Supporting Information

Modified Julia-Kocienski reagents for a stereoselective introduction of trisubstituted double bonds: a formal total synthesis of Limazepine E and Barmumycin

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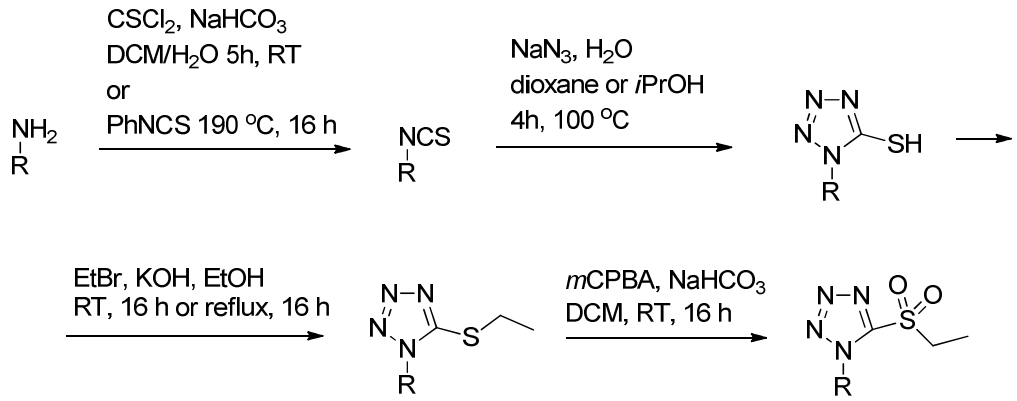
Sulfones 14 were synthesized according to the general scheme:



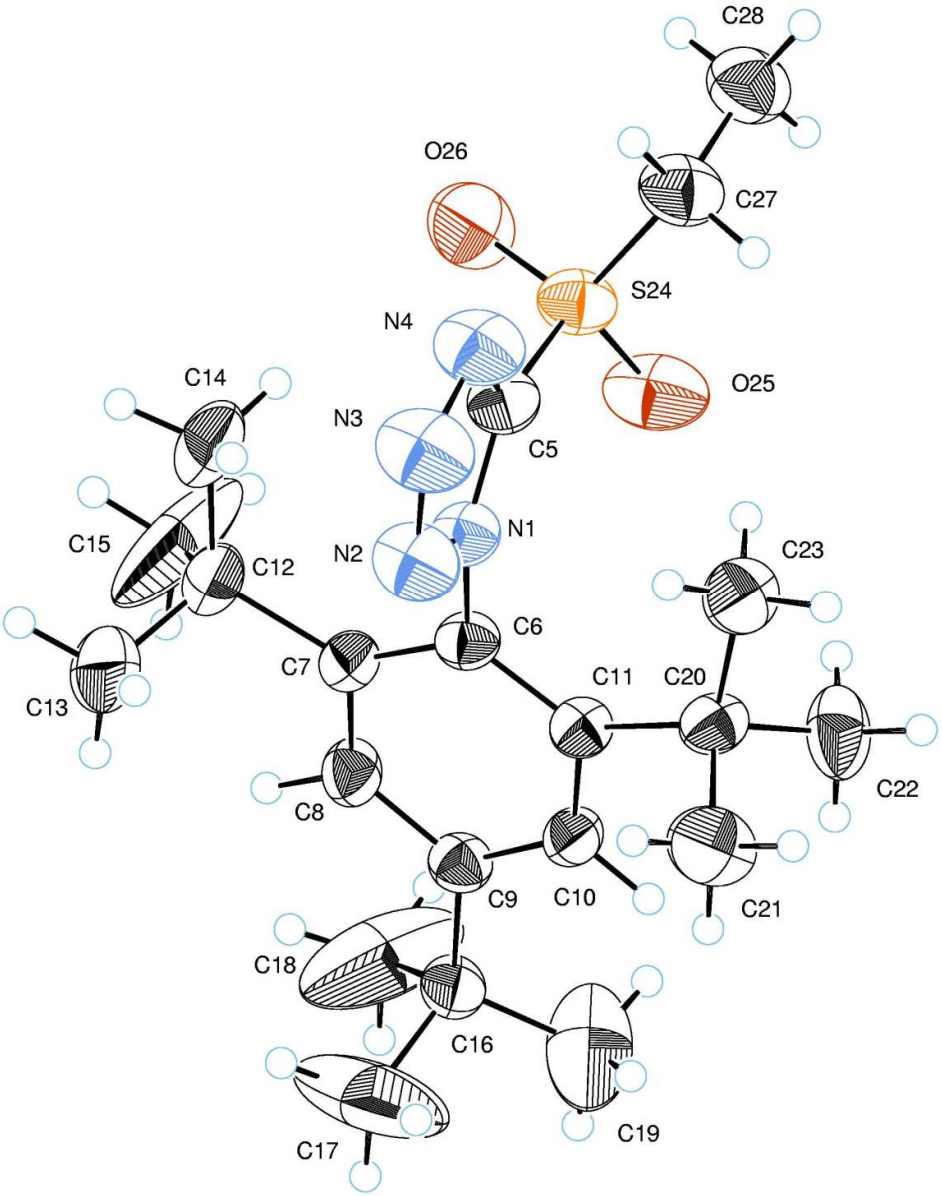


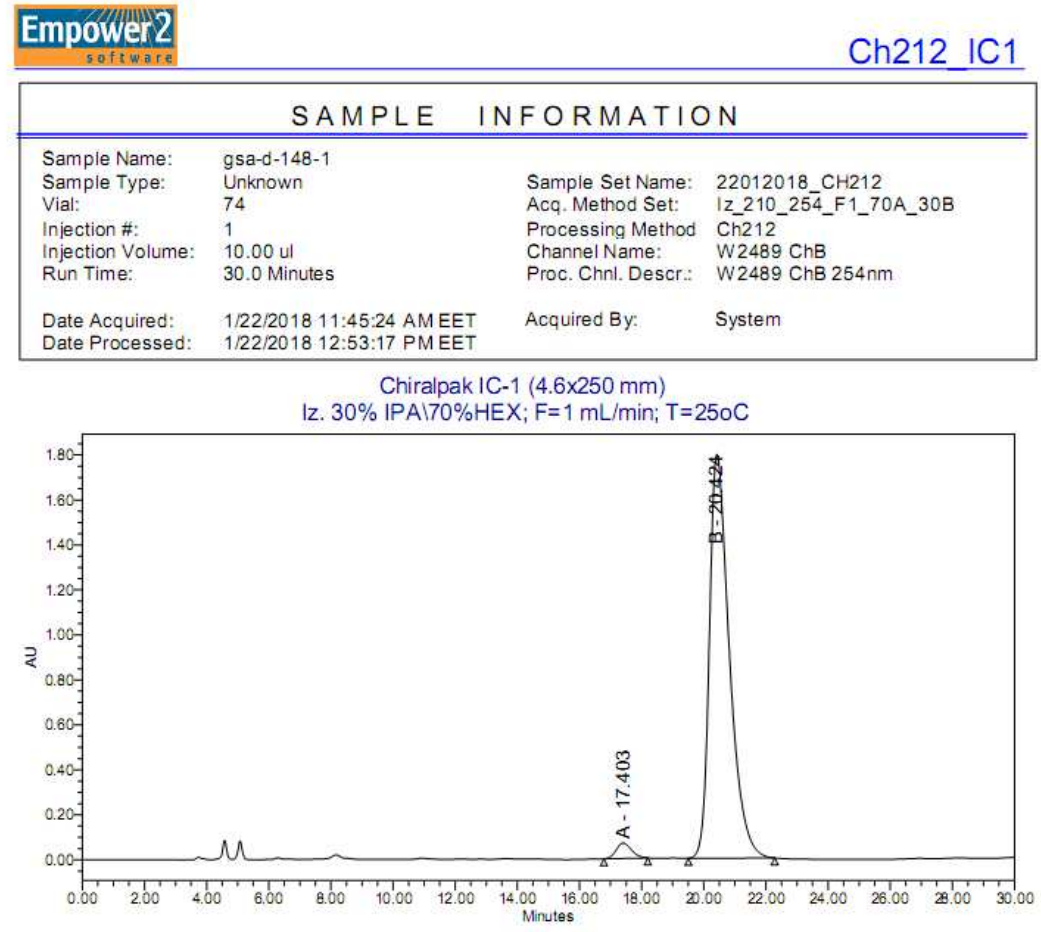
Figure 1. ORTEP molecular structure of compound **14h**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

For single crystal X-ray diffraction good enough, cut edged crystals of **14h** were grown from methylcyclohexane/CCl_4. The X-ray analysis was carried out using a Nonius KappaCCD automatic diffractometer (accumulated at room temperature, molybdenum radiation with λ = 0.71073 Å, graphite monochromator, and φ and ω scanning). Crystal data for **13h**: monoclinic; a = 9.7134(2), b = 25.2530(6), c = 9.8342(3) Å, β = 104.9223(9)°; V = 2330.8(1) Å^3, Z = 4, μ = 0.161 mm^{-1}, D_{calc} = 1.159 g·cm^{-3}; space group is $P2_1/n$. A total of 10034 reflection intensities were collected up to $2\theta_{max}$ = 56°; for structure refinement 3107 independent reflections with $I > 2\sigma(I)$ were used. The structure was solved by a direct method with refinement in a full matrix least squares method using the SHELX package [1]. All nonhydrogen atoms were refined in anisotropical approximation. H-atoms were refined by riding model with Uiso(H) = 1.2Ueq(C). The final R-factor is 0.0732.

[1] G. M. Sheldrick, A short history of SHELX, Acta Crystallogr. A64 (2008) 112-122.

Representative examples of HPLC plots used for determination of *E*-/*Z*-ratio in Julia-Kocienski olefination of ketone 13 with sulphones 14.

A HPLC plot of Julia-Kocienski olefination of ketone **13** with sulphone **14j** (KHMDS as a base).



	Peak Name	RT	Area	% Area	Height	EP Plate Count	Resolution	Selectivity	Width @ 50%	K Prime
1	A	17.403	2346472	2.85	68527	5963			0.530	4.355
2	B	20.424	80015490	97.15	1795991	5222	2.981	1.213	0.665	5.284

1

A HPLC plot of Julia-Kocienski olefination of ketone **13** with sulphone **14c** (LiHMDS as a base).

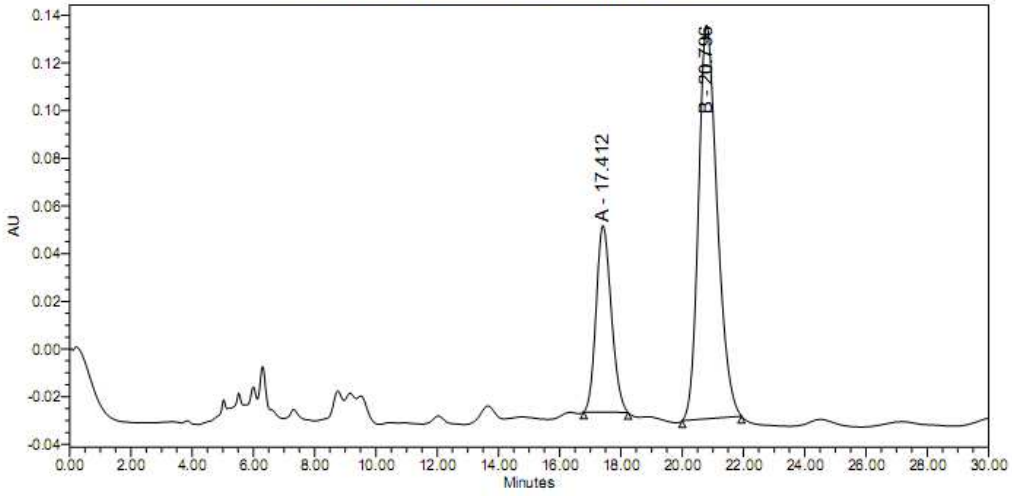
Empower 2 software

Ch212_IC1

SAMPLE INFORMATION

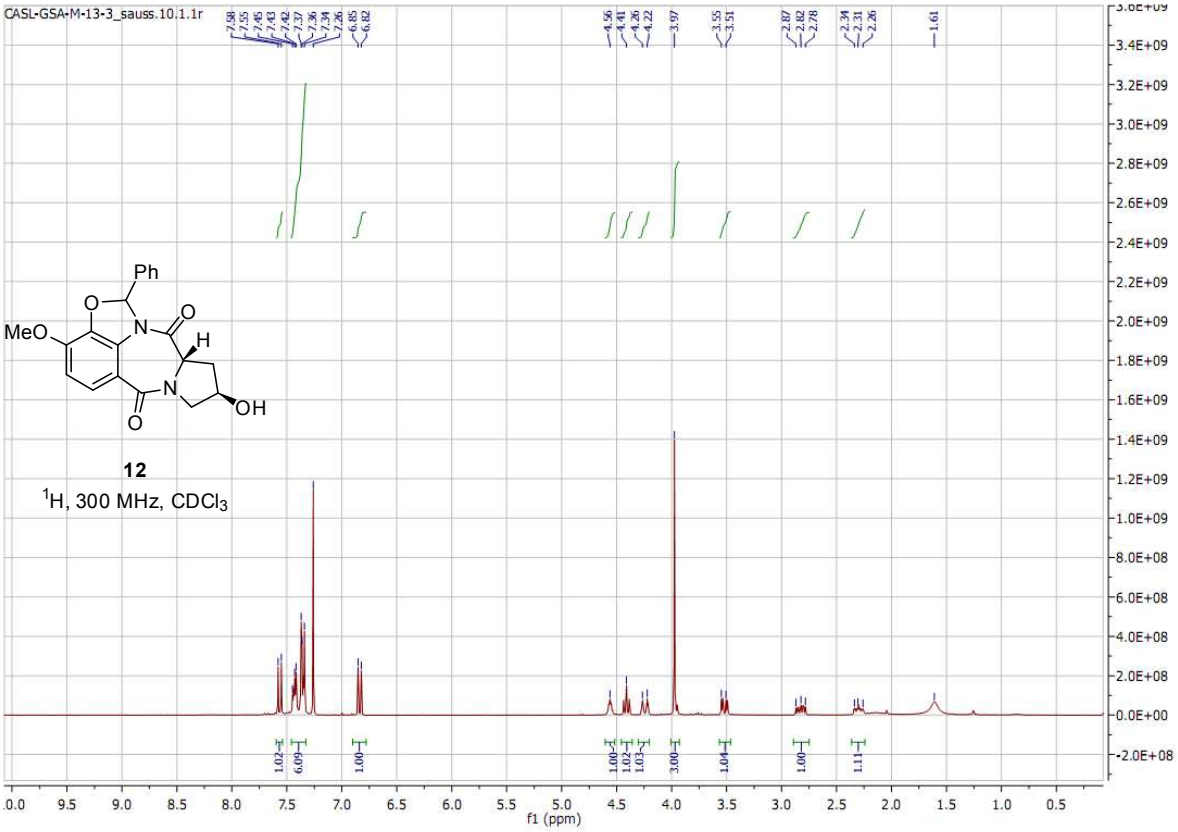
Sample Name:	gsa-d-74		
Sample Type:	Unknown	Sample Set Name:	22012018_CH212
Vial:	75	Acq. Method Set:	Iz_210_254_F1_70A_30B
Injection #:	1	Processing Method	Ch212
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 254nm
Date Acquired:	1/22/2018 12:16:27 PM EET	Acquired By:	System
Date Processed:	1/22/2018 12:53:17 PM EET		

Chiralpak IC-1 (4.6x250 mm)
Iz. 30% IPA\70%HEX; F=1 mL/min; T=25oC



	Peak Name	RT	Area	% Area	Height	EP Plate Count	Resolution	Selectivity	Width @ 50%	K Prime
1	A	17.412	2693160	27.71	78152	5855			0.536	4.358
2	B	20.796	7025166	72.29	165129	5649	3.365	1.239	0.651	5.399

1



12

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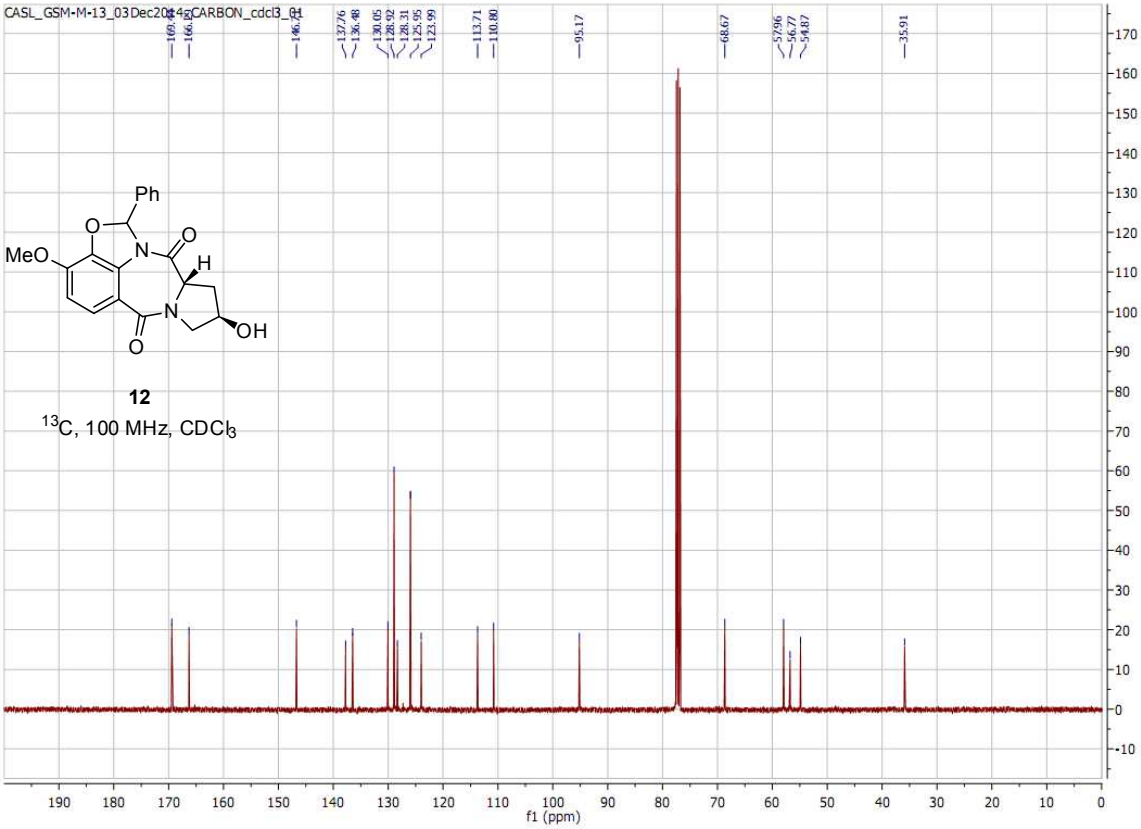

12

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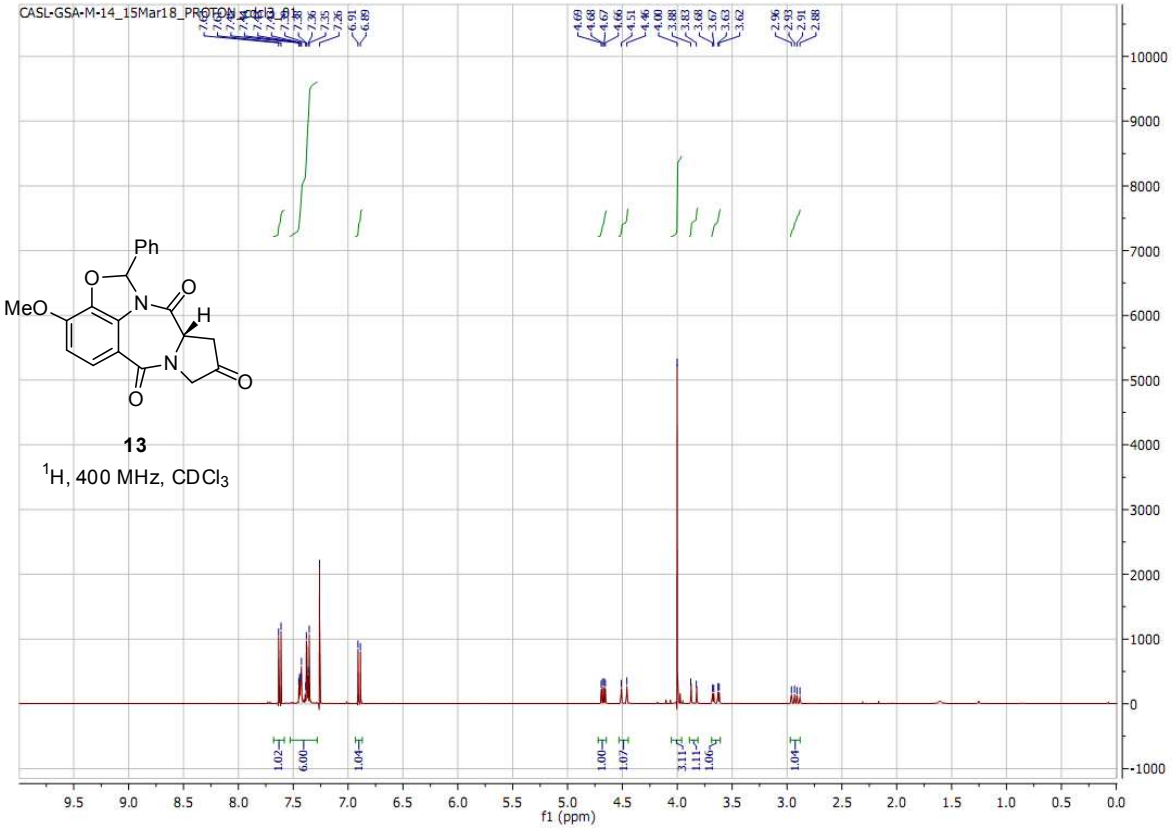

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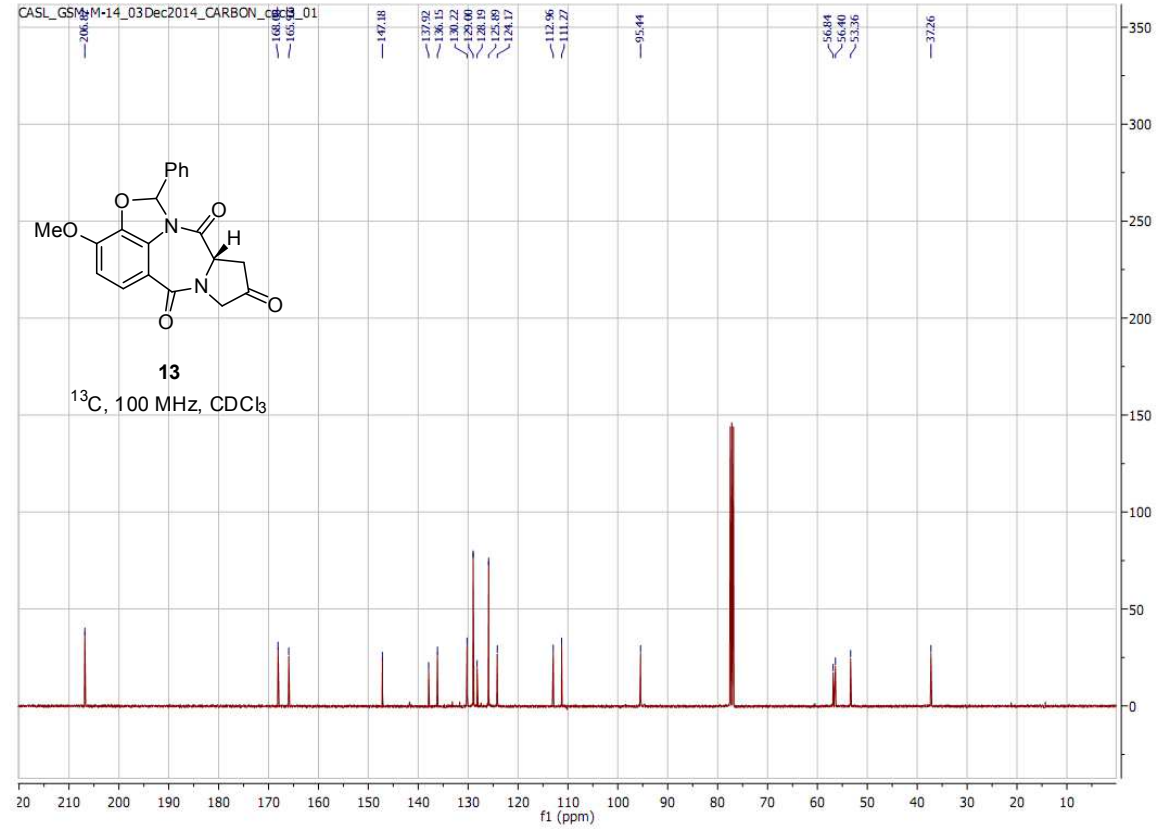

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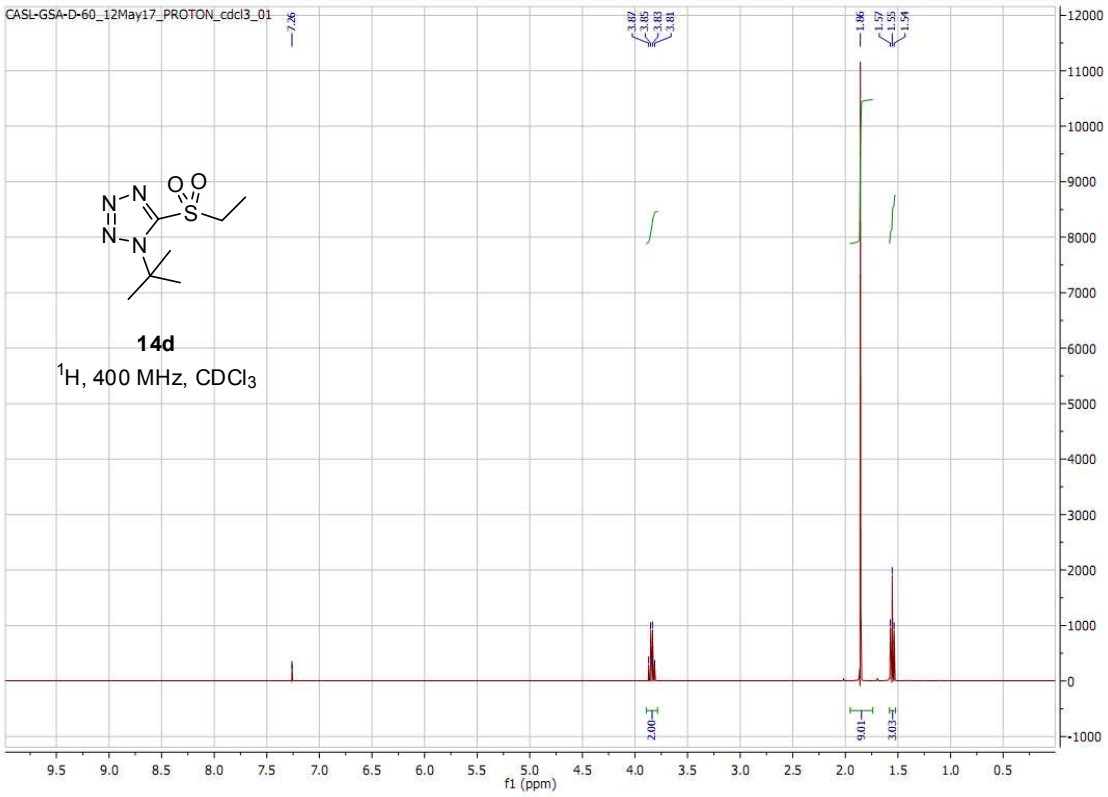

14d

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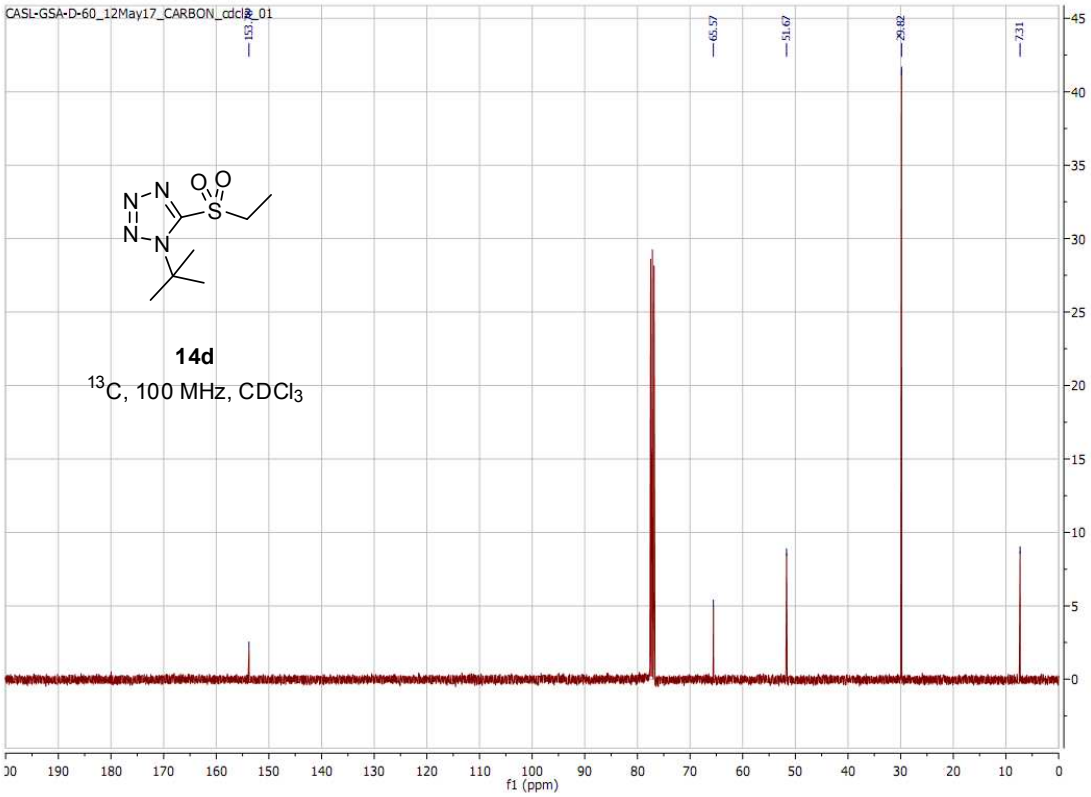

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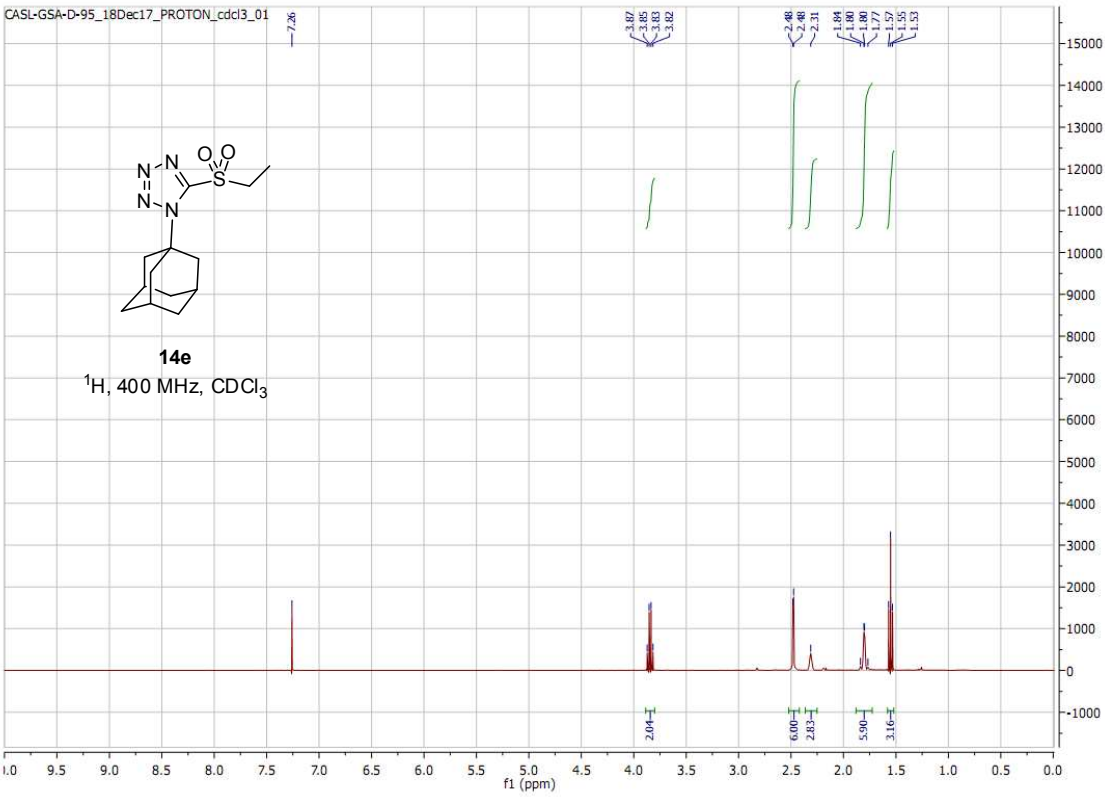

14e

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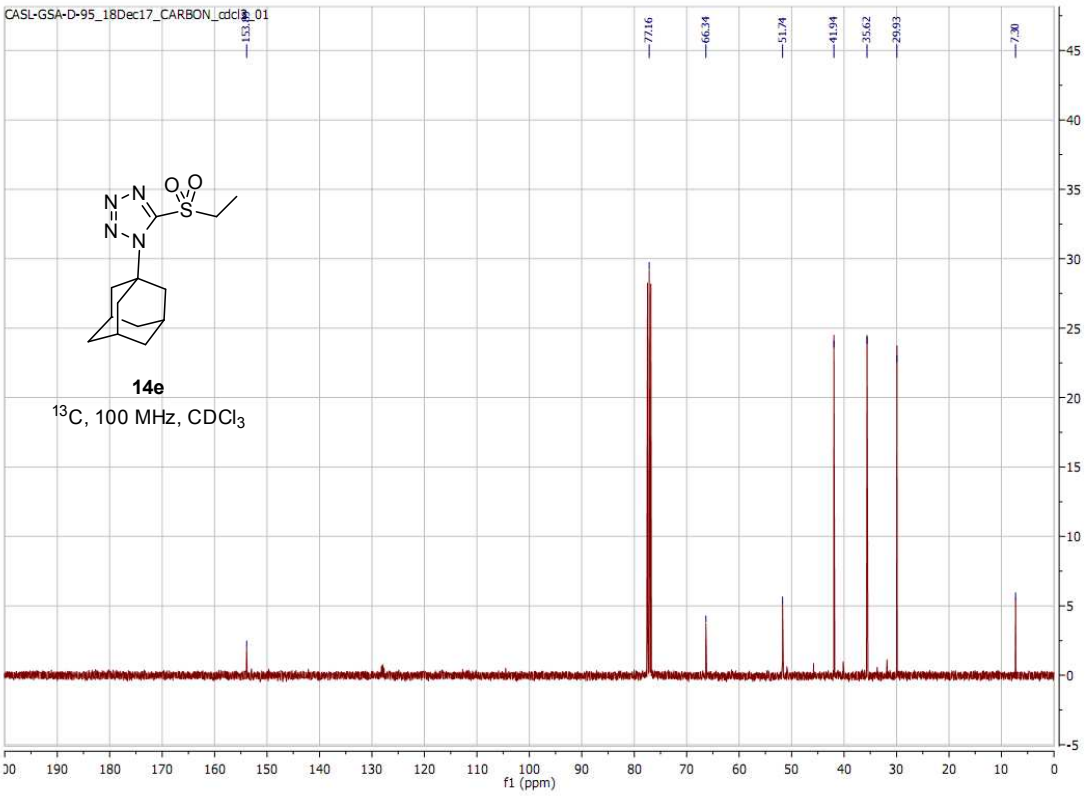

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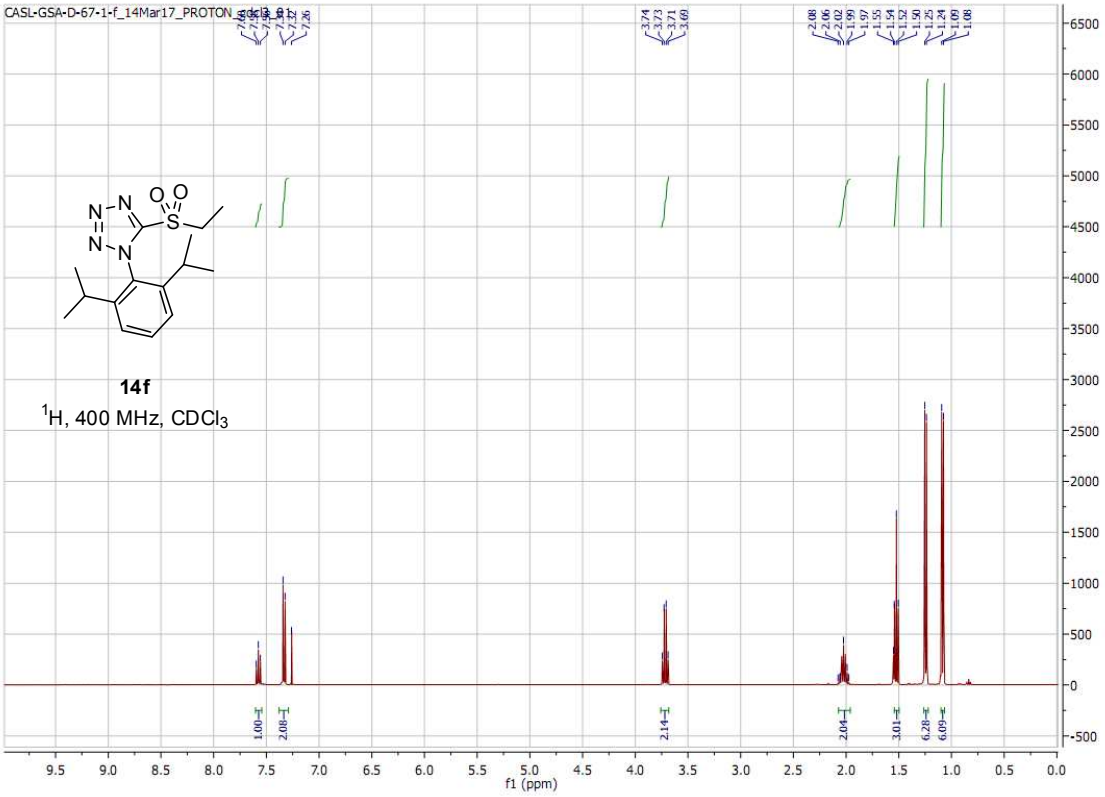

14f

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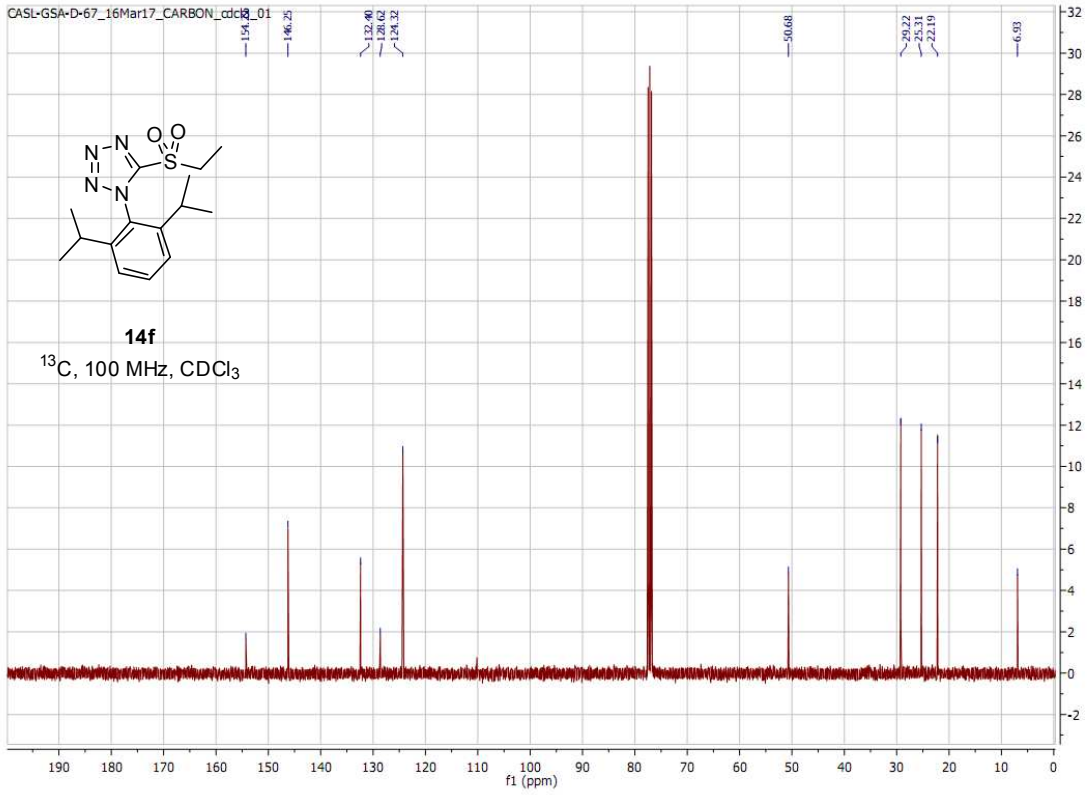

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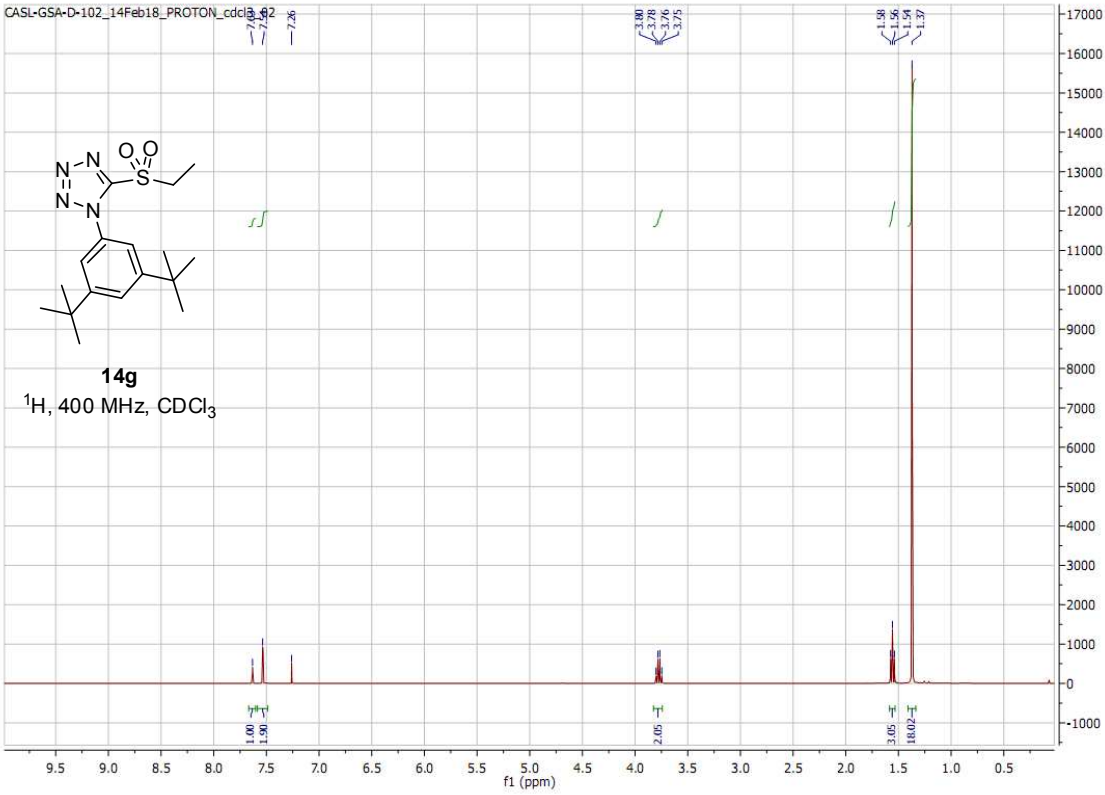

14g

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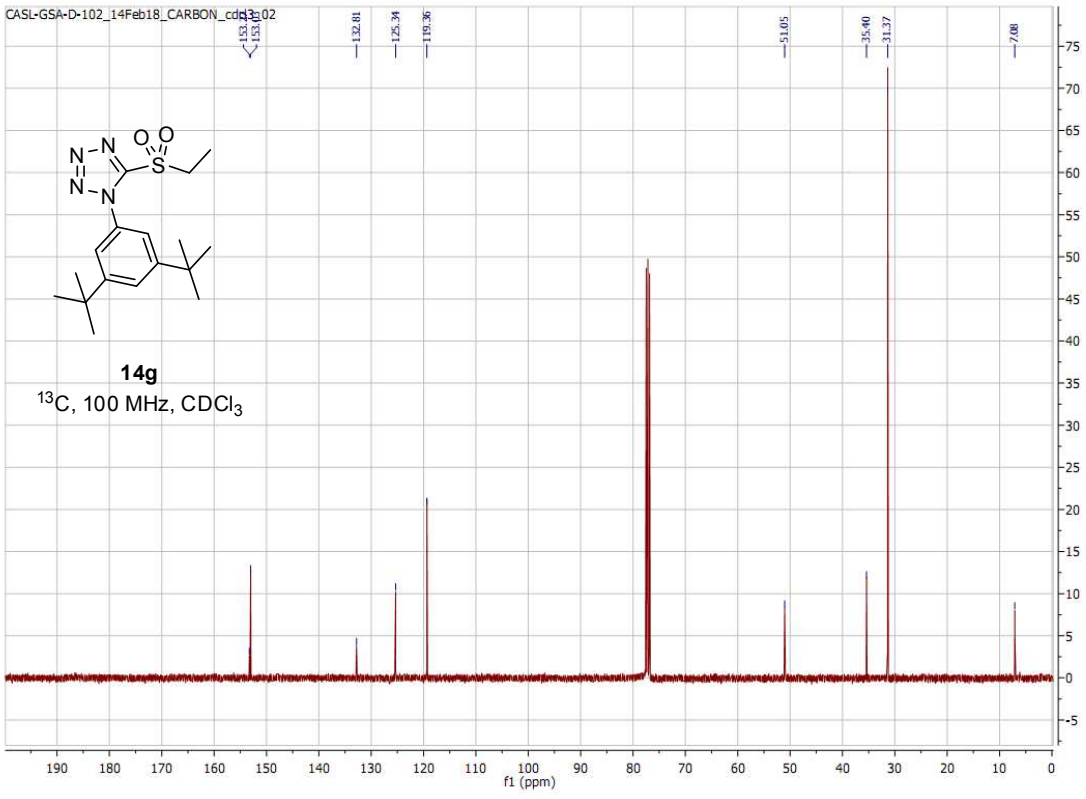

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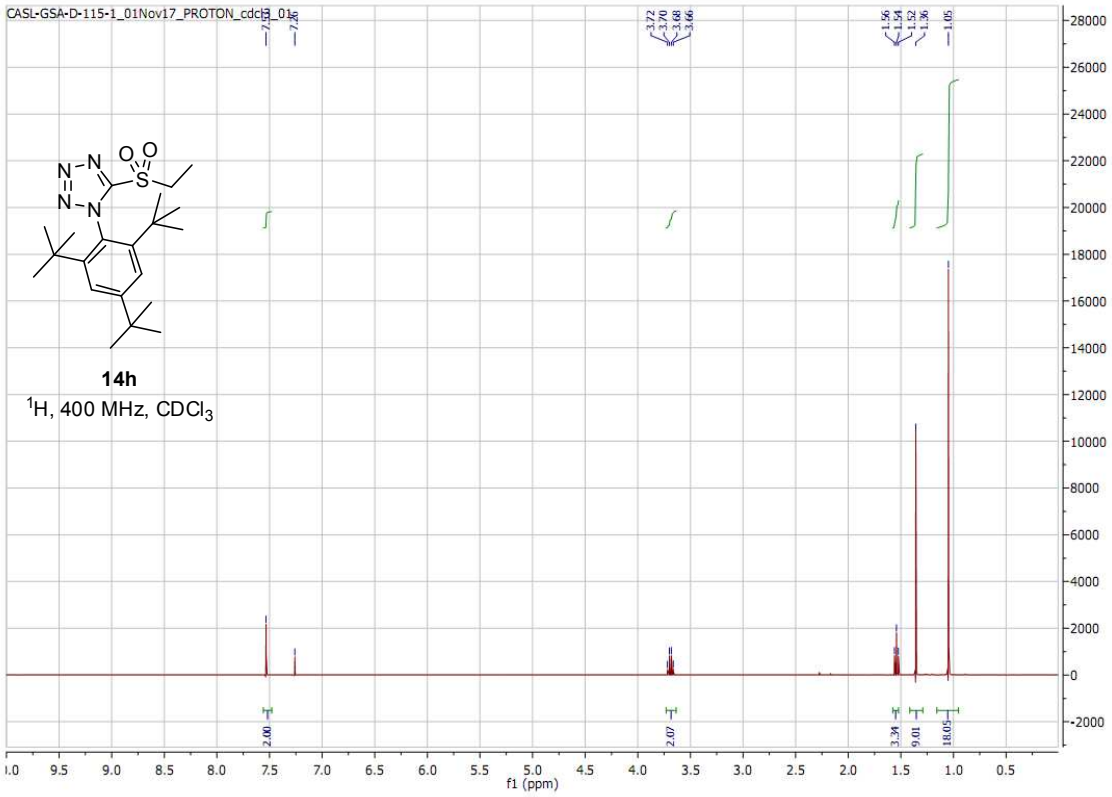

14h

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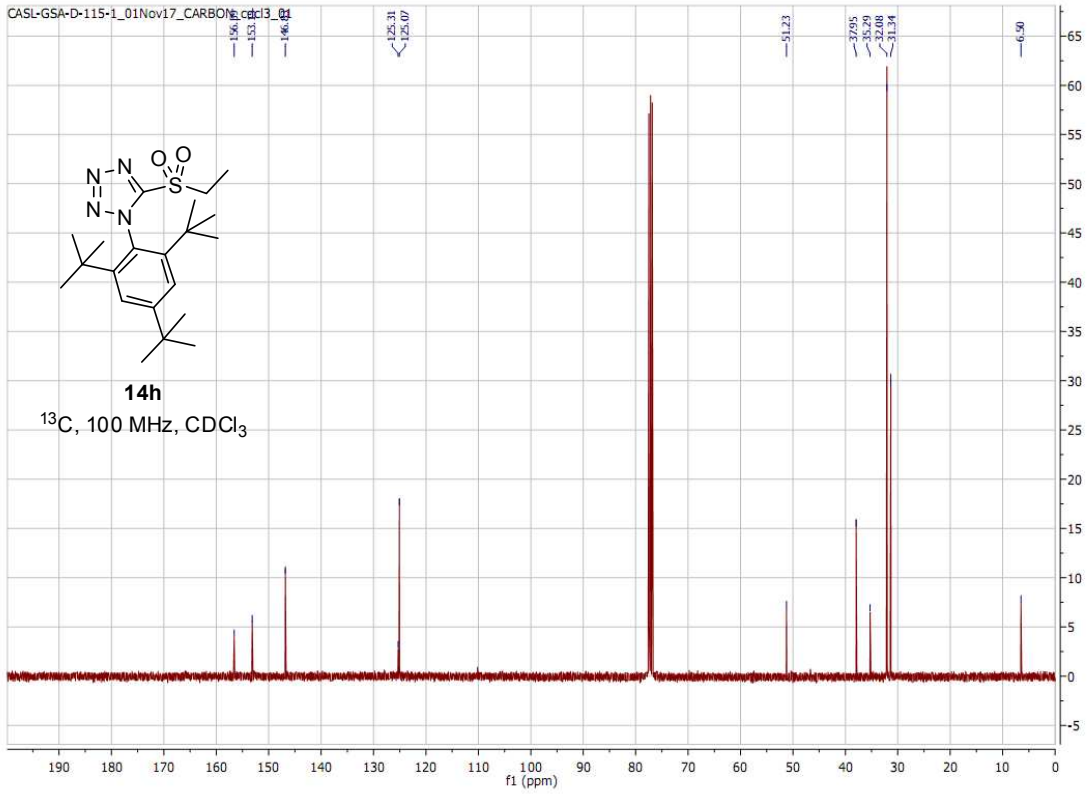

14h

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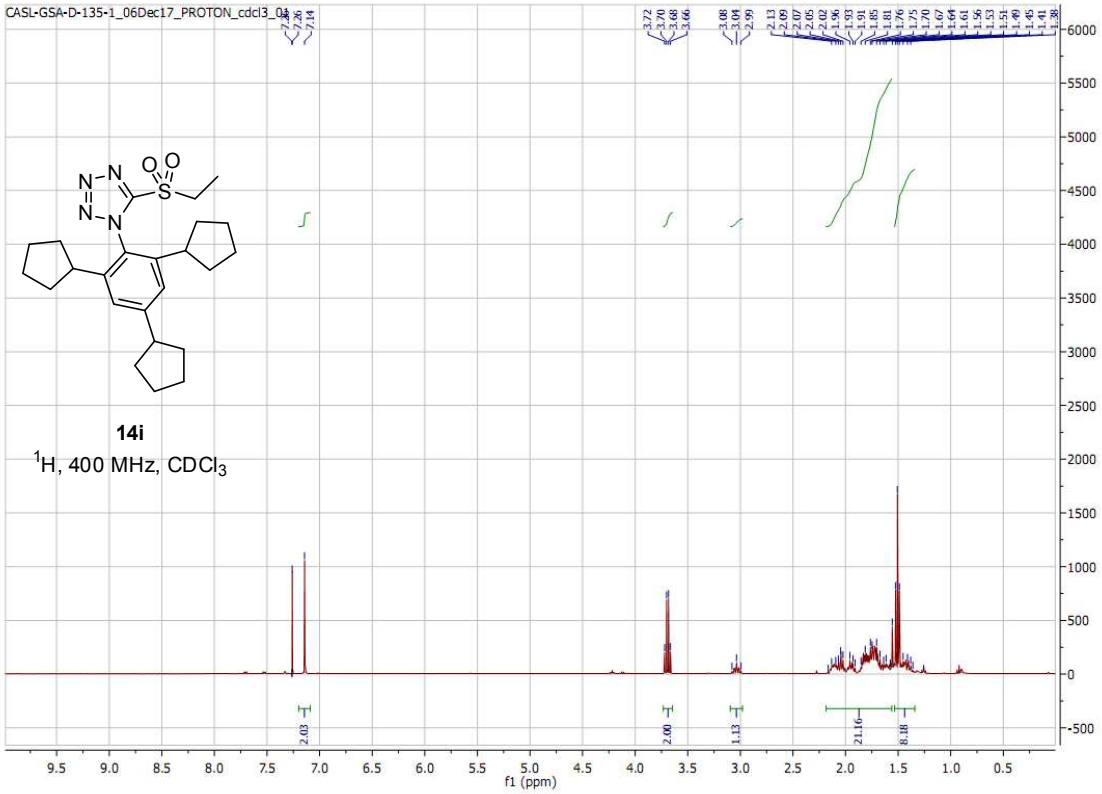

14i

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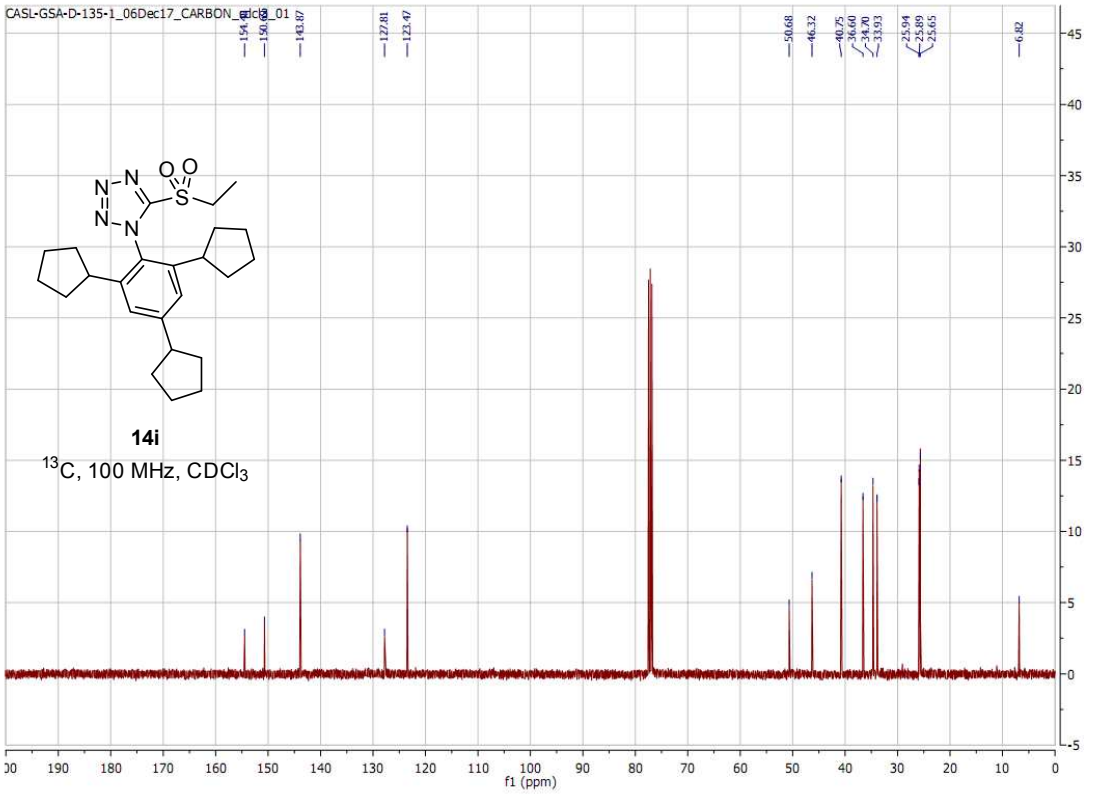

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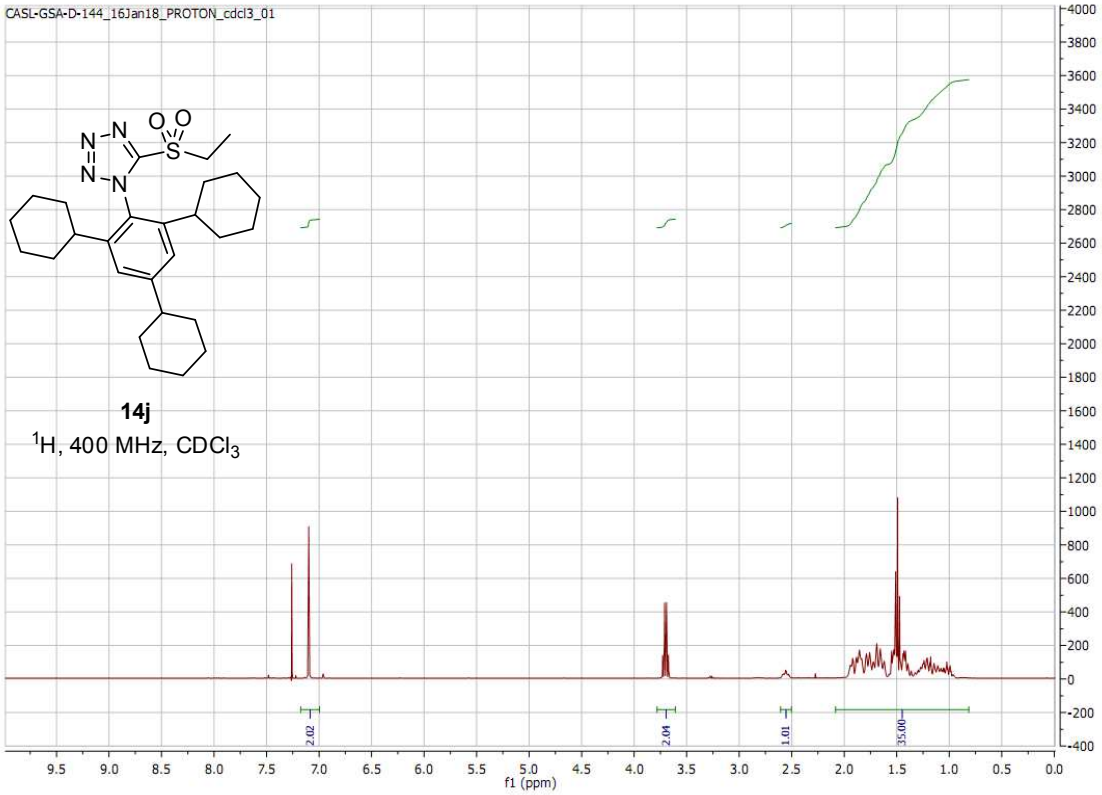
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14j
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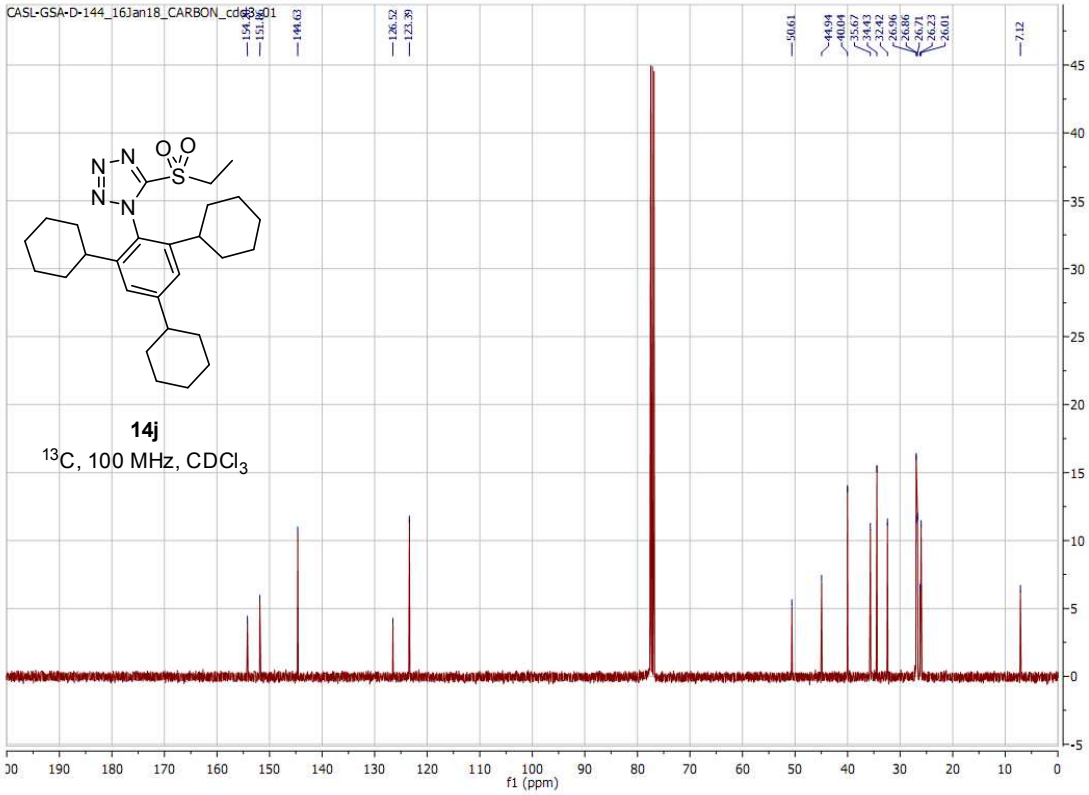
f1 (ppm)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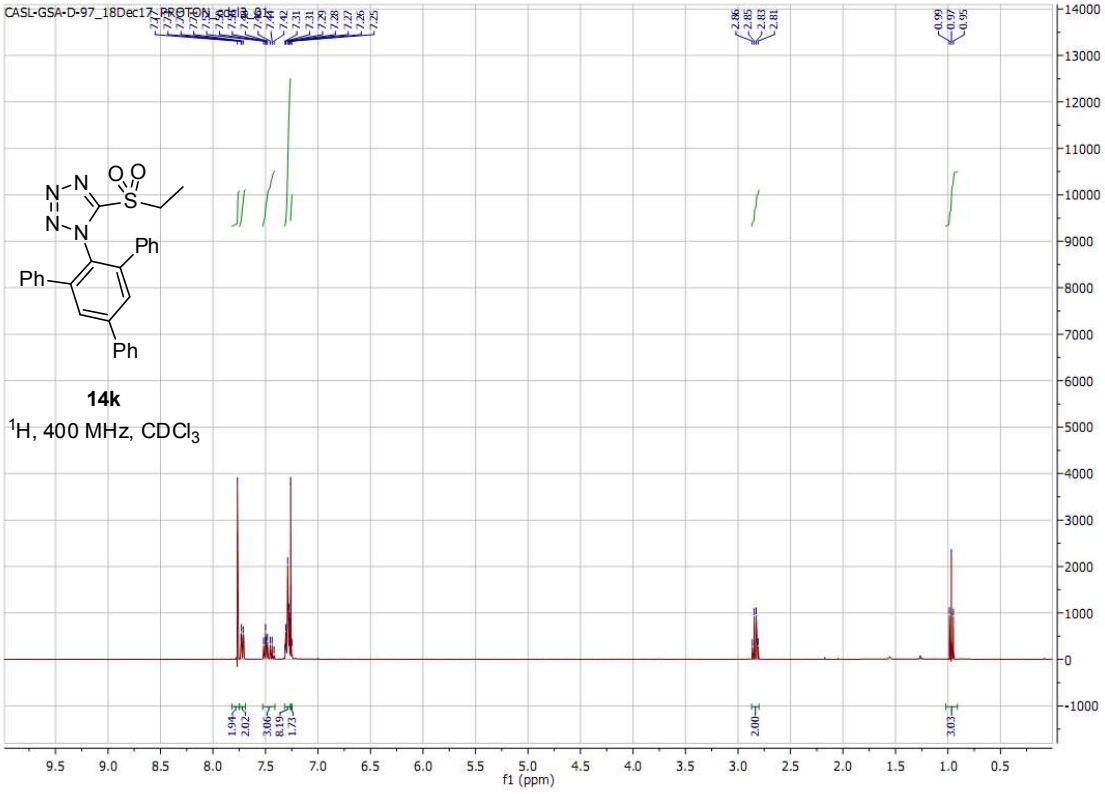
f1 (ppm)



14k

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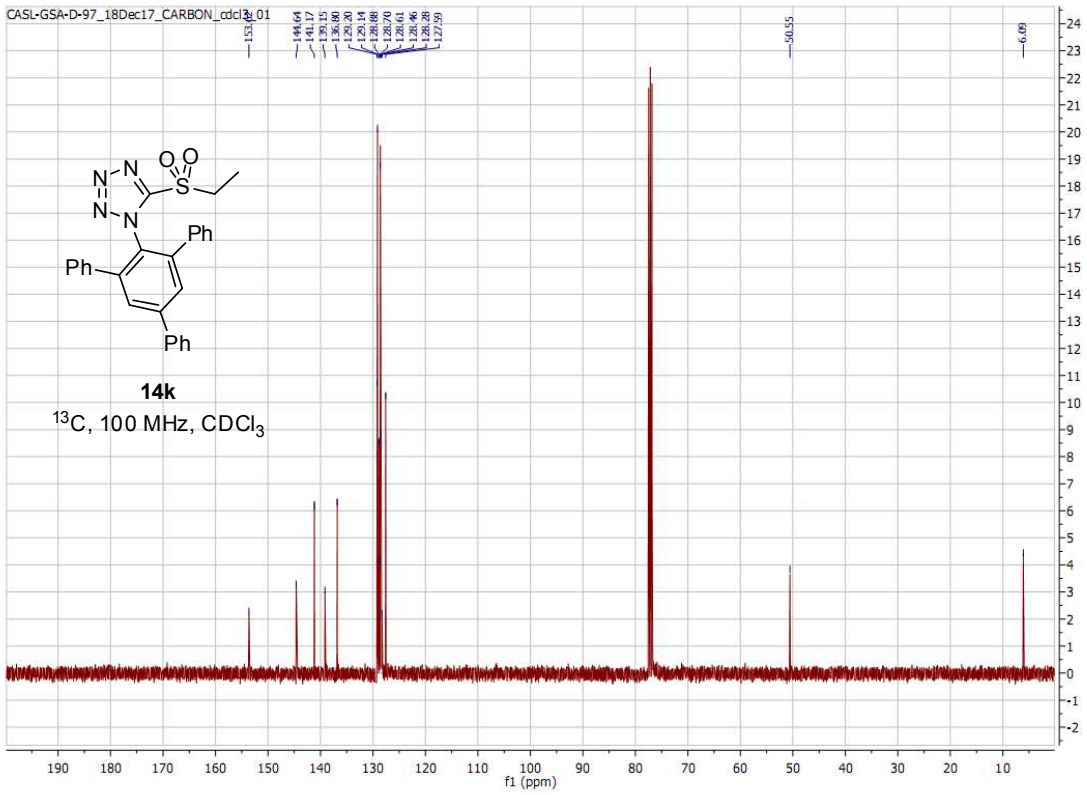
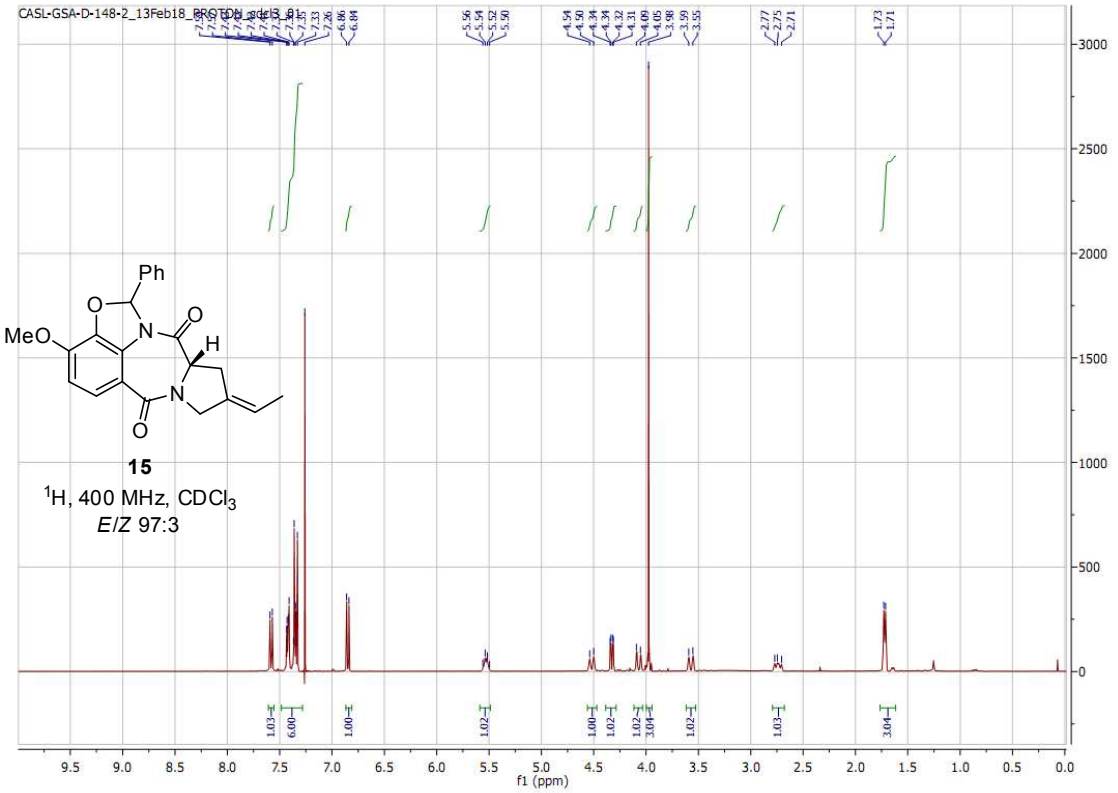


14k

^{13}C, 100 MHz, $CDCl_3$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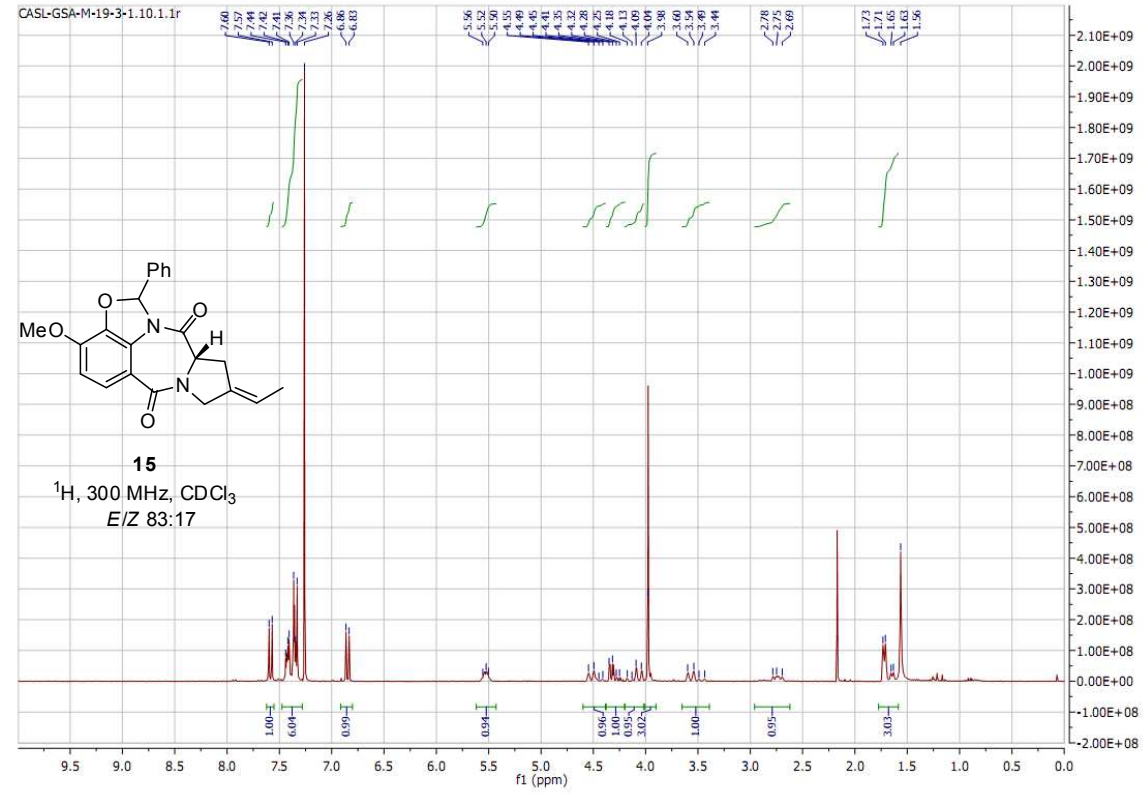
O
MeO
H
N
O
15
1H, 400 MHz, CDCl3
E/Z 97:3
f1 (ppm)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Ph
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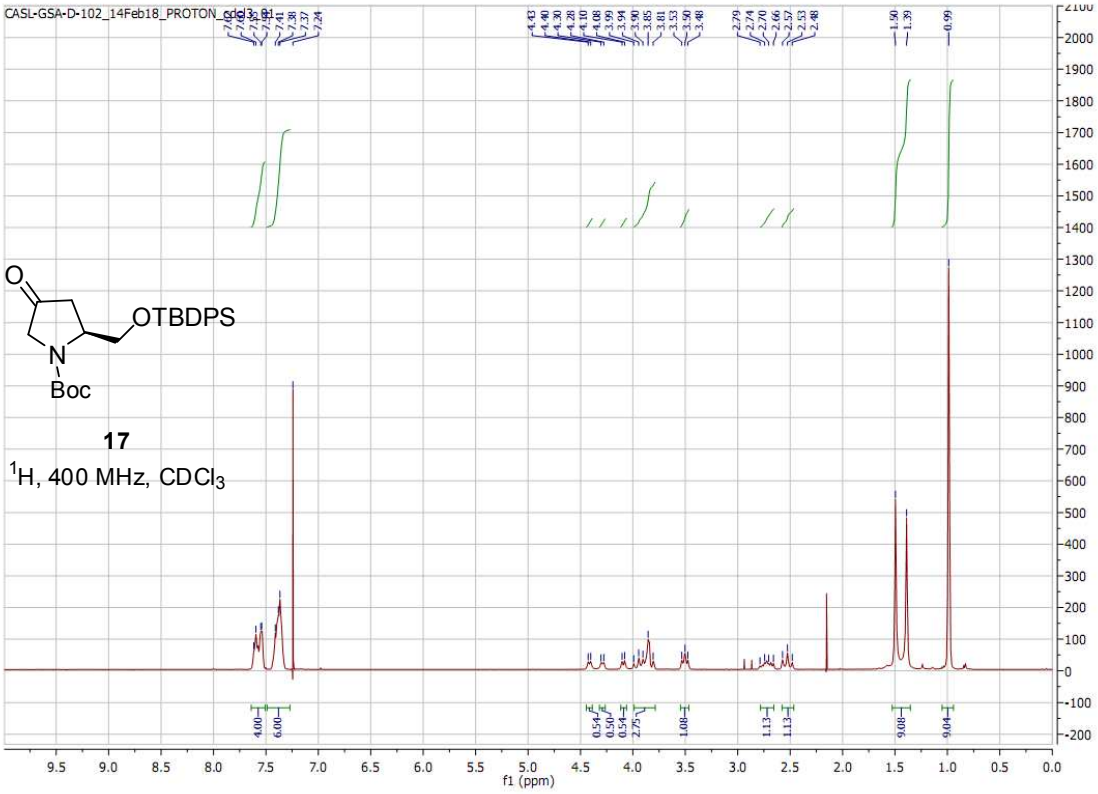
N
O
MeO
H
N
O
15
1H, 300 MHz, CDCl3
E/Z 83:17
f1 (ppm)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OTBDPS
N
Boc
17
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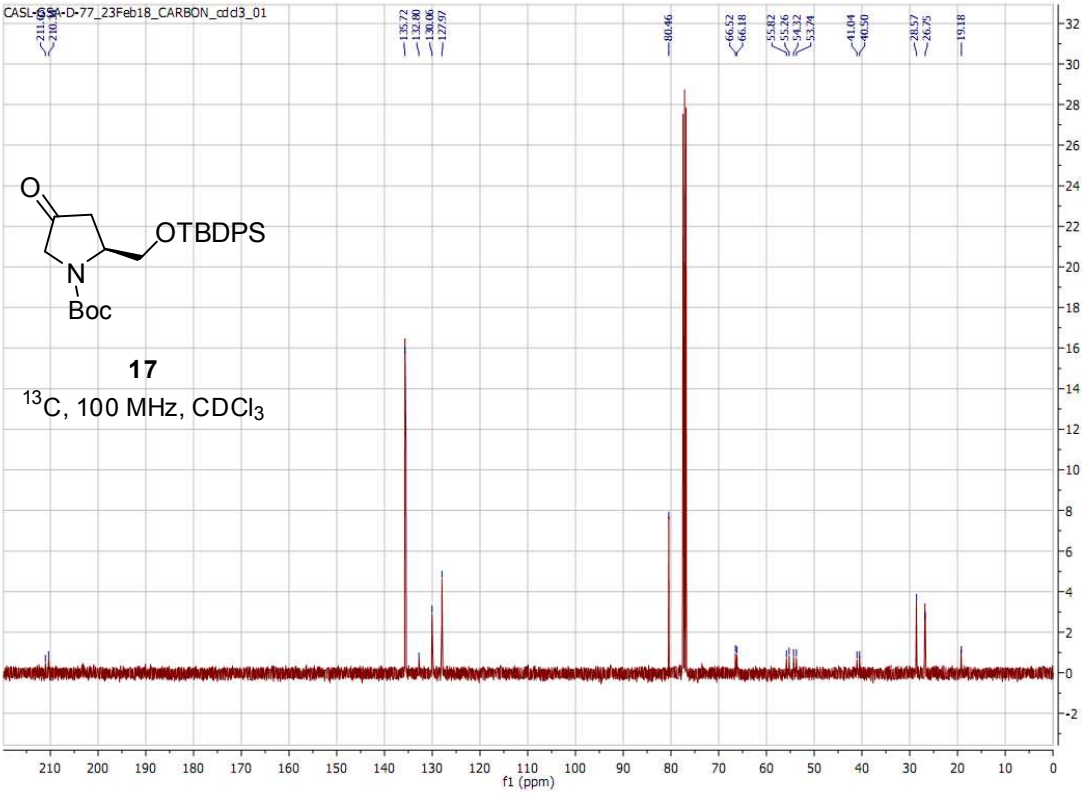
f1 (ppm)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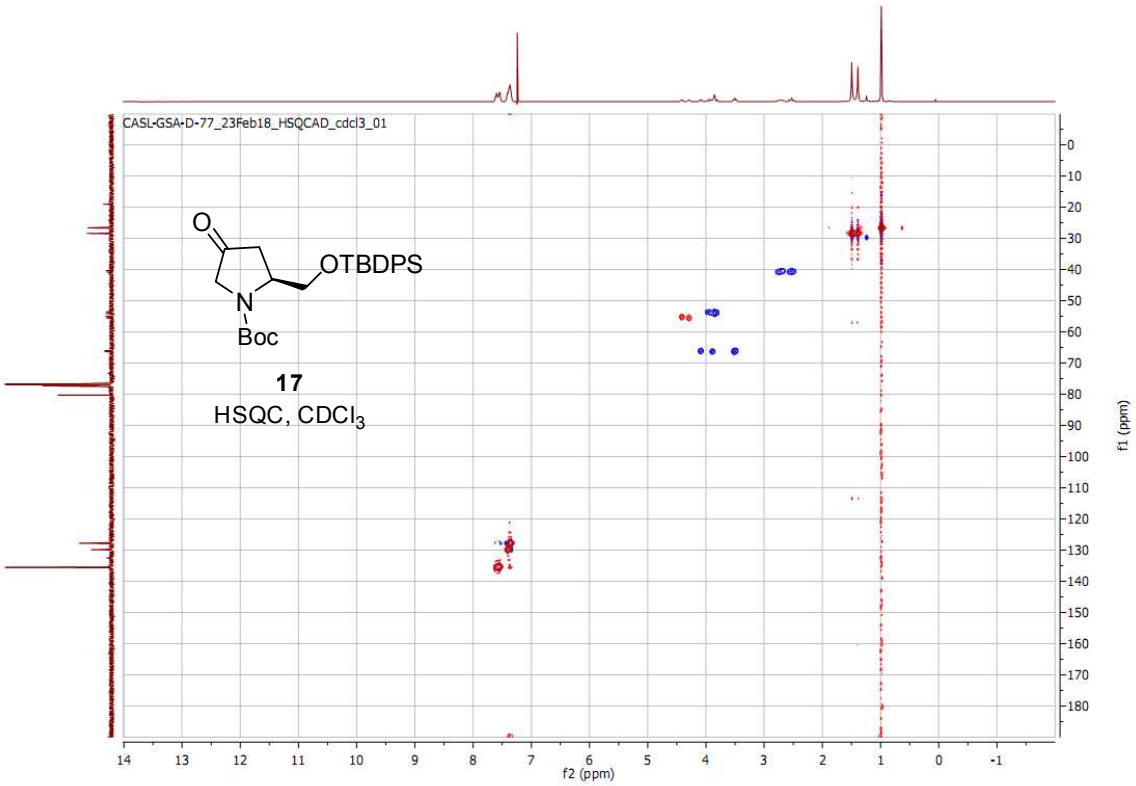
f1 (ppm)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Boc
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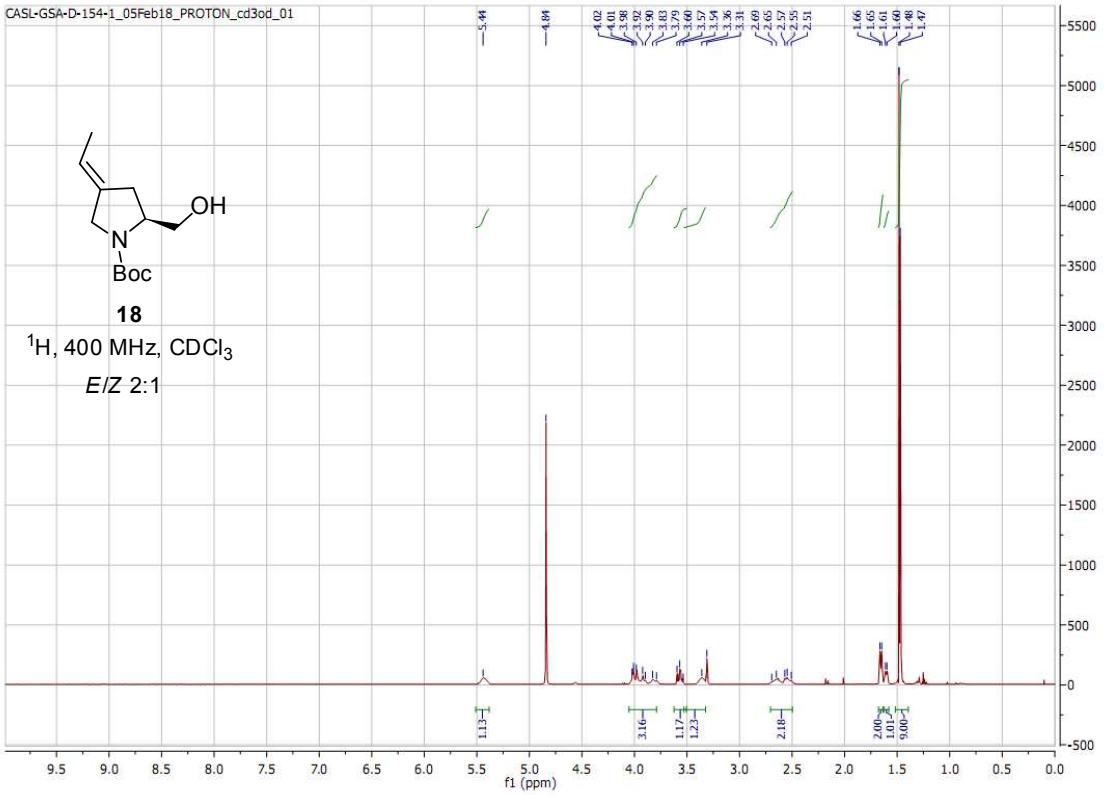
HSQC, CDCl3
f2 (ppm)
f1 (ppm)



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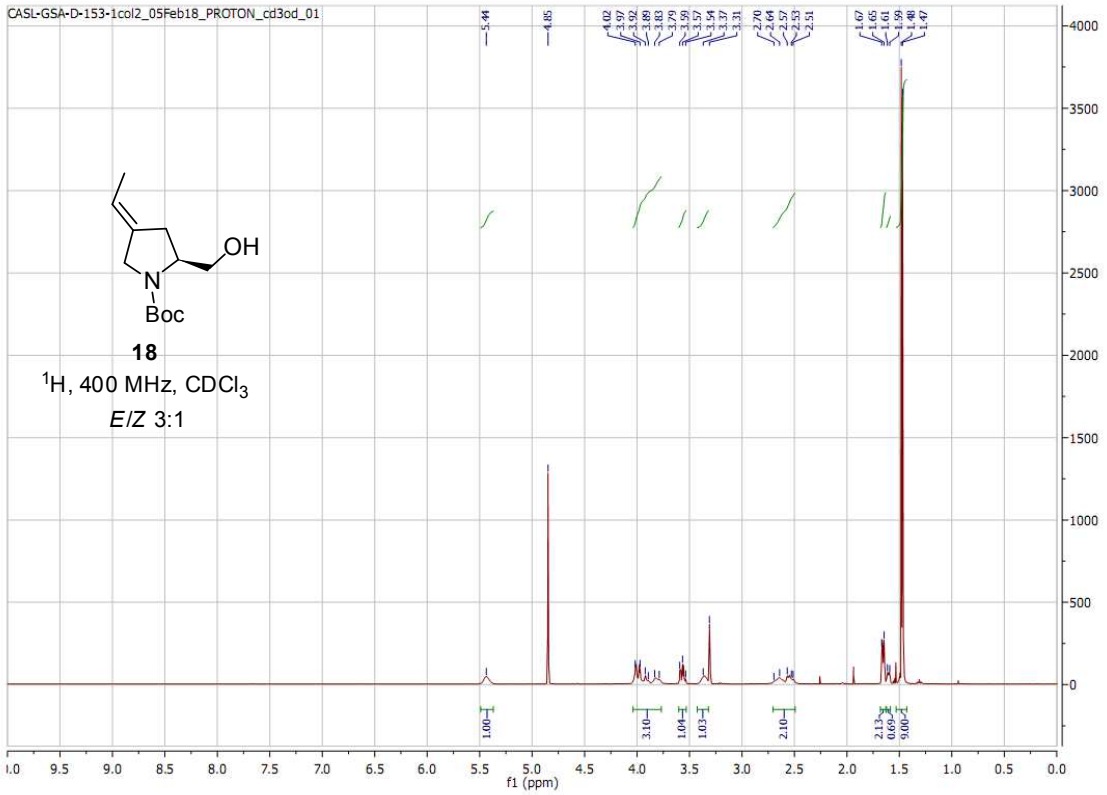
E/*Z* 2:1



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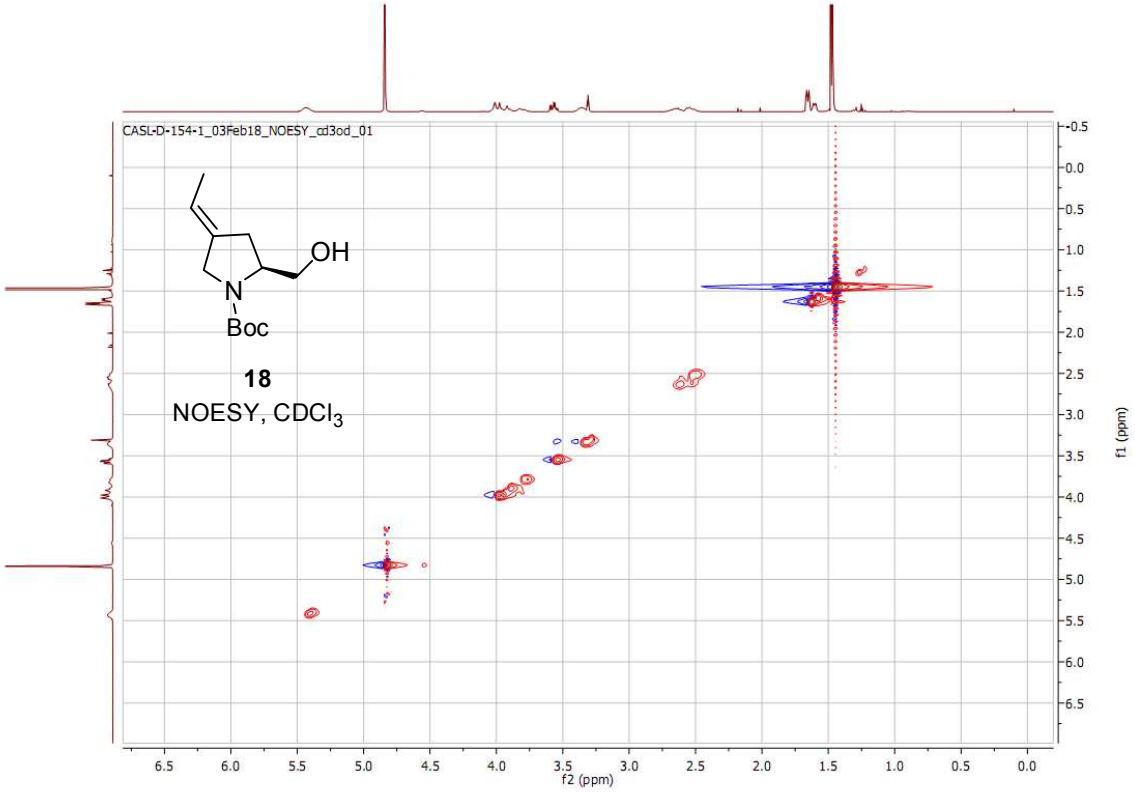
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OH
N
Boc
18
NOESY, CDCl3
f2 (ppm)
f1 (ppm)