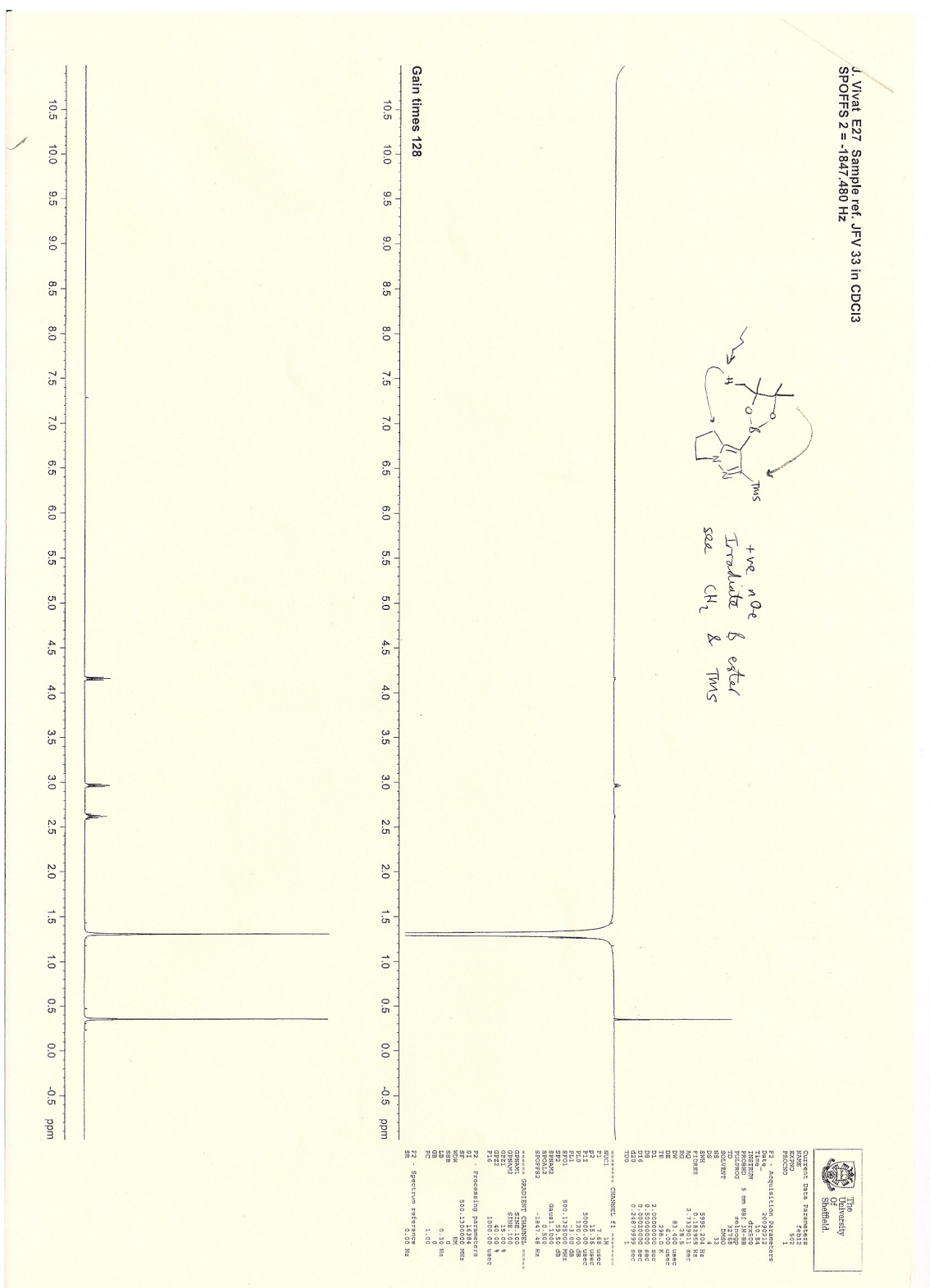


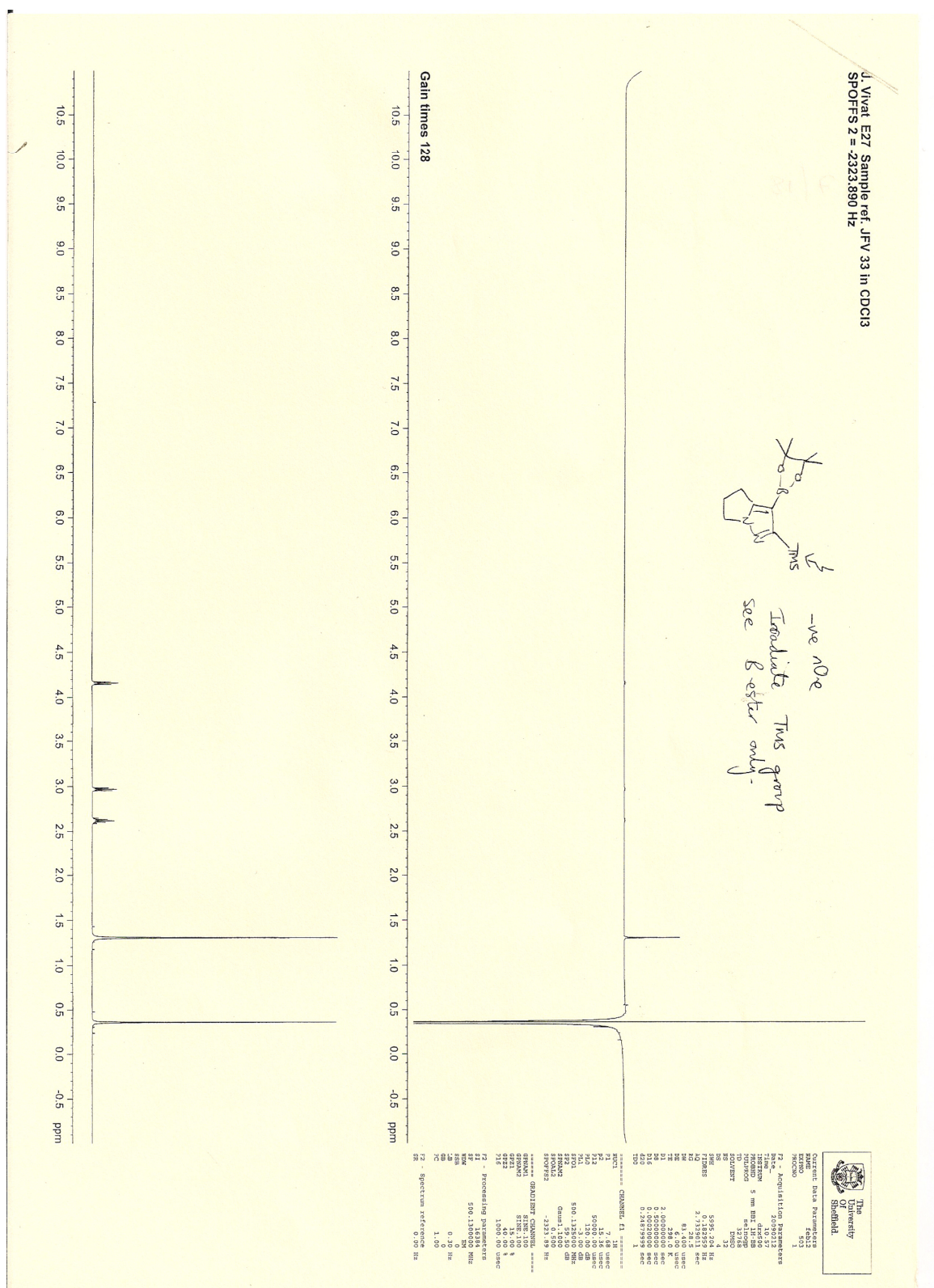
Regiochemical assignment of **31a/b** by nOe

Regiochemical assignment of **31a/b** by nOe

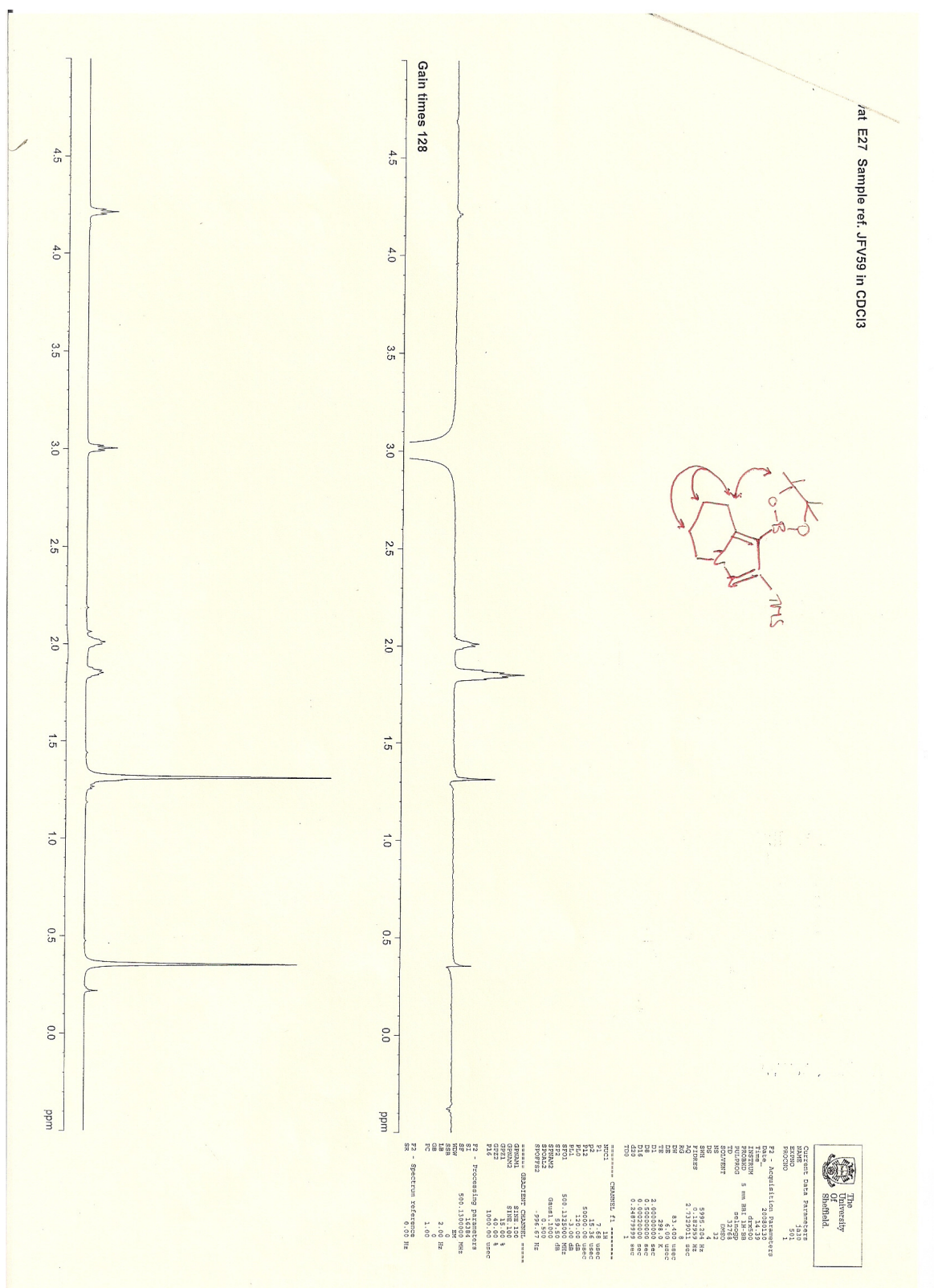


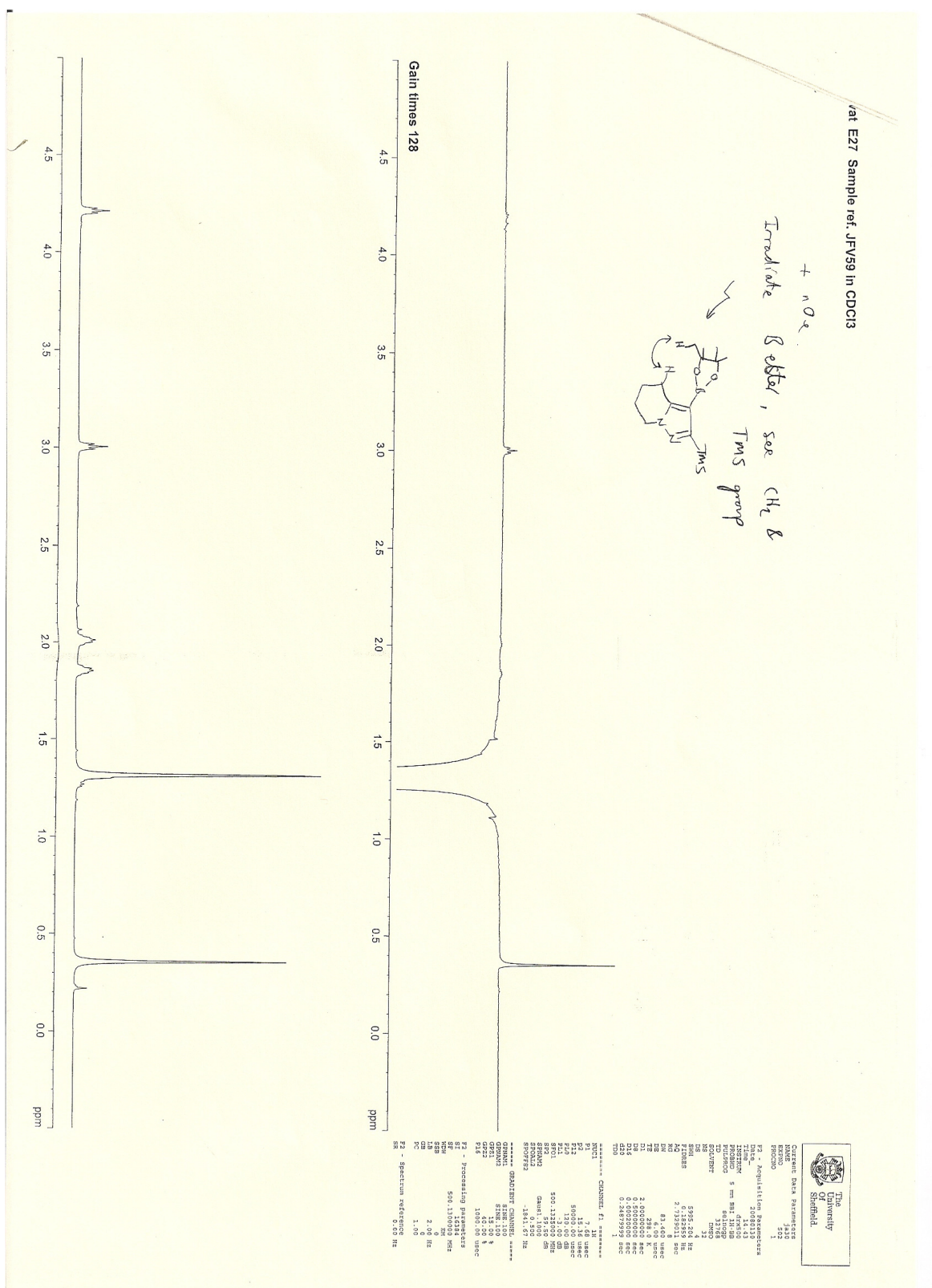








Regiochemical assignment of **36** by nOe

Regiochemical assignment of **36** by nOe



Regiochemical assignment of **36** by nOe