

Selective Reduction of Peptide Isothiazolidin-3-ones

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General Procedures

Anhydrous solvents and reagents were purchased from commercial vendors and were used as received. Flash chromatography was performed with Merck 60 grade silica gel, and preparative-scale HPLC was performed with a C₈ or C₁₈ reverse phase column, eluting with water-acetonitrile with 0.1% TFA added.

¹H NMR were acquired at 400 MHz at Sunesis Pharmaceuticals, Inc, ¹³C NMR were acquired at 100 MHz at Acorn NMR, Pleasanton, CA. High resolution mass spectral analysis was performed at UC Berkeley, Berkeley, CA.

Improved Procedure for Synthesis of Compounds 2a-2b.

To a solution of **1a** or **1b** (7 mmol) in 100 mL dry CH₂Cl₂ was added pyridine (10 mL). The solution was cooled to -78 °C under N₂ and stirred for 15 min, and bromine (2.5 eq) in dry CH₂Cl₂ (to 1.0 M) was added dropwise over 30 min. The solution was allowed to warm to 0 °C over 2 h, and then quenched by the addition of 50 mL 10 mM sodium thiosulfate in H₂O. The organic phase was separated, washed 3x 75 mL 10% NaHSO₄, 1x 100 mL sat. NaCl, dried on MgSO₄, and evaporated *in vacuo*. Flash chromatography (1:1 EtOAc:hexanes) afforded the product as a white solid. Spectral characteristics of **2a** and **2b** were identical to those in reference 9. **2a**: 46% (70% based on recovered s.m.), **2b**: 55% (58% based on recovered s.m.)

Synthesis of coumarin thioacid 5.

A 25 mL round bottom flask was charged with 771.7 mg (4.058 mmol) of coumarin-3-carboxylate and 10 mL SOCl₂ added under inert atmosphere. The solution was heated to reflux (~80 °C) for 2 h, cooled, and evaporated *in vacuo*. The white residue was taken up in 10 mL dry CH₂Cl₂ and added dropwise via addition funnel, to a solution of NaSH•H₂O (456.3 mg, 6.160 mmol) in 10 mL MeOH (0 °C). The solution is stirred for 10 min on ice, then warmed to RT and stirred for 30 min, evaporated, and redissolved in 50 mL H₂O. The aqueous solution is acidified to pH 3 with 10 M HCl and extracted 3x 50 mL CH₂Cl₂. The organic phases were combined, dried on MgSO₄, and

evaporated *in vacuo*. Flash chromatography (2:100 MeOH:CH₂Cl₂) afforded the product (375.4 mg, 1.822 mmol) as a yellow solid.

General Procedure for Synthesis of Compounds 3a-3l and 6 (for characterization)

To a solution of **2a** or **2b** (10-100 mg) in CH₂Cl₂ (to 0.1 M) was added the nucleophile (1.05 eq). The solution was stirred at room temperature for 15 min, and then evaporated. Products were purified by RP-HPLC (0-90% CH₃CN + 0.1% TFA). Fractions containing product were concentrated to remove acetonitrile, and then NaOH added to neutralize the aqueous solution (except with compounds **3f** and **3j** which were untreated). The aqueous solutions were extracted 3x with CH₂Cl₂, and the organic phases were combined, dried on MgSO₄, and evaporated *in vacuo* to give the products, generally as white solids or clear oils.

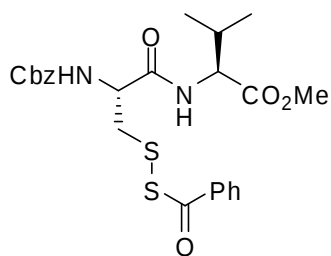
Compound	Yield
3a	47.0%
3b	55.2%
3c	61.1%
3d	52.7%
3e	43.8%
3f	60.2%
3g	82.8%
3h	60.3%
3i	61.4%
3j	90.8%
3k	64.0%
3l	65.3%

General Procedure for Analysis of Reaction Selectivity (Reaction of 1b and 2b to give products 3a-3l)

To a solution of **1b** or **2b** (1-10 mg) in 4:1 MeOH:buffer (50 mM HEPES, 100 mM NaCl, 1 mM EDTA, pH 7.0) was added the nucleophile (1.05 eq). The solution was monitored by RP-LCMS for formation of the adduct.

For reactions involving compound **2b**, a reaction was judged to have taken place if less than 5% of the starting material remained and more than 95% of product **3a-3l** was present after 24 h (note that the nucleophiles reported in this paper generally gave quantitative conversion in less than 10 min).

For reactions involving compound **1b**, a reaction was judged to have taken place if more than 5% of the adduct forms in 24 h or if less than 95% of the starting material remained after 24 h.

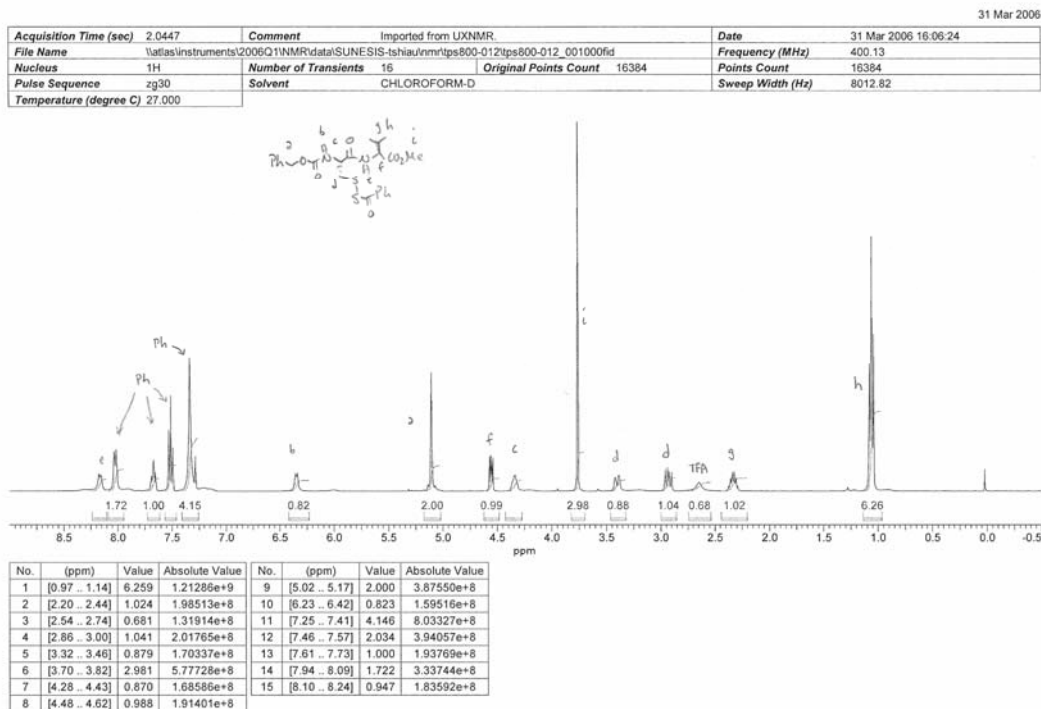


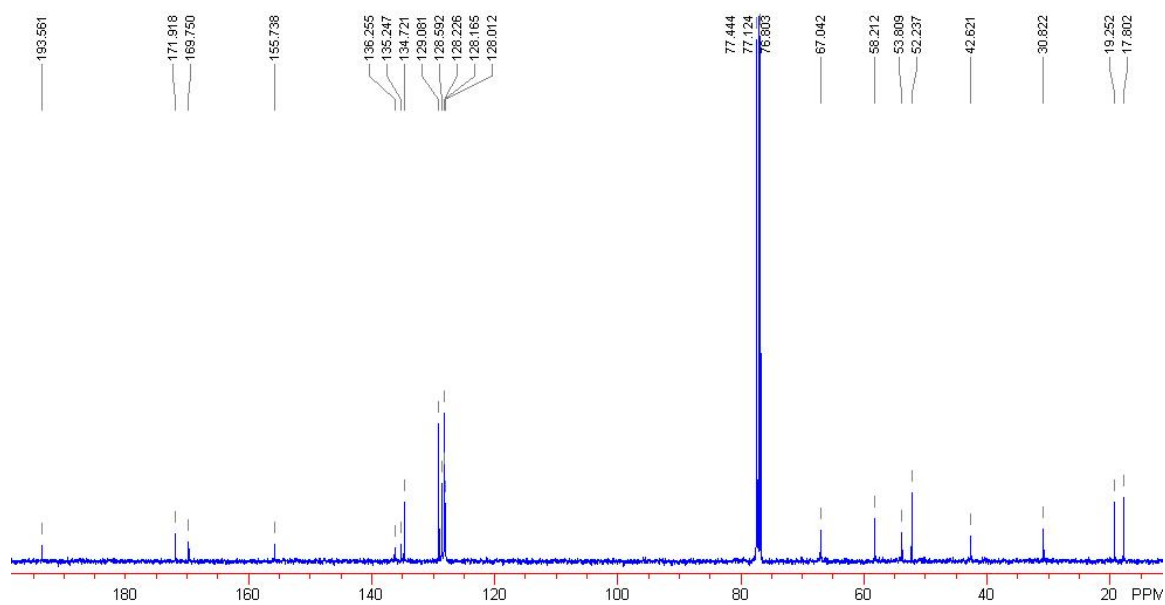
Compound **3a**

Chemical Formula: $C_{24}H_{28}N_2O_6S_2$

Exact Mass: 504.1389

Compound **3a**. ^1H NMR (400 MHz, CDCl_3) δ 1.06 (m, 6H), 2.34 (m, 1H), 2.93 (dd, $J=8.3, 14.1$ Hz, 1H), 3.40 (dd, $J=2.9, 14.2$ Hz, 1H), 3.76 (s, 3H), 4.34 (m, 1H), 4.56 (dd, $J=4.9, 8.4$ Hz, 1H), 5.11 (s, 2H), 6.35 (d, $J=6.8$ Hz, 1H), 7.34 (m, 5H), 7.51 (t, $J=7.8$, 2H), 7.67 (m, 1H), 8.02 (m, 2H), 8.16 (d, $J=7.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 17.80, 19.25, 30.82, 42.62, 52.24, 53.81, 58.21, 67.04, 128.0, 128.16, 128.23, 128.59, 129.08, 134.72, 135.24, 136.26, 155.74, 169.75, 171.92, 193.56. MH^+ predicted for $C_{24}H_{28}N_2O_6S_2$: 505.1462, found: 505.1480.





Elemental Composition

Date : 21-APR-2006

File:N1094 Ident:3_7 SMO(1,9) PKD(9,4,9,0.01%,0.0,30.00%,F,F)

ZAB-SEQ FAB+ Voltage 8pI:3942912 TIC:313466112 Flags:NORM

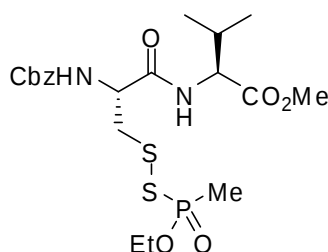
File Text:SHIAU TPS-524-071 NBA

Heteroatom Max: 20 Ion: Both Even and Odd

Limits:

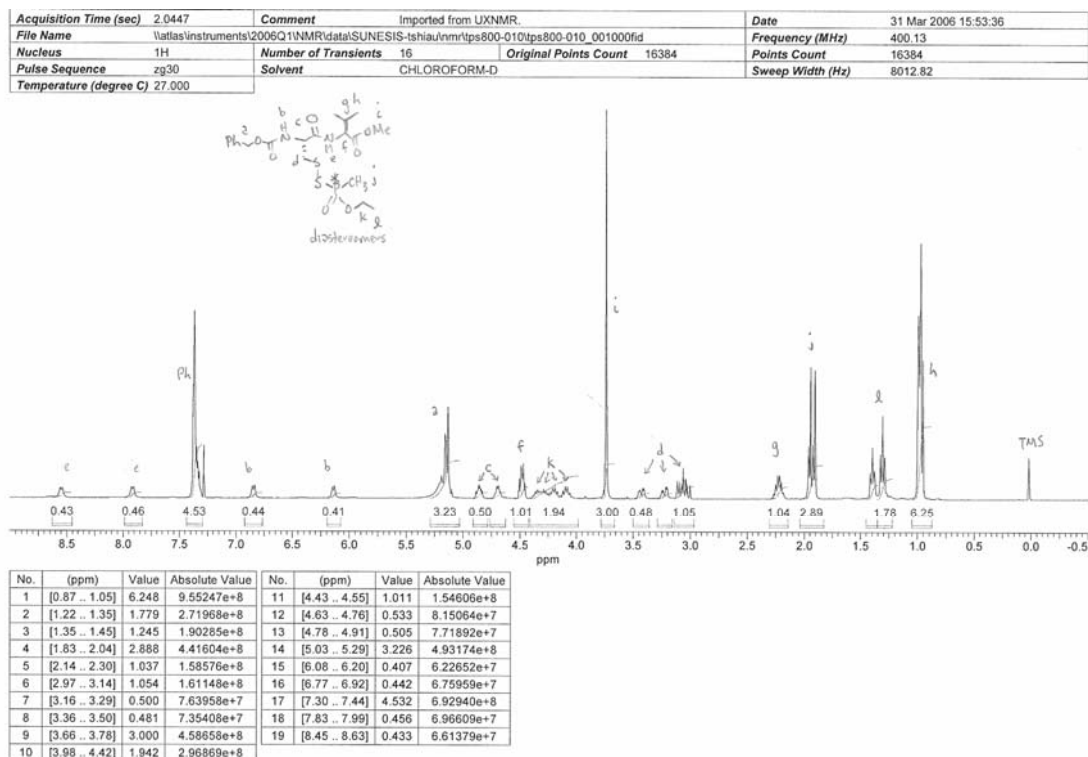
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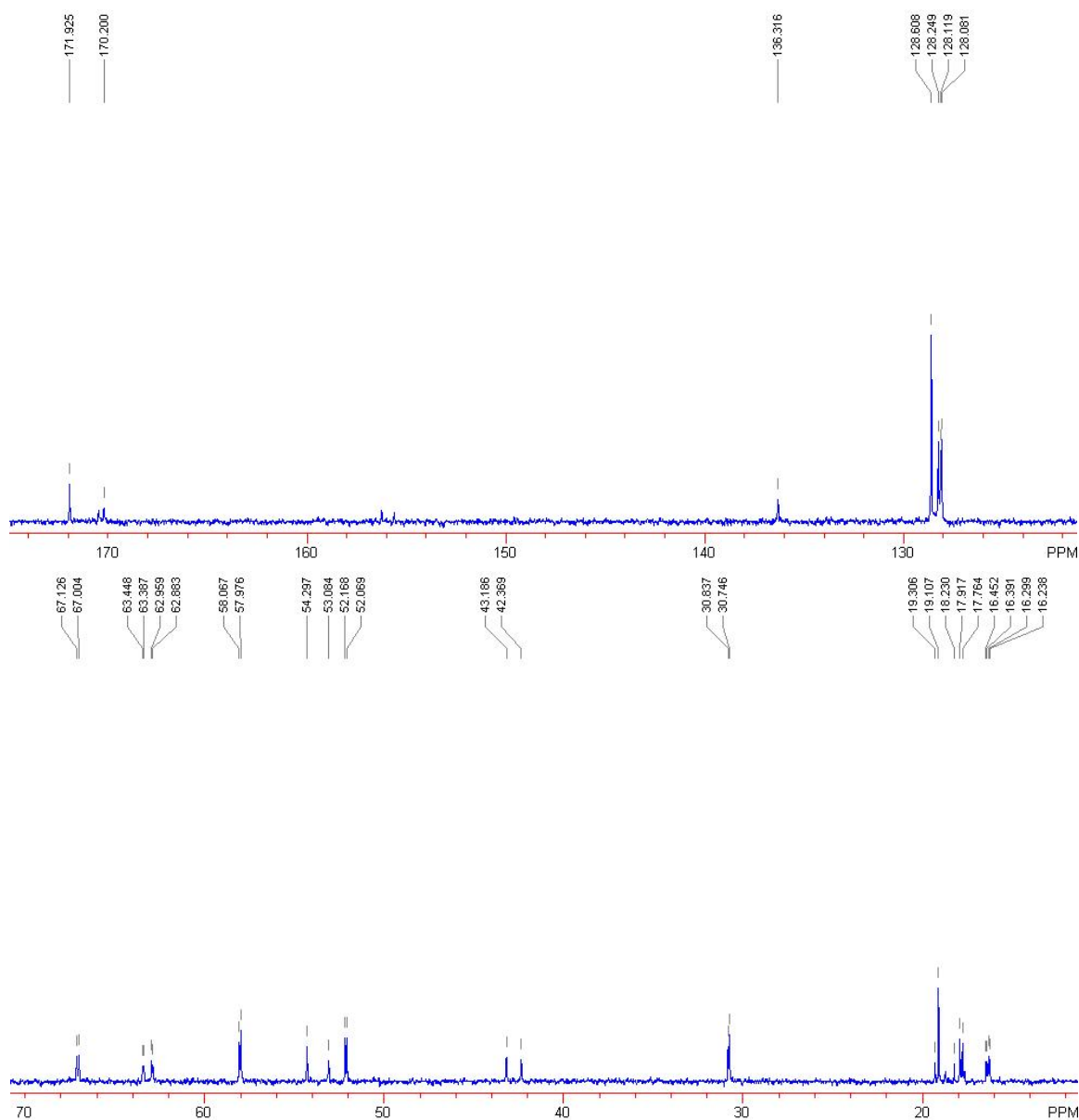
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			-12.8	-6.5	506.143943	25.5	32		20	5		1
			-13.2	-6.7	506.143764	17.0	25		22	4	8	
			13.4	6.8	506.157211	15.5	27		28	3	3	2
			13.4	6.8	506.157230	26.0	31	1	19	5	2	
			13.5	6.8	506.157271	7.5	17	1	29	6	7	2
			-14.1	-7.1	506.143317	21.5	29	1	21	2	6	
			-14.1	-7.1	506.143297	11.0	25		30		7	2
			14.7	7.4	506.157861	24.5	35		24	1	1	1
			14.8	7.5	506.157922	16.5	25	1	25	4	5	1
			-15.0	-7.6	506.142844	21.0	28	1	23	5		2
			-15.4	-7.8	506.142666	12.5	21	1	25	4	8	1
			-15.5	-7.8	506.142605	20.5	31		24	1	4	1
			15.7	7.9	506.158369	12.0	21		26	6	7	1
			16.0	8.1	506.158553	15.0	29		30		4	2
			16.1	8.1	506.158573	25.5	33	1	21	2	3	
			16.2	8.2	506.158614	7.0	19	1	31	3	8	2
			-16.7	-8.5	506.141974	22.0	27	1	19	5	5	
			-16.8	-8.5	506.141955	11.5	23		28	3	6	2
			-16.8	-8.5	506.141913	30.0	37		18	2	1	
			17.0	8.6	506.159020	21.0	29		22	4	5	
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			-18.1	-9.2	506.141263	21.0	29		22	4	3	1
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			18.7	9.5	506.159891	20.0	30		26	4		2
			-19.0	-9.6	506.140815	25.5	33	1	21	2	1	1
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			19.6	9.9	506.160363	20.5	31		24	1	6	
505.147952	100.0		0.2	0.1	505.148043	16.5	25		25	6	2	2
			0.2	0.1	505.148068	21.5	30	1	22	1	6	
			-0.7	-0.4	505.147595	21.0	29	1	24	4		2
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			1.1	0.6	505.148515	17.0	26		23	3	8	
			-1.2	-0.6	505.147356	20.5	32		25		4	1
			1.5	0.7	505.148694	25.5	33		21	4		1
			-1.5	-0.8	505.147172	17.5	24		21	6	7	
			2.0	1.0	505.148938	20.5	31	1	26	1	1	2
			-2.4	-1.2	505.146725	22.0	28	1	20	4	5	
			-2.5	-1.2	505.146706	11.5	24		29	2	6	2
			-2.5	-1.3	505.146664	30.0	38		19	1	1	
			2.8	1.4	505.149386	16.0	27		27	3	3	2
			2.9	1.5	505.149405	26.5	31	1	18	5	2	
			3.0	1.5	505.149446	8.0	17	1	28	6	7	2



Compound **3b** (1:1 d.r.)
 Chemical Formula: C₂₀H₃₁N₂O₇PS₂
 Exact Mass: 506.1310

Compound **3b**. ¹HNMR (400 MHz, CDCl₃) δ 0.97 (m, 6H), 1.31 (t, 1.5 H, J=7.4 Hz), 1.40 (t, 1.5 H, J=6.9 Hz), 1.93 (m, 3H), 2.23 (m, 1H), 3.06 (m, 1H), 3.21 (m, 0.5 H), 3.42 (m, 0.5 H), 3.74 (s, 3H), 4.05-4.35 (m, 2H), 4.48 (m, 1H), 4.70 (m, 1H), 4.85 (m, 1H), 5.15 (m, 2H), 6.14 (d, 0.5 H, J=7.4 Hz), 6.84 (d, 0.5 H, J=7.8 Hz), 7.37 (m, 5H), 7.92 (d, 0.5 H, J=8 Hz), 8.55 (d, 0.5 H, J=8 Hz). ¹³CNMR (100 MHz, CDCl₃) δ 16.24, 16.30, 16.40, 15.45, 17.76, 17.92, 18.23, 19.11, 19.31, 30.75, 30.84, 42.37, 43.19, 52.07, 52.17, 53.08, 54.30, 58.00, 58.07, 62.88, 62.96, 63.39, 63.45, 67.04, 67.13, 128.08, 128.12, 128.25, 128.61, 136.32, 170.20, 171.93. MH⁺ predicted for C₂₀H₃₁N₂O₇PS₂: 507.1383, found: 507.1381.



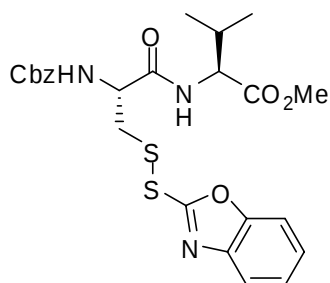


Elemental Composition

Date : 20-APR-2006

Heteroatom Max: 20 Ion: Both Even and Odd
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	0.9	0.5	507.138505	29.5	38	19		2			
	1.0	0.5	507.138546	11.0	24	29	1	7		2	
	-1.1	-0.5	507.137516	7.0	18	30	5	6	1	2	
	-1.1	-0.6	507.137475	25.5	32	20	4	1	1		
	1.5	0.8	507.138818	25.0	34	22	1	2	1		
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	-1.7	-0.8	507.137204	11.5	22	27	4	6		2	
	-1.8	-0.9	507.137162	30.0	36	17	3	1			
	1.9	1.0	507.139013	17.0	24	21	5	8			
	-2.1	-1.0	507.137008	19.5	32	28			1	2	
	2.3	1.1	507.139192	25.5	31	19	6			1	
	-2.4	-1.2	507.136824	16.5	24	24	6	3	1	1	
	2.5	1.3	507.139326	12.5	20	24	6	8	1		
	2.9	1.5	507.139510	15.5	28	28		5	1	1	
	-3.0	-1.5	507.136512	21.0	28	21	5	3		1	
	3.6	1.8	507.139884	16.0	25	25	5	3		2	
	-3.8	-1.9	507.136138	20.5	31	24		5	1		
	4.2	2.1	507.140196	11.5	21	28	6	3	1	2	
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	-5.7	-2.9	507.135174	16.0	27	25	1	7		1	
	6.3	3.2	507.141226	15.5	27	27	2	4		2	
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	6.9	3.5	507.141539	11.0	23	30	3	4	1	2	
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	7.5	3.8	507.141877	24.5	35	23		2		1	
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	8.9	4.5	507.142564	20.5	28	23	6			2	
	-9.1	-4.6	507.133452	21.5	27	20	6	3	1		
	9.2	4.6	507.142697	7.5	17	28	6	8	1	1	
	9.5	4.8	507.142881	10.5	25	32		5	1	2	
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	9.8	5.0	507.143036	21.0	29	21	3	6			
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	10.4	5.3	507.143348	16.5	25	24	4	6	1		
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	11.5	5.9	507.143906	20.0	30	25	3	1		2	
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Compound **3c**

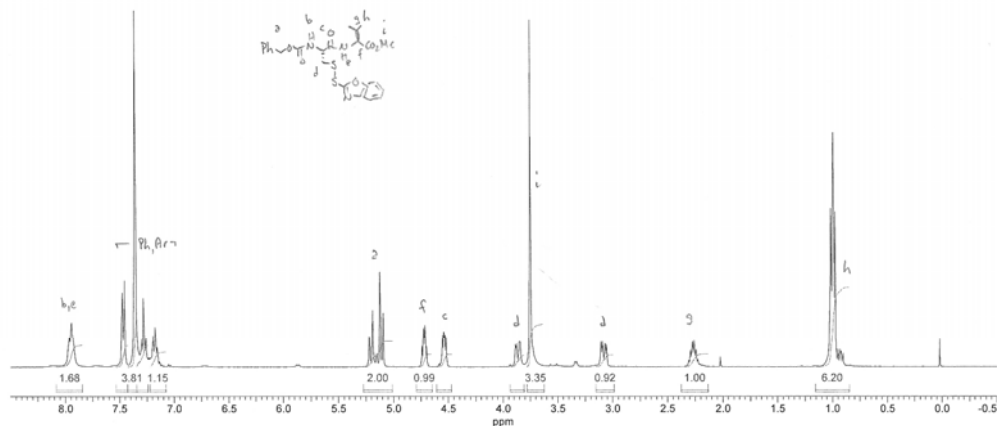
Chemical Formula: $C_{24}H_{27}N_3O_6S_2$

Exact Mass: 517.1341

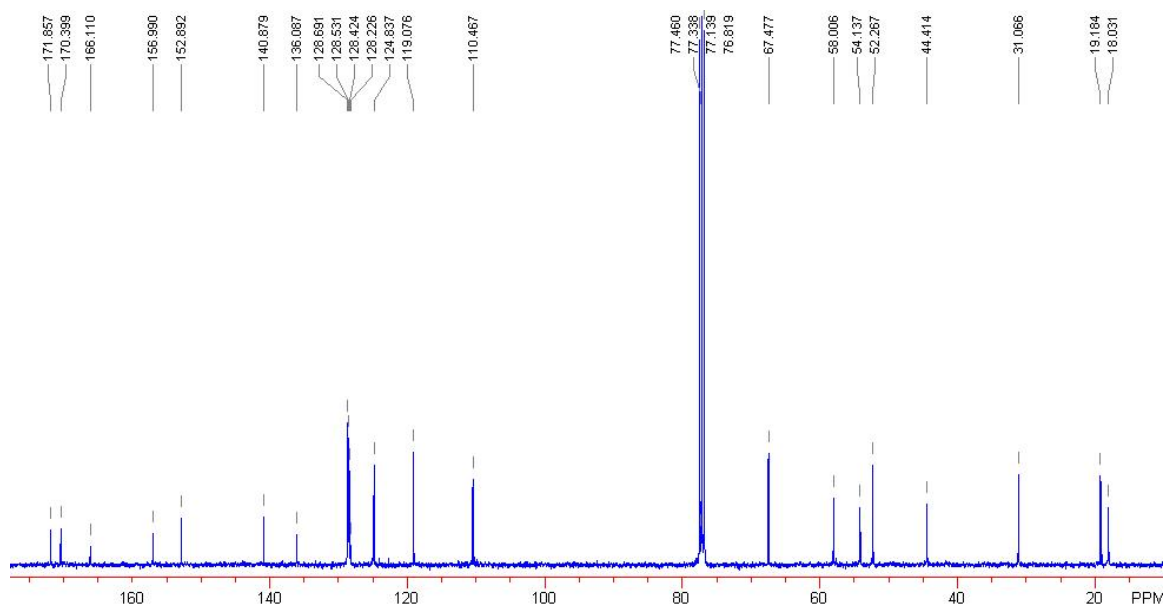
Compound **3c**. 1H NMR (400 MHz, $CDCl_3$) δ 1.00 (m, 6H), 2.27 (m, 1H), 3.08 (dd, 1H, $J=5.8, 14.2$ Hz), 3.75 (s, 3H), 3.87 (dd, 1H, $J=3.9, 14.2$ Hz), 4.54 (m, 1H), 4.72 (m, 1H), 5.10 (d, 1H, $J=11.7$ Hz), 5.20 (d, 1H, $J=12.2$ Hz), 7.1-7.5 (m, 9H), 7.95 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 18.03, 19.19, 31.07, 44.41, 52.27, 54.14, 58.01, 67.48, 110.47, 119.08, 124.84, 128.23, 128.42, 128.53, 128.69, 136.09, 140.68, 152.69, 156.99, 166.11, 170.40, 171.86. MH^+ predicted for $C_{24}H_{27}N_3O_6S_2$: 518.1414, found: 518.1426.

Acquisition Time (sec)	2.0447	Comment	Imported from LUXNMR.	Date	31 Mar 2006 16:12:48
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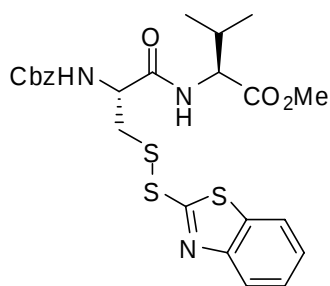


No.	(ppm)	Value	Absolute Value	No.	(ppm)	Value	Absolute Value
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2	[2.13 .. 2.38]	1.002	2.46061e+8	9	[7.08 .. 7.23]	1.150	2.82520e+8
3	[2.99 .. 3.15]	0.915	2.24832e+8	10	[7.24 .. 7.34]	1.689	4.15047e+8
4	[3.63 .. 3.78]	3.351	8.23293e+8	11	[7.35 .. 7.43]	3.810	9.36015e+8
5	[3.81 .. 3.94]	0.901	2.21459e+8	12	[7.43 .. 7.54]	1.650	4.05437e+8
6	[4.47 .. 4.61]	0.977	2.39958e+8	13	[7.85 .. 8.08]	1.682	4.13134e+8
7	[4.65 .. 4.79]	0.987	2.42401e+8				



Metereatom Max: 20 Ion: Both Even and Odd
Limits:

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	-1.3	-0.7	518.141955	12.5	24	28	3	6	2
	1.3	0.7	518.143297	12.0	26	30		7	2
	-1.3	-0.7	518.141913	31.0	38	18	2	1	
	2.2	1.2	518.143764	18.0	26	22	4	8	
	2.6	1.3	518.143943	26.5	33	20	5		1
	-2.6	-1.3	518.141263	22.0	30	22	4	3	1
	-3.9	-2.0	518.140612	13.0	22	26	6	5	2
	3.9	2.0	518.144635	17.0	27	26	4	3	2
	-3.9	-2.0	518.140571	31.5	36	16	5		
	5.2	2.7	518.145285	26.0	35	22	2	1	1
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	6.5	3.4	518.145977	16.5	29	28	1	4	2
	-6.5	-3.4	518.139233	26.5	35	20	1	4	
	7.4	3.8	518.146444	22.5	29	20	5	5	
	-7.8	-4.0	518.138583	17.5	27	24	3	6	1
	8.7	4.5	518.147136	13.0	23	26	4	8	1
	-9.0	-4.7	518.137932	8.5	19	28	5	8	2
	9.1	4.7	518.147315	21.5	30	24	5		2
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	11.7	6.0	518.148657	21.0	32	26	2	1	2
	-11.7	-6.1	518.136553	22.0	32	22		7	
	12.6	6.5	518.149124	27.0	32	18	6	2	
	-12.6	-6.5	518.136081	21.5	31	24	3	1	2
	13.9	7.2	518.149816	17.5	26	24	5	5	1
	-14.3	-7.4	518.135211	22.5	30	20	3	6	
	15.2	7.9	518.150467	26.5	34	20	3	3	
	-15.2	-7.9	518.134739	22.0	29	22	6		2
	15.2	7.9	518.150508	8.0	20	30	4	8	2
	-15.5	-8.1	518.134560	13.5	22	24	5	8	1
	16.5	8.5	518.151159	17.0	28	26	2	6	1
	-16.5	-8.6	518.134052	26.0	36	22		2	1
	-16.9	-8.7	518.133868	23.0	28	18	6	5	
	17.8	9.2	518.151809	26.0	36	22		4	
	-17.8	-9.2	518.133401	17.0	28	26	2	4	2
	19.1	9.9	518.152496	22.0	29	22	6	2	1
	-19.1	-9.9	518.132709	26.5	34	20	3	1	1

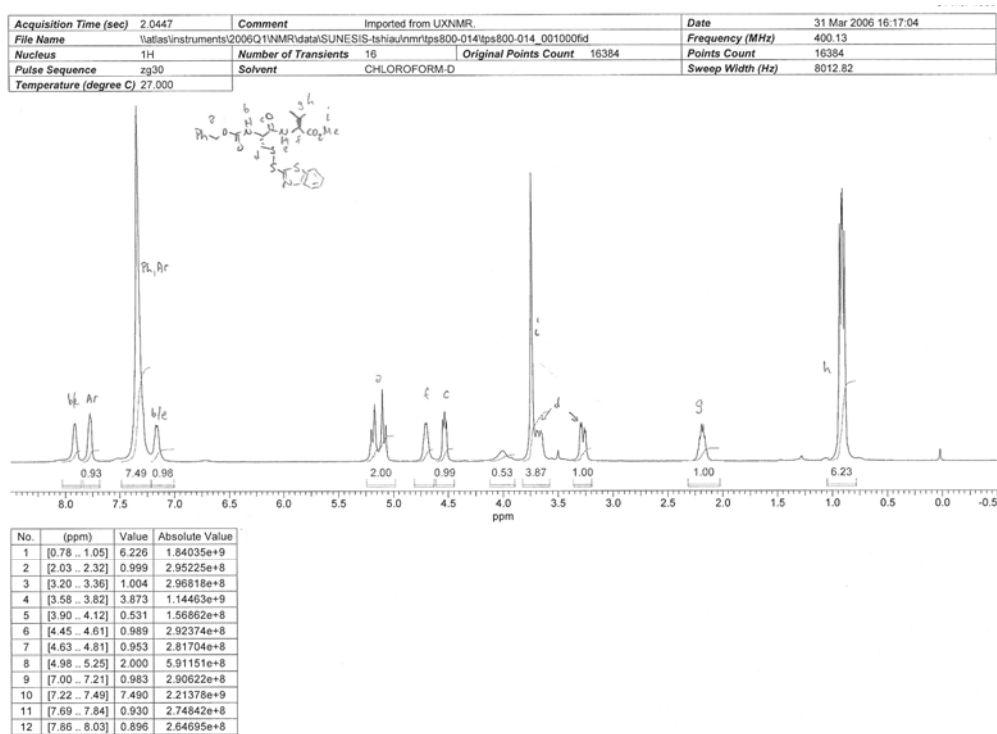


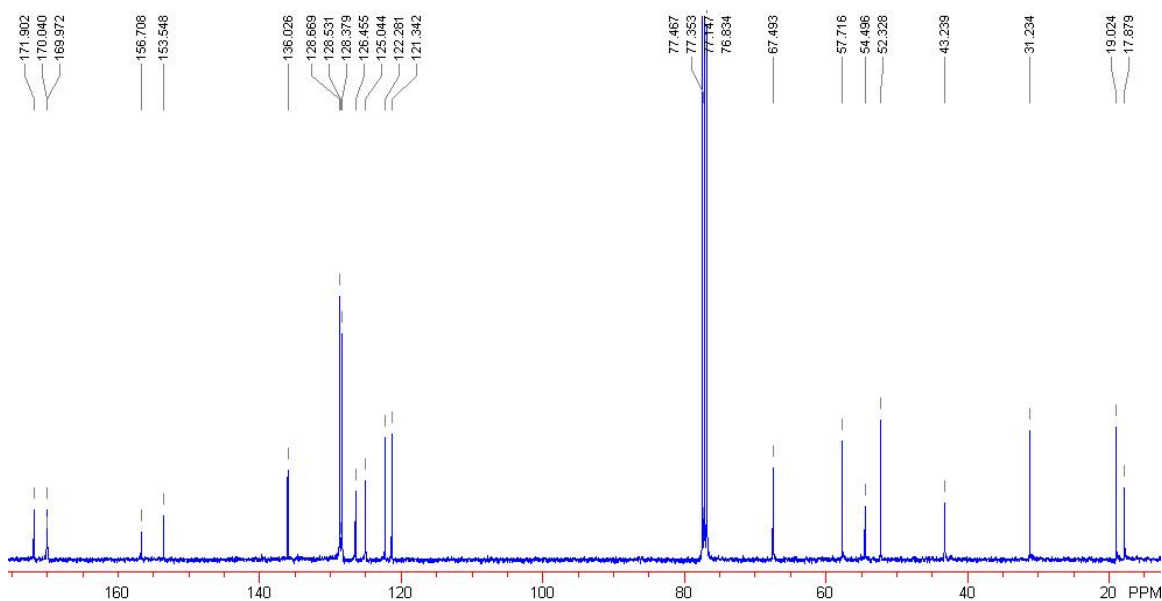
Compound **3d**

Chemical Formula: $C_{24}H_{27}N_3O_5S_3$

Exact Mass: 533.1113

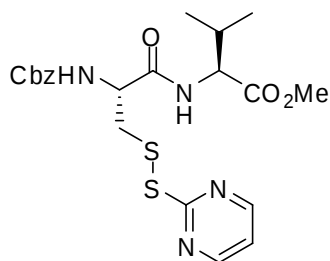
Compound **3d**. 1H NMR (400 MHz, $CDCl_3$) δ 0.91 (m, 6H), 2.18 (m, 1H), 3.27 (dd, 1H, $J=4.8, 14.1$ Hz), 3.6-3.7 (m, 4H), 4.54 (m, 1H), 4.70 (m, 1H), 5.0-5.1 (m, 2H), 7.16 (d, 1H, $J=4.1$ Hz), 7.34 (m, 8H), 7.77 (s, 1H), 7.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.88, 19.02, 31.23, 43.24, 52.33, 54.50, 57.72, 67.49, 121.34, 122.28, 125.04, 126.46, 128.38, 128.53, 128.67, 136.03, 153.55, 156.71, 169.97, 170.04, 171.90. MH^+ predicted for $C_{24}H_{27}N_3O_5S_3$: 534.1186, found: 534.1181.





Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

534.118050	10.0	-0.5	0	0	0	0	0	0	0
		40.0	200	400	6	8	3		
Mass	PPH	mDa	Calc. Mass	DBE	C	H	N	O	S
534.118050	-0.5	-0.3	534.117769	13.0	22	26	6	4	3
	0.7	0.4	534.118420	22.0	30	22	4	2	2
	-0.9	-0.5	534.117549	23.0	29	18	4	7	
	1.6	0.8	534.118892	22.5	31	20	1	8	
	-1.8	-1.0	534.117082	17.0	29	26		6	2
	1.9	1.0	534.119071	31.0	38	18	2		1
	2.0	1.1	534.119112	12.5	24	28	3	5	3
	-3.0	-1.6	534.116432	8.0	21	30	2	8	3
	-3.1	-1.7	534.116391	26.5	35	20	1	3	1
	3.2	1.7	534.119762	21.5	32	24	1	3	2
	4.1	2.2	534.120229	27.5	32	16	5	4	
	-4.3	-2.3	534.115740	17.5	27	24	3	5	2
	-4.4	-2.4	534.115699	36.0	41	14	2		
	4.5	2.4	534.120454	12.0	26	30		6	3
	5.4	2.9	534.120921	18.0	26	22	4	7	1
	-5.5	-3.0	534.115089	8.5	19	28	5	7	3
	-5.6	-3.0	534.115048	27.0	33	18	4	2	1
	-6.5	-3.5	534.114581	21.0	33	26		1	3
	6.6	3.5	534.121572	27.0	34	18	2	5	
	-6.8	-3.7	534.114397	18.0	25	22	6	4	2
	7.0	3.7	534.121792	17.0	27	26	4	2	3
	7.9	4.2	534.122264	17.5	28	24	1	8	1
	-8.1	-4.3	534.113711	22.0	32	22		6	1
	8.2	4.4	534.122442	26.0	35	22	2		2
	-9.0	-4.8	534.113238	21.5	31	24	3		3
	9.1	4.9	534.122909	32.0	35	14	6	1	
	-9.3	-5.0	534.113060	13.0	24	26	2	8	2
	-9.4	-5.0	534.113019	31.5	38	16	1	3	
	9.5	5.1	534.123134	16.5	29	28	1	3	3
	10.4	5.6	534.123601	22.5	29	20	5	4	1
	-10.6	-5.7	534.112368	22.5	30	20	3	5	1
	11.6	6.2	534.124252	31.5	37	16	3	2	
	11.7	6.2	534.124293	13.0	23	26	4	7	2
	-11.9	-6.3	534.111717	13.5	22	24	5	7	2
	-11.9	-6.4	534.111676	32.0	36	14	4	2	
	-12.8	-6.8	534.111209	26.0	36	22		1	2
	12.9	6.9	534.124944	22.0	31	22	2	5	1
	-13.2	-7.0	534.111025	23.0	28	18	6	4	1
	-14.0	-7.5	534.110558	17.0	28	26	2	3	3
	14.1	7.5	534.125595	31.0	39	18		3	
	14.2	7.6	534.125636	12.5	25	28	1	8	2
	-14.4	-7.7	534.110339	27.0	35	18		6	
	14.5	7.8	534.125814	21.0	32	26	2		3
	-15.3	-8.2	534.109866	26.5	34	20	3		2
	15.4	8.2	534.126281	27.0	32	18	6	1	1
	-15.7	-8.4	534.109688	18.0	27	22	2	8	1
	-16.5	-8.8	534.109216	17.5	26	24	5	2	3
	16.7	8.9	534.126973	17.5	26	24	5	4	2



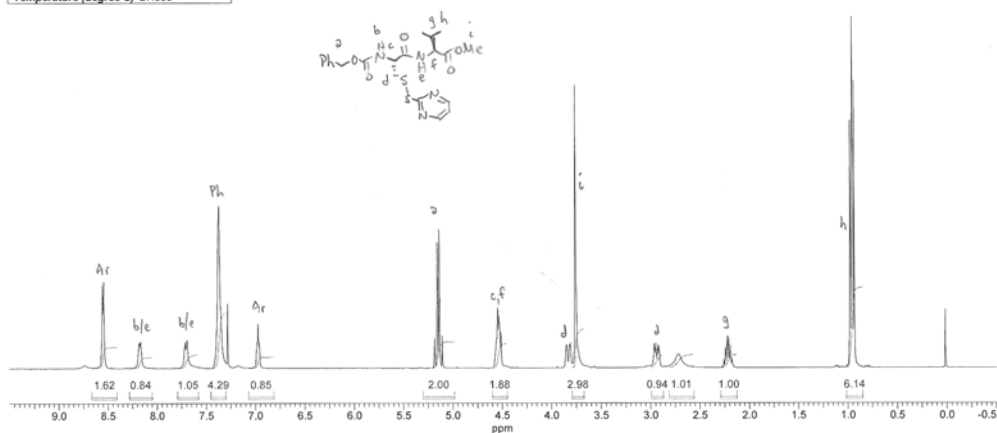
Compound **3e**

Chemical Formula: $C_{21}H_{26}N_4O_5S_2$

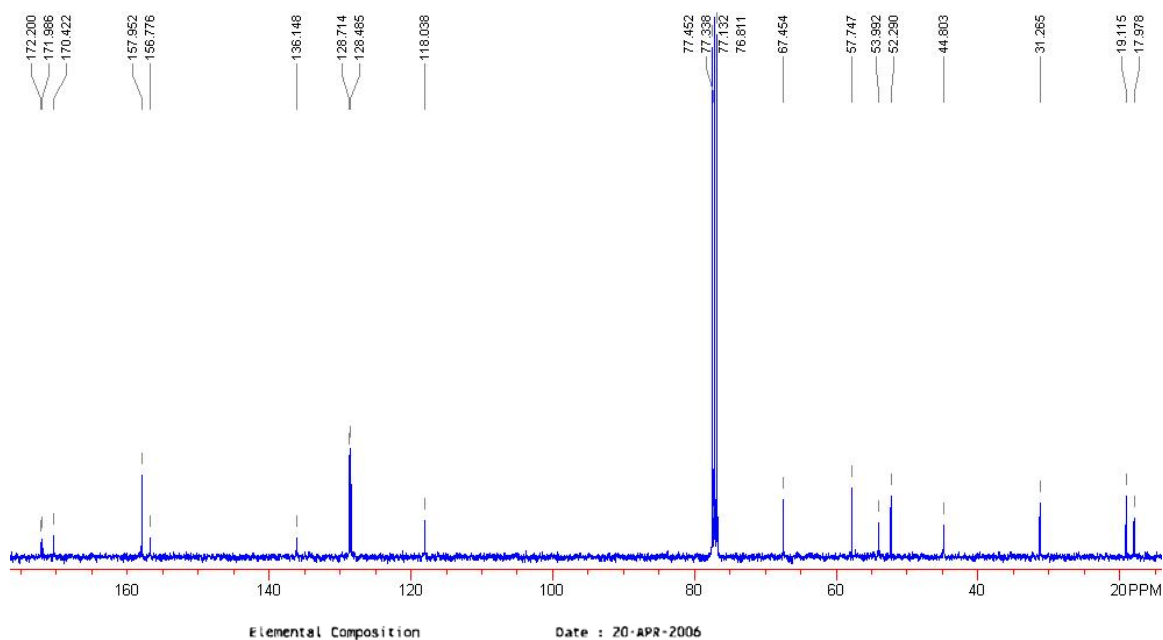
Exact Mass: 478.1345

Compound **3e**. 1H NMR (400 MHz, $CDCl_3$) δ 0.96 (m, 6H), 2.22 (m, 1H), 2.94 (dd, 1H, 5.4, 13.7 Hz), 3.76 (s, 3H), 3.83 (dd, 1H, $J=3.9, 14.1$ Hz), 4.54 (m, 2H), 5.15 (m, 2H), 6.97 (m, 1H), 7.37 (m, 5H), 7.71 (m, 1H), 8.17 (m, 1H), 8.55 (d, 2H, $J=4.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.98, 19.12, 31.27, 44.81, 52.29, 53.99, 57.75, 67.45, 118.04, 126.49, 126.71, 136.15, 156.78, 157.95, 170.42, 171.99, 172.20. MH^+ predicted for $C_{21}H_{26}N_4O_5S_2$: 479.1417, found: 479.1411.

Acquisition Time (sec)	2.0447	Comment	Imported from UXXNMR	Date	25 Mar 2006 23:51:28
File Name	Y:\data\instruments\2006Q1\NMR\data\SUNESIS-tshiau\nmr\tps653-060_001000fid			Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	64	Original Points Count	16384
Pulse Sequence	zg30	Solvent	CHLOROFORM-D	Sweep Width (Hz)	8012.82
Temperature (degree C)	27.000				

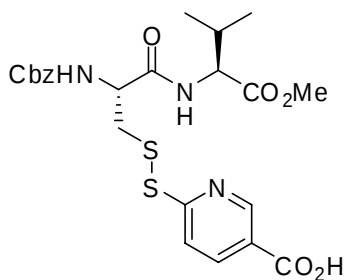


No.	(ppm)	Value	Absolute Value
1	[0.85 .. 1.02]	6.144	6.44134e+9
2	[2.13 .. 2.29]	0.996	1.04376e+9
3	[2.56 .. 2.81]	1.013	1.06154e+9
4	[2.87 .. 2.99]	0.942	9.87944e+8
5	[3.67 .. 3.79]	2.985	3.12915e+9
6	[4.45 .. 4.60]	1.876	1.96722e+9
7	[4.98 .. 5.30]	2.000	2.09681e+9
8	[6.81 .. 7.07]	0.852	8.92864e+8
9	[7.30 .. 7.45]	4.294	4.50143e+9
10	[7.58 .. 7.79]	1.050	1.10047e+9
11	[8.05 .. 8.28]	0.844	8.84414e+8
12	[8.41 .. 8.67]	1.615	1.69337e+9



Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

479.141050		10.0		-0.5	0	0	0	0	0
				40.0	200	400	6	8	2
Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
479.141050	1.1	0.5	479.141597	20.0	27	21	5	2	1
	-1.6	-0.8	479.140260	15.0	26	25	1	6	1
	2.5	1.2	479.142248	29.0	35	17	3		
	2.6	1.2	479.142289	10.5	21	27	4	5	2
	-3.0	-1.4	479.139609	6.0	18	29	3	8	2
	-3.1	-1.5	479.139568	24.5	32	19	2	3	
	3.9	1.9	479.142940	19.5	29	23	2	3	1
	-4.5	-2.1	479.138917	15.5	24	23	4	5	1
	5.3	2.5	479.143590	28.5	37	19		1	
	5.4	2.6	479.143632	10.0	23	29	1	6	2
	-5.8	-2.8	479.138266	6.5	16	27	6	7	2
	-5.9	-2.8	479.138225	25.0	30	17	5	2	
	6.4	3.0	479.144098	16.0	23	21	5	7	
	-6.9	-3.3	479.137758	19.0	30	25	1	1	2
	8.2	3.9	479.144969	15.0	24	25	5	2	2
	-8.7	-4.2	479.136888	20.0	29	21	1	6	
	9.2	4.4	479.145441	15.5	25	23	2	8	
	9.5	4.6	479.145620	24.0	32	21	3		1
	-9.7	-4.6	479.136416	19.5	28	23	4		2
	-10.0	-4.8	479.136237	11.0	21	25	3	8	1
	11.0	5.3	479.146312	14.5	26	27	2	3	2
	-11.5	-5.5	479.135545	20.5	27	19	4	5	
	12.0	5.7	479.146778	20.5	26	19	6	4	
	12.3	5.9	479.146962	23.5	34	23		1	1
	-12.5	-6.0	479.135078	14.5	27	27		4	2
	-12.8	-6.2	479.134894	11.5	19	23	6	7	1
	13.4	6.4	479.147470	11.0	20	25	5	7	1
	-13.9	-6.7	479.134386	24.0	33	21	1	1	1
	14.8	7.1	479.148121	20.0	28	21	3	5	
	-15.3	-7.3	479.133736	15.0	25	25	3	3	2
	16.2	7.8	479.148813	10.5	22	27	2	8	1
	16.6	7.9	479.148992	19.0	29	25	3		2
	-16.7	-8.0	479.133044	24.5	31	19	4		1
	-17.1	-8.2	479.132865	16.0	24	21	3	8	
	17.6	8.4	479.149464	19.5	30	23		6	
	-18.1	-8.7	479.132393	15.5	23	23	6	2	2
	19.0	9.1	479.150150	15.5	23	23	6	4	1
	19.4	9.3	479.150334	18.5	31	27		1	2
	-19.5	-9.3	479.131706	19.5	30	23		4	1
	-19.9	-9.5	479.131522	16.5	22	19	6	7	
	20.4	9.8	479.150801	24.5	31	19	4	2	
	20.4	9.8	479.150842	6.0	17	29	5	7	2
	-20.9	-10.0	479.131056	10.5	22	27	2	6	2



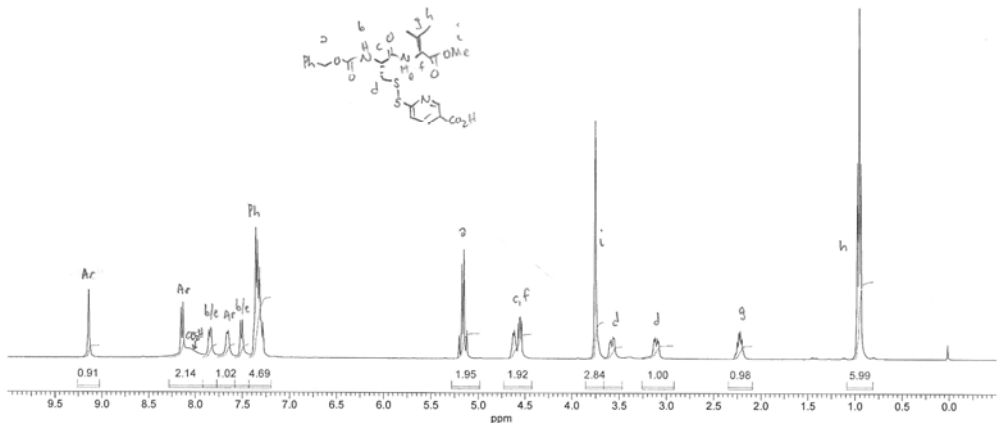
Compound **3f**

Chemical Formula: $C_{23}H_{27}N_3O_7S_2$

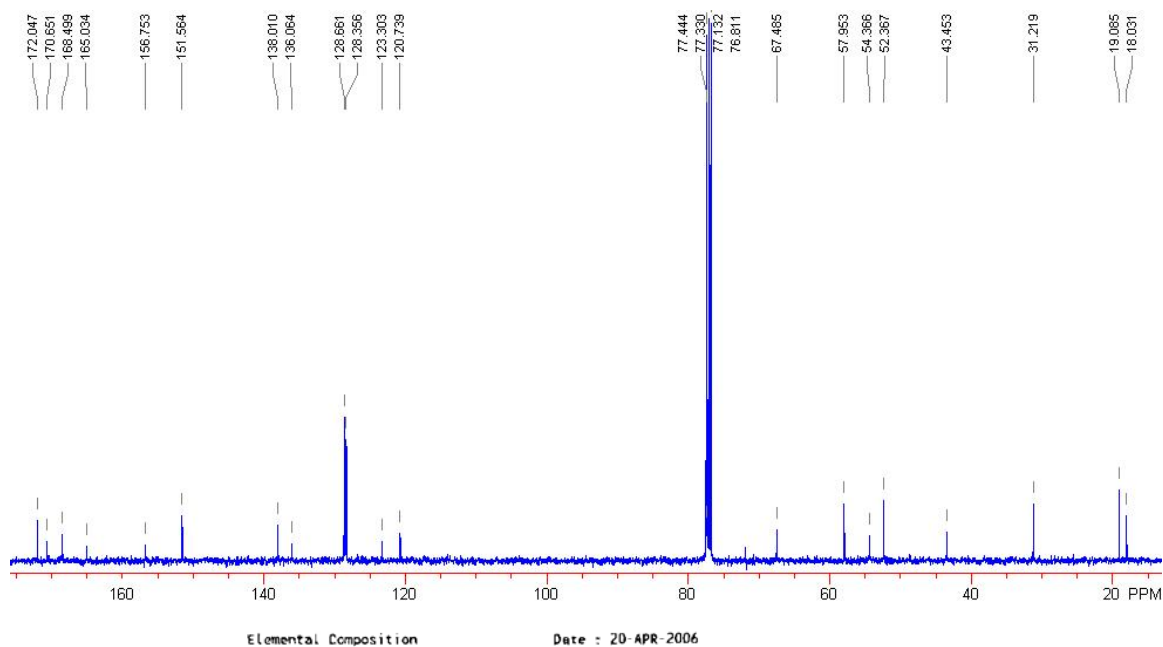
Exact Mass: 521.1290

Compound **3f**. 1H NMR (400 MHz, $CDCl_3$) δ 0.96 (m, 6H), 2.23 (m, 1H), 3.11 (dd, 1H, $J=5.9, 14.2$ Hz), 3.58 (dd, 1H, $J=4.4, 13.7$ Hz), 3.76 (s, 3H), 4.5-4.7 (m, 2H), 5.16 (m, 2H), 7.2-7.4 (m, 5H), 7.51 (d, 1H, $J=8.3$ Hz), 7.65 (m, 1H), 7.85 (m, 1H), 7.9-8.3 (br, 1H), 8.15 (d, 1H, $J=8.3$ Hz), 9.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.03, 19.09, 31.22, 43.45, 52.37, 54.37, 57.95, 67.49, 120.74, 123.30, 128.36, 128.68, 136.06, 138.01, 151.56, 156.76, 165.03, 168.50, 170.65, 172.05. MH^+ predicted for $C_{23}H_{27}N_3O_7S_2$: 522.1363, found: 522.1355.

Acquisition Time (sec)	2.0447	Comment	Imported from LUXNMR.	Date	25 Mar 2006 23:57:52
File Name	\\atlant\instruments\20060211\NMR\data\SUNESIS-Ishtiaq\nmr\tps653-061_001006fid			Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	64	Original Points Count	16384
Pulse Sequence	zg30	Solvent	CHLOROFORM-D	Points Count	16384
Temperature (degree C)	27.000			Sweep Width (Hz)	8012.82

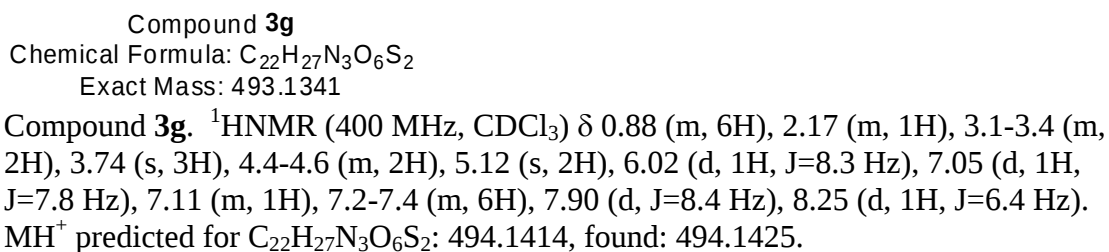


No.	(ppm)	Value	Absolute Value	No.	(ppm)	Value	Absolute Value
1	[0.81 .. 1.09]	5.992	6.64969e+9	8	[7.20 .. 7.43]	4.686	5.20083e+9
2	[2.09 .. 2.35]	0.979	1.08598e+9	9	[7.43 .. 7.58]	1.023	1.13528e+9
3	[2.92 .. 3.26]	0.998	1.10717e+9	10	[7.58 .. 7.77]	1.018	1.13028e+9
4	[3.47 .. 3.66]	0.912	1.01227e+9	11	[7.77 .. 7.92]	0.994	1.10294e+9
5	[3.67 .. 3.86]	2.843	3.15527e+9	12	[7.92 .. 8.28]	2.144	2.37946e+9
6	[4.43 .. 4.73]	1.916	2.12626e+9	13	[9.03 .. 9.26]	0.905	1.00462e+9
7	[4.96 .. 5.28]	1.954	2.16823e+9				

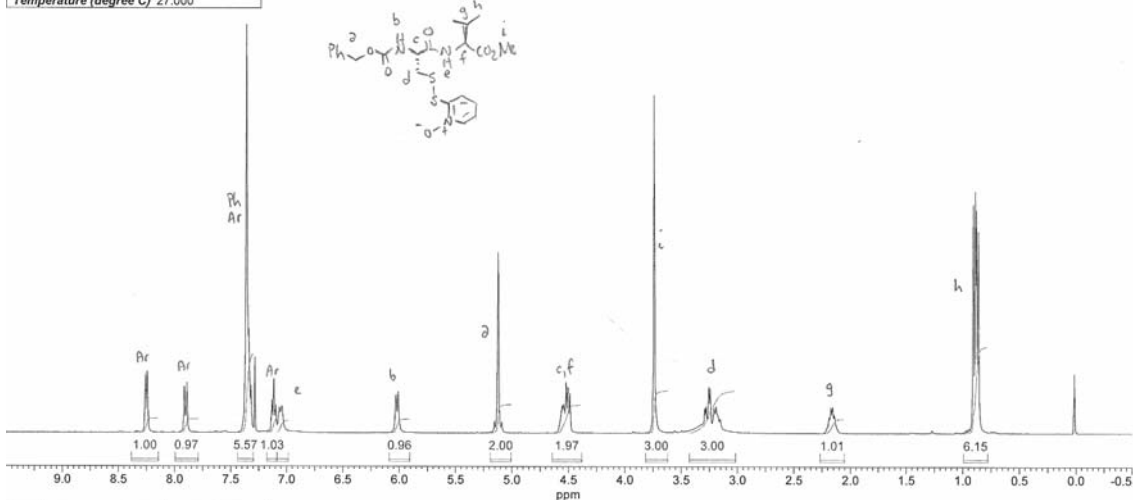


Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

522.135460	10.0	-0.5	0	0	0	0	0	0	0
		40.0	200	400	6	8	2		
Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
522.135460	0.0	0.0	522.135485	30.5	35	16	5	1	
	0.1	0.1	522.135527	12.0	21	26	6	6	2
	-0.8	-0.4	522.135019	24.5	35	24	1		2
	-1.2	-0.6	522.134840	16.0	28	26		8	1
	1.4	0.7	522.136177	21.0	29	32	4	4	1
	-2.5	-1.3	522.134148	25.5	34	20	1	5	
	2.6	1.4	522.136828	30.0	37	18	2	2	
	2.7	1.4	522.136869	11.5	23	28	3	7	2
	-3.8	-2.0	522.133497	16.5	26	24	3	7	1
	3.9	2.1	522.137520	20.5	31	24	1	5	1
	-5.1	-2.7	522.132805	26.0	32	18	4	4	
	5.3	2.8	522.138212	11.0	25	30		8	2
	-6.0	-3.1	522.132339	20.0	32	26		3	2
	-6.3	-3.3	522.132155	17.0	24	22	6	6	1
	6.5	3.4	522.138857	25.5	32	20	5	1	1
	-7.3	-3.8	522.131647	29.5	38	20	1		1
	-7.6	-4.0	522.131468	21.0	31	22		8	
	7.8	4.1	522.139549	16.0	26	26	4	4	2
	-8.5	-4.5	522.130996	20.5	30	24	3	2	2
	9.1	4.7	522.140200	25.0	34	22	2	2	1
	-10.2	-5.3	522.130125	21.5	29	20	3	7	
	10.3	5.4	522.140851	34.0	42	18			
	10.4	5.4	522.140892	15.5	28	28	1	5	2
	-11.1	-5.8	522.129653	21.0	28	22	6	1	2
	11.3	5.9	522.141359	21.5	28	20	5	6	
	-12.4	-6.5	522.128967	25.0	35	22		3	1
	-12.8	-6.7	522.128783	22.0	27	18	6	6	
	13.0	6.8	522.142229	20.5	29	24	5	1	2
	-13.7	-7.1	522.128316	16.0	27	26	2	5	2
	-13.8	-7.2	522.128275	34.5	41	16	1		
	13.9	7.2	522.142701	21.0	30	22	2	7	
	-15.0	-7.8	522.127624	25.5	33	20	3	2	1
	15.5	8.1	522.143572	20.0	31	26	2	2	2
	-16.3	-8.5	522.126973	16.5	25	24	5	4	2
	16.4	8.6	522.144039	26.0	31	18	6	3	
	16.8	8.8	522.144223	29.0	39	22			1
	-17.6	-9.2	522.126281	26.0	31	18	6	1	1
	17.8	9.3	522.144731	16.5	25	24	5	6	1
	-18.8	-9.8	522.125636	11.5	24	28	1	8	2
	-18.9	-9.9	522.125595	30.0	38	18		3	
	19.0	9.9	522.145381	25.5	33	20	3	4	



Acquisition Time (sec)	2.0447	Comment	Imported from UXMNR.	Date	25 Mar 2006 23:19:28
File Name	\data\instruments\200601\NM1\data\SUNESIS-tshau\nmr\tps524-173\tps524-173_001000fid			Frequency (MHz)	400.13
Nucleus	¹ H	Number of Transients	64	Original Points Count	16384
Pulse Sequence	zg30	Solvent	CHLOROFORM-D	Points Count	16384
Temperature (degree C)	27.000			Sweep Width (Hz)	8012.82



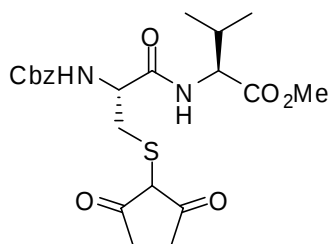
No.	(ppm)	Value	Absolute Value
1	[0.78, 0.99]	6.147	5.0640e+06
2	[2.05, 2.27]	1.006	8.2911e+08
3	[3.02, 3.43]	2.996	2.46862e+9
4	[3.62, 3.82]	3.000	2.47189e+9
5	[4.38, 4.64]	1.973	1.6250e+9
6	[5.01, 5.19]	2.000	1.64794e+9
7	[5.91, 6.09]	0.965	7.95076e+8
8	[6.98, 7.08]	0.873	7.19115e+8
9	[7.09, 7.18]	1.533	8.51085e+8
10	[7.30, 7.44]	5.074	4.59283e+9
11	[7.79, 7.99]	1.003	8.01327e+8
12	[8.14, 8.38]	0.972	8.25486e+8

Elemental Composition

Date : 20-APR-2006

Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

494.142480		10.0		-0.5	0	0	0	0	0
				40.0	200	400	6	8	2
Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
494.142480	0.3	0.1	494.142605	19.5	30	24	1	4	1
	-1.1	-0.5	494.141955	10.5	22	28	3	6	2
	-1.1	-0.6	494.141913	29.0	36	18	2	1	
	1.7	0.8	494.143297	10.0	24	30		7	2
	-2.5	-1.2	494.141263	20.0	28	22	4	3	1
	2.6	1.3	494.143764	16.0	24	22	4	8	
	3.0	1.5	494.143943	24.5	31	20	5		1
	-3.8	-1.9	494.140612	11.0	20	26	6	5	2
	-3.9	-1.9	494.140571	29.5	34	16	5		
	4.4	2.2	494.144635	15.0	25	26	4	3	2
	-5.2	-2.6	494.139925	15.0	27	26		7	1
	5.7	2.8	494.145285	24.0	33	22	2	1	1
	-6.6	-3.2	494.139233	24.5	33	20	1	4	
	7.1	3.5	494.145977	14.5	27	28	1	4	2
	-7.9	-3.9	494.138583	15.5	25	24	3	6	1
	8.0	4.0	494.146444	20.5	27	20	5	5	
	-9.2	-4.5	494.137932	6.5	17	28	5	8	2
	-9.3	-4.6	494.137891	25.0	31	18	4	3	
	9.4	4.7	494.147136	11.0	21	26	4	8	1
	9.8	4.8	494.147315	19.5	28	24	5		2
	-10.2	-5.1	494.137424	19.0	31	26		2	2
	-10.6	-5.2	494.137240	16.0	23	22	6	5	1
	10.7	5.3	494.147787	20.0	29	22	2	6	
	-12.0	-5.9	494.136553	20.0	30	22		7	
	12.5	6.2	494.148657	19.0	30	26	2	1	2
	-12.9	-6.4	494.136081	19.5	29	24	3	1	2
	13.4	6.6	494.149124	25.0	30	18	6	2	
	-14.7	-7.3	494.135211	20.5	28	20	3	6	
	14.8	7.3	494.149816	15.5	24	24	5	5	1
	-15.7	-7.7	494.134739	20.0	27	22	6		2
	-16.0	-7.9	494.134560	11.5	20	24	5	8	1
	16.2	8.0	494.150467	24.5	32	20	3	3	
	16.2	8.0	494.150508	6.0	18	30	4	8	2
	-17.1	-8.4	494.134052	24.0	34	22		2	1
	-17.4	-8.6	494.133868	21.0	26	18	6	5	
	17.6	8.7	494.151159	15.0	26	26	2	6	1
	-18.4	-9.1	494.133401	15.0	26	26	2	4	2
	18.9	9.3	494.151809	24.0	34	22		4	
	-19.8	-9.8	494.132709	24.5	32	20	3	1	1

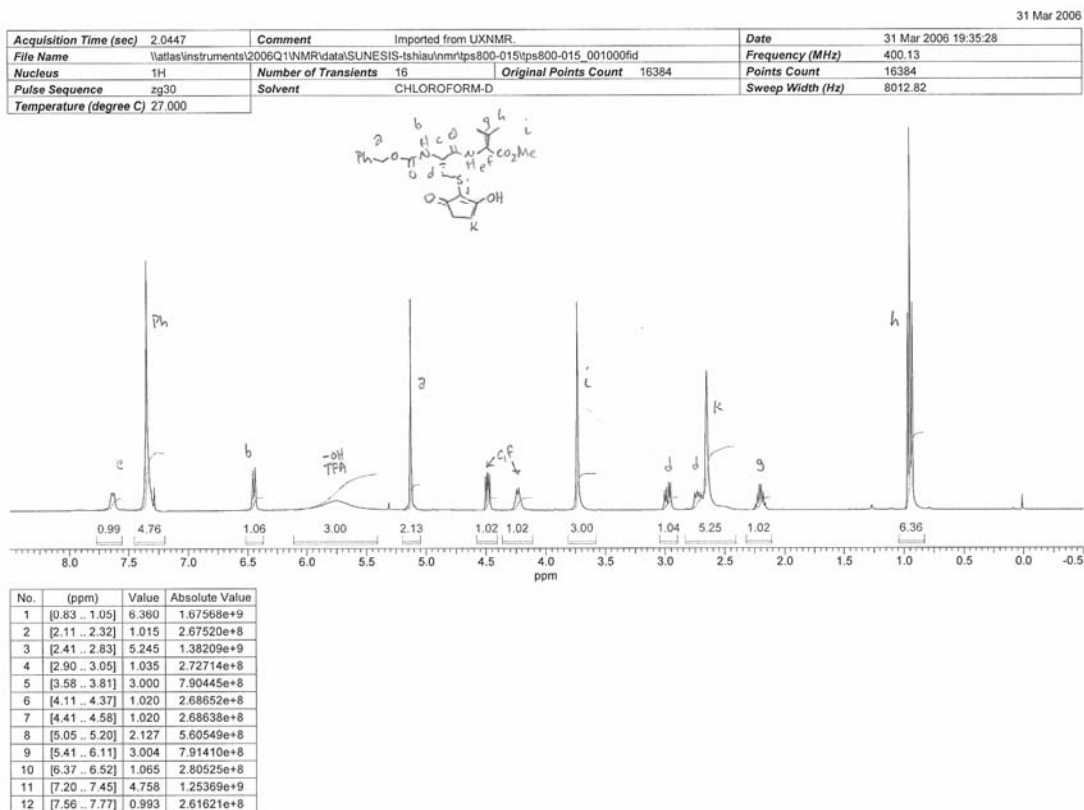


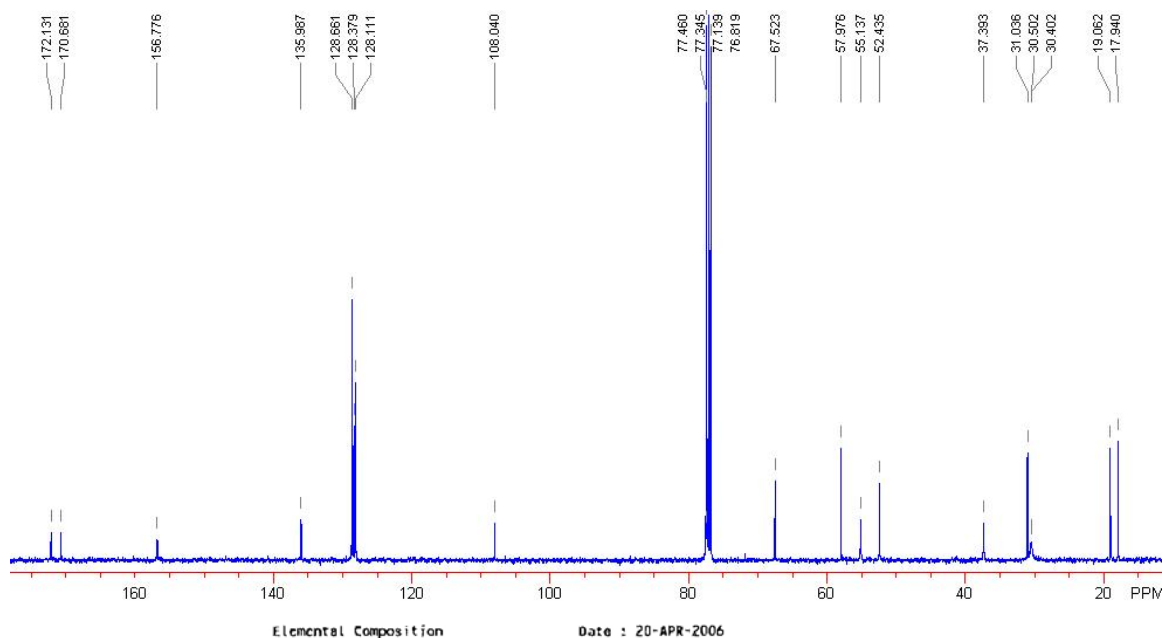
Compound **3h**

Chemical Formula: C₂₂H₂₈N₂O₇S

Exact Mass: 464.1617

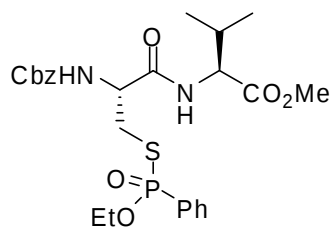
Compound **3h**. ¹HNMR (400 MHz, CDCl₃) δ 0.95 (m, 6H), 2.20 (m, 1H), 2.65 (s, 4H), 2.72 (dd, 1H, J=7.3, 13.7 Hz), 2.98 (dd, 1H, J=5.9, 13.7 Hz), 3.74 (s, 3H), 4.23 (m, 1H), 4.48 (dd, 1H, J=5.4, 8.3 Hz), 5.13 (s, 2H), 5.75 (br, 2H), 6.44 (d, 1H, J=7.4 Hz), 7.3 (m, 5H), 7.63 (d, 1H, J=7.4 Hz). ¹³CNMR (100 MHz, CDCl₃) δ 17.94, 19.06, 30.40, 30.50, 31.04, 37.40, 52.44, 55.14, 57.98, 67.52, 106.04, 128.11, 128.38, 128.68, 135.99, 156.78, 170.68, 172.13. MH⁺ predicted for C₂₂H₂₈N₂O₇S: 465.1690, found: 465.1704.





Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

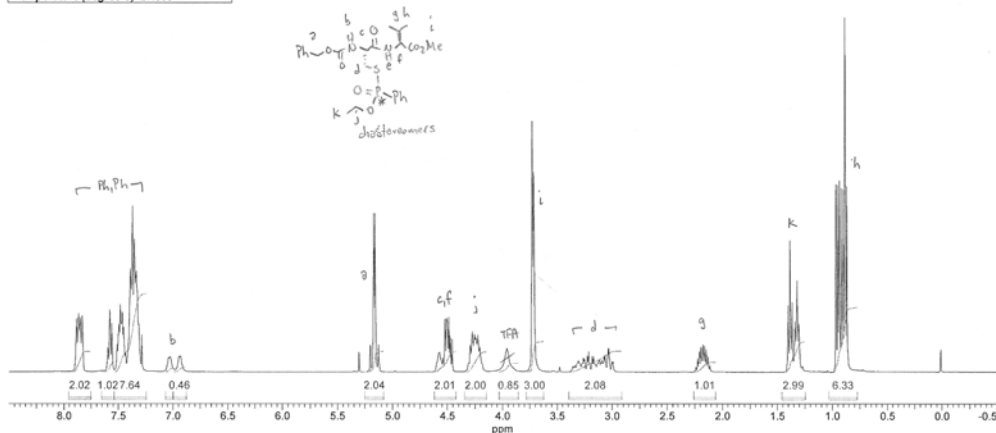
465.170350	10.0	-0.5	0	0	0	0	0	0	
		40.0	200	400	6	8		1	
Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
465.170350	-0.3	-0.2	465.170199	18.5	30	25		5	
	1.2	0.5	465.170886	14.5	23	25	6	3	1
	-1.7	-0.8	465.169548	9.5	22	29	2	7	1
	2.6	1.2	465.171537	23.5	31	21	4	1	
	-3.2	-1.5	465.168857	19.0	28	23	3	4	
	4.0	1.9	465.172228	14.0	25	27	3	4	1
	-4.6	-2.1	465.168206	10.0	20	27	5	6	1
	5.4	2.5	465.172879	23.0	33	23	1	2	
	-5.7	-2.7	465.167698	22.5	34	25			1
	-6.1	-2.8	465.167514	19.5	26	21	6	3	
	6.5	3.0	465.173387	10.5	19	25	6	8	
	6.9	3.2	465.173571	13.5	27	29		5	1
	-9.0	-4.2	465.166176	14.5	25	25	2	7	
	9.8	4.6	465.174908	18.5	28	25	4	1	1
	-11.9	-5.5	465.164834	15.0	23	23	5	6	
	12.7	5.9	465.176251	18.0	30	27	1	2	1
	-13.0	-6.0	465.164326	27.5	37	21			
	13.8	6.4	465.176759	5.5	16	29	6	8	1
	-14.3	-6.7	465.163675	18.5	29	25	2	2	1
	15.2	7.1	465.177410	14.5	24	25	4	6	
	-17.2	-8.0	465.162332	19.0	27	23	5	1	1
	18.1	8.4	465.178753	14.0	26	27	1	7	
	-20.1	-9.4	465.160995	14.0	26	27	1	5	1
	20.9	9.7	465.180090	19.0	27	23	5	3	



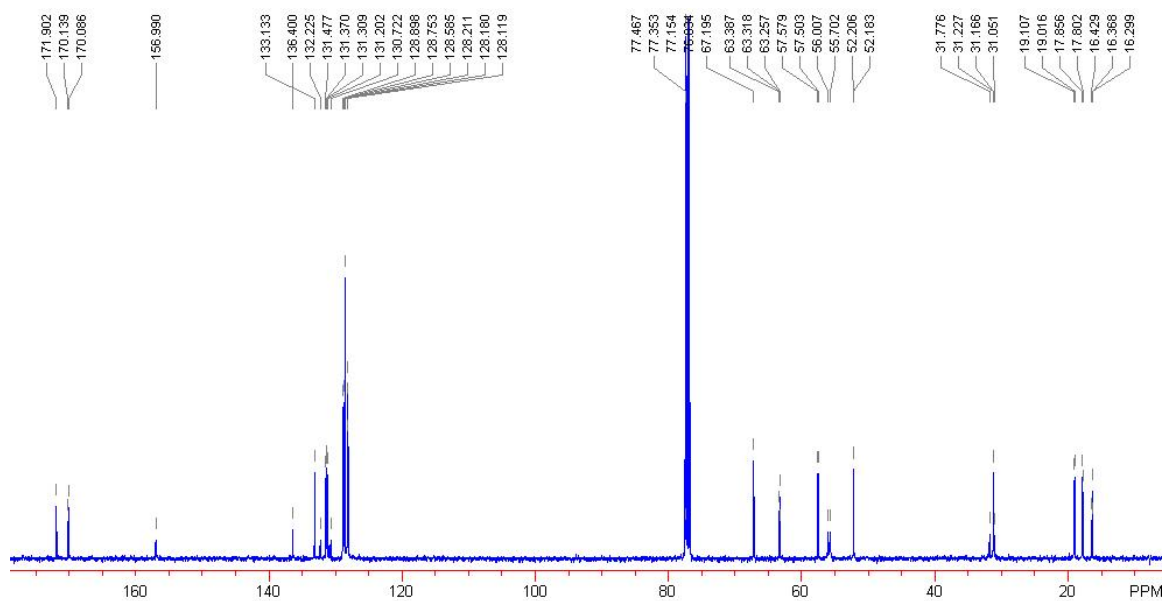
Compound **3i** (1:1 d.r.)
 Chemical Formula: C₂₅H₃₃N₂O₇PS
 Exact Mass: 536.1746

Compound **3i**. ¹HNMR (400 MHz, CDCl₃) δ 0.87-0.97 (m, 6H), 1.31-1.40 (m, 3H), 2.13-2.22 (m, 1H), 3.0-3.4 (m, 2H), 3.71-3.73 (m, 3H), 4.23-4.31 (m, 2H), 4.47-4.58 (m, 2H), 5.16 (m, 2H), 6.94 (d, 0.5H, J=4 Hz), 7.03 (d, 0.5H, J=8 Hz), 7.3-7.6 (m, 8H), 7.58 (m, 1H), 7.86 (m, 2H). ¹³CNMR (100 MHz, CDCl₃) δ 16.30, 16.37, 16.43, 17.80, 17.86, 19.02, 19.11, 31.05, 31.17, 31.23, 31.77, 52.18, 52.21, 55.70, 56.01, 57.50, 57.58, 63.26, 63.32, 63.39, 67.20, 128.12, 128.18, 128.21, 128.59, 128.75, 128.90, 130.72, 131.20, 131.31, 131.37, 131.48, 132.22, 133.13, 136.40, 156.99, 170.09, 170.14, 171.90. MH⁺ predicted for C₂₅H₃₃N₂O₇PS: 537.1819, found: 537.1817.

Acquisition Time (sec)	2.0447	Comment	Imported from UXXNMR	Date	31 Mar 2006 16:00:00
File Name	\atlantis\instruments\2006Q1\NMR\data\SUNESIS-tshia\nmr\tps800-011\tps800-011_001000fid			Frequency (MHz)	400.13
Nucleus	¹ H	Number of Transients	16	Original Points Count	16384
Pulse Sequence	zg30	Solvent	CHLOROFORM-D	Points Count	16384
Temperature (degree C)	27.000			Sweep Width (Hz)	8012.82



No.	(ppm)	Value	Absolute Value	No.	(ppm)	Value	Absolute Value
1	[0.78 .. 1.03]	6.334	1.24013e+9	8	[4.42 .. 4.62]	2.013	3.94068e+8
2	[1.25 .. 1.46]	2.985	5.84493e+8	9	[5.08 .. 5.25]	2.037	3.98837e+8
3	[2.06 .. 2.26]	1.008	1.97348e+8	10	[6.88 .. 7.00]	0.457	8.93875e+7
4	[2.91 .. 3.39]	2.082	4.07635e+8	11	[7.00 .. 7.07]	0.391	7.64811e+7
5	[3.63 .. 3.79]	3.000	5.87346e+8	12	[7.25 .. 7.54]	7.643	1.49642e+9
6	[3.86 .. 4.03]	0.854	1.67231e+8	13	[7.54 .. 7.65]	1.022	2.00135e+8
7	[4.15 .. 4.34]	1.997	3.90930e+8	14	[7.75 .. 7.96]	2.016	3.94617e+8



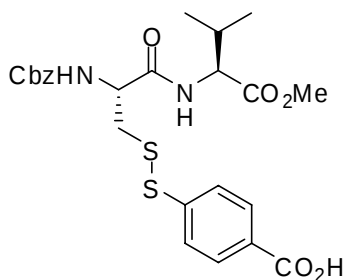
Elemental Composition

Date : 20-APR-2006

Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	P	S
537.181710	0.1	0.0	537.181745	20.0	31	28	3	4	1	
	-0.5	-0.3	537.181433	24.5	35	25	2	4		
	0.8	0.4	537.182125	15.0	29	31	1	7		1
	-1.1	-0.6	537.181094	11.0	23	32	5	6	1	1
	1.4	0.7	537.182437	10.5	25	34	2	7	1	1
	-1.7	-0.9	537.180782	15.5	27	29	4	6		1
	2.0	1.1	537.182770	29.5	36	21	6			
	-2.1	-1.1	537.180586	23.5	37	30			1	1
	-2.4	-1.3	537.180402	20.5	29	26	6	3	1	
	2.6	1.4	537.183088	19.5	33	30		5	1	
	-2.9	-1.6	537.180131	6.5	19	33	6	8		2
	-3.0	-1.6	537.180090	25.0	33	23	5	3		
	3.3	1.8	537.183462	20.0	30	27	5	3		1
	-3.3	-1.8	537.179936	14.5	29	34	2	2	1	2
	3.8	2.1	537.183774	15.5	26	30	6	3	1	1
	-3.9	-2.1	537.179623	19.0	33	31	1	2		2
	4.2	2.2	537.183958	18.5	34	34			1	2
	4.5	2.4	537.184113	29.0	38	23	3	1		
	4.5	2.4	537.184154	10.5	24	33	4	6		2
	-4.9	-2.6	537.179065	15.5	28	30	2	7	1	
	5.1	2.7	537.184425	24.5	34	26	4	1	1	
	5.1	2.8	537.184466	6.0	20	36	5	6	1	2
	-5.5	-3.0	537.178753	20.0	32	27	1	7		
	5.8	3.1	537.184805	19.5	32	29	2	4		1
	-5.8	-3.1	537.178593	15.0	27	32	5	1	1	2
	6.3	3.4	537.185117	15.0	28	32	3	4	1	1
	-6.4	-3.4	537.178280	19.5	31	29	4	1		2
	7.0	3.7	537.185455	28.5	40	25		2		
	7.0	3.8	537.185496	10.0	26	35	1	7		2
	-7.4	-4.0	537.177722	16.0	26	28	5	6	1	
	7.6	4.1	537.185768	24.0	36	28	1	2	1	
	7.6	4.1	537.185809	5.5	22	38	2	7	1	2
	7.9	4.3	537.185963	16.0	26	27	5	8		
	-8.0	-4.3	537.177410	20.5	30	25	4	6		
	8.3	4.4	537.186142	24.5	33	25	6			1
	-8.3	-4.5	537.177256	10.0	26	36	1	5	1	2
	-8.4	-4.5	537.177214	28.5	40	26			1	
	8.5	4.6	537.186276	11.5	22	30	6	8	1	
	8.8	4.7	537.186460	14.5	30	34		5	1	1
	-8.9	-4.8	537.176943	14.5	30	33		5		2
	-9.2	-5.0	537.176759	11.5	22	29	6	8		1
	9.5	5.1	537.186834	15.0	27	31	5	3		2
	-9.6	-5.1	537.176564	19.5	32	30	2	2	1	1
	10.1	5.4	537.187146	10.5	23	34	6	3	1	2
	-10.2	-5.5	537.176251	24.0	36	27	1	2		1
	10.7	5.8	537.187485	24.0	35	27	3	1		1
	-10.8	-5.8	537.175913	10.5	24	34	4	4	1	2
	11.3	6.1	537.187797	19.5	31	30	4	1	1	1

- 1 -

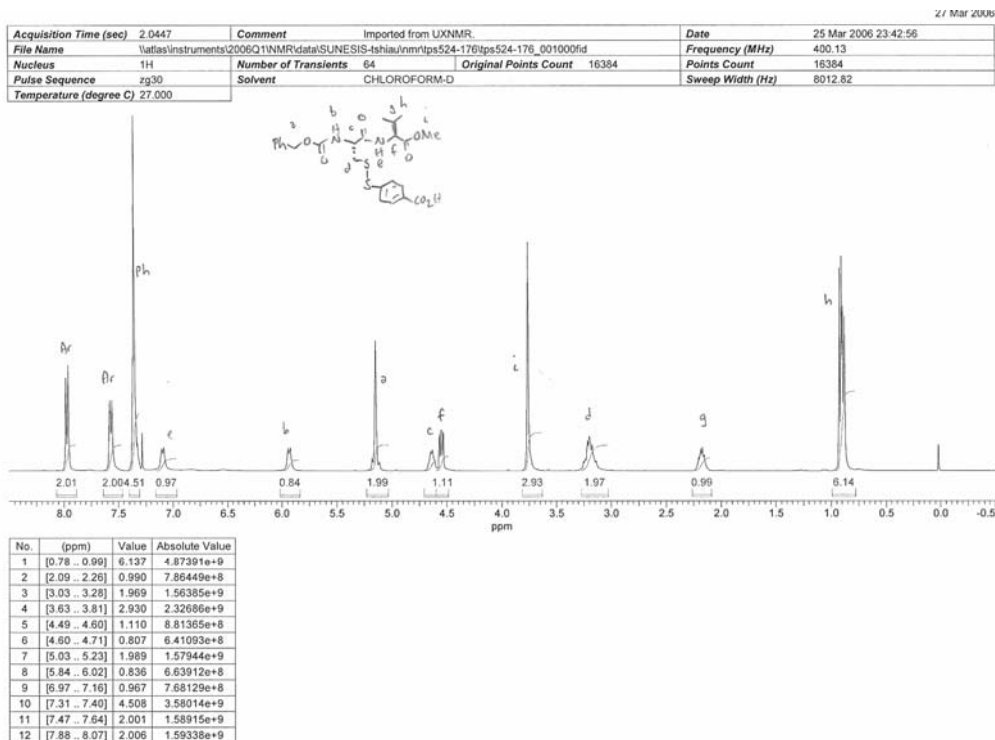


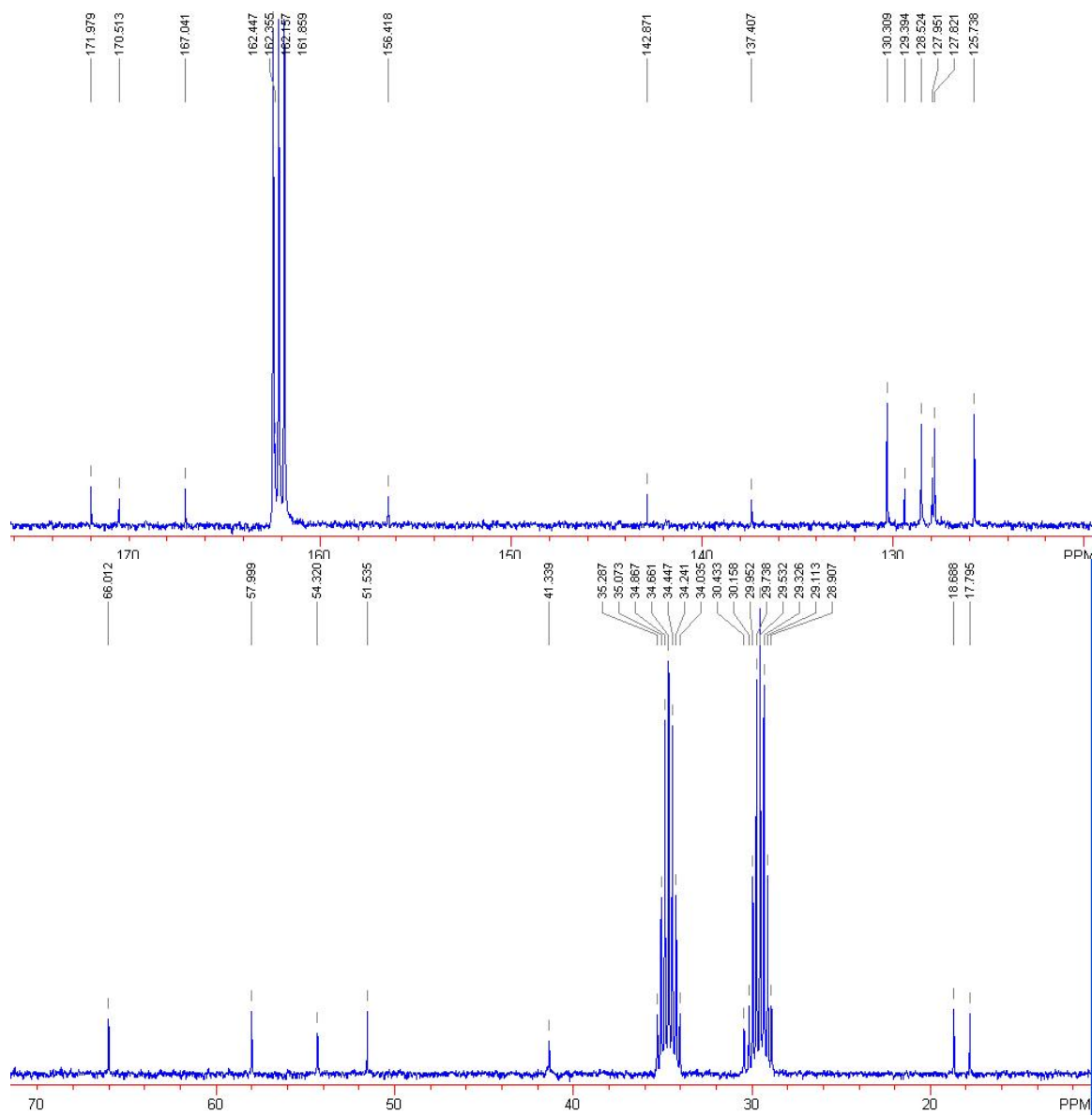
Compound **3j**

Chemical Formula: $C_{24}H_{28}N_2O_7S_2$

Exact Mass: 520.1338

Compound **3j**. ^1H NMR (400 MHz, CDCl_3) δ 0.90 (m, 6H), 2.18 (m, 1H), 3.20 (m, 2H), 3.76 (s, 3H), 4.56 (dd, 1H, $J=5.9, 8.3$ Hz), 4.64 (m, 1H), 5.15 (m, 2H), 5.93 (d, 1H, $J=7.3$ Hz), 7.10 (d, 1H, $J=8.3$ Hz), 7.36 (m, 5H), 7.57 (d, 2H, $J=8.3$ Hz), 7.97 (d, 2H, $J=8.3$ Hz). ^{13}C NMR (100 MHz, d_7 -DMF) δ 17.80, 18.69, 41.34, 51.54, 54.32, 58.00, 66.01, 125.74, 127.82, 127.95, 128.52, 129.39, 130.31, 137.41, 142.67, 167.42, 167.04, 170.51, 171.98. MH^+ predicted for $C_{24}H_{28}N_2O_7S_2$: 521.1411, found: 521.1421.



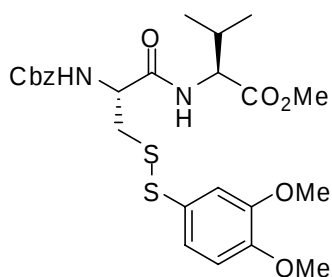


Elemental Composition

Date : 21-APR-2006

Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

521.142070	10.0			-0.5	0	0	0	0	0
				40.0	200	400	6	8	2
Mass	PPM	mPa	Calc. Mass	DBE	C	H	N	O	S
521.142070	0.0	0.0	521.142087	17.5	24	21	6	8	
	0.4	0.2	521.142271	20.5	32	25		5	1
	-0.9	-0.4	521.141620	11.5	24	29	2	7	2
	-0.9	-0.5	521.141579	30.0	38	19	1	2	
	1.7	0.9	521.142958	16.5	25	25	6	3	2
	-2.2	-1.1	521.140928	21.0	30	23	3	4	1
	3.0	1.5	521.143608	25.5	33	21	4	1	1
	-3.4	-1.8	521.140278	12.0	22	27	5	6	2
	-3.5	-1.8	521.140236	30.5	36	17	4	1	
	4.3	2.2	521.144300	16.0	27	27	3	4	2
	-4.4	-2.3	521.139770	24.5	36	25			2
	-4.8	-2.5	521.139586	21.5	28	21	6	3	1
	5.5	2.9	521.144951	25.0	35	23	1	2	1
	-6.1	-3.2	521.138899	25.5	35	21		5	
	6.5	3.4	521.145459	12.5	21	25	6	8	1
	6.9	3.6	521.145643	15.5	29	29		5	2
	-7.3	-3.8	521.138248	16.5	27	25	2	7	1
	7.8	4.0	521.146110	21.5	29	21	4	6	
	-8.7	-4.5	521.137556	26.0	33	19	3	4	
	9.4	4.9	521.146980	20.5	30	25	4	1	2
	-9.9	-5.2	521.136906	17.0	25	23	5	6	1
	10.3	5.4	521.147452	21.0	31	23	1	7	
	-10.9	-5.7	521.136398	29.5	39	21			1
	-11.2	-5.9	521.136214	26.5	31	17	6	3	
	12.0	6.3	521.148323	20.0	32	27	1	2	2
	-12.1	-6.3	521.135747	20.5	31	25	2	2	2
	12.9	6.7	521.148790	26.0	32	19	5	3	
	13.0	6.8	521.148831	7.5	18	29	6	8	2
	-13.8	-7.2	521.134876	21.5	30	21	2	7	
	14.2	7.4	521.149482	16.5	26	25	4	6	1
	-14.7	-7.7	521.134404	21.0	29	23	5	1	2
	15.5	8.1	521.150132	25.5	34	21	2	4	
	-16.4	-8.5	521.133534	22.0	28	19	5	6	
	16.8	8.8	521.150824	16.0	28	27	1	7	1
	-17.3	-9.0	521.133067	16.0	28	27	1	5	2
	-17.4	-9.0	521.133026	34.5	42	17			
	18.0	9.4	521.151470	30.5	35	17	6		
	-18.6	-9.7	521.132375	25.5	34	21	2	2	1



Compound **3k**

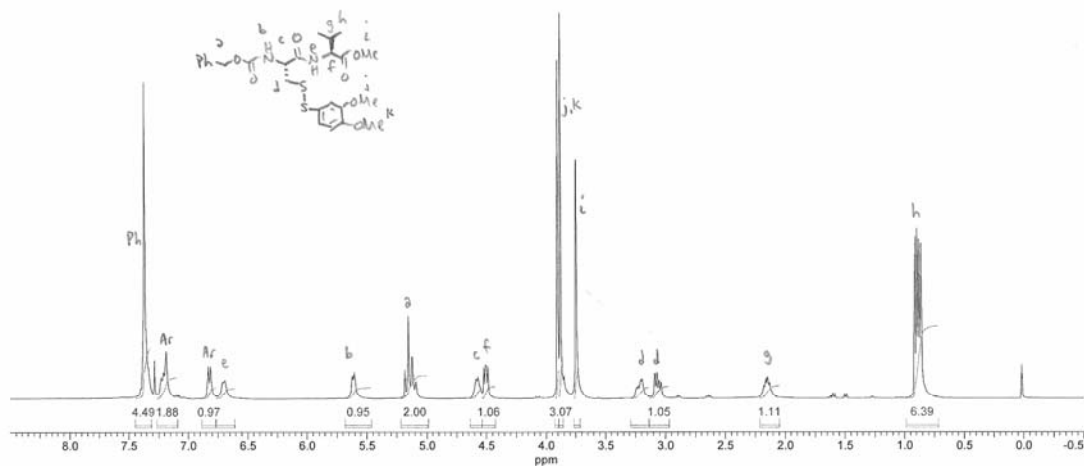
Chemical Formula: $C_{25}H_{32}N_2O_7S_2$

Exact Mass: 536.1651

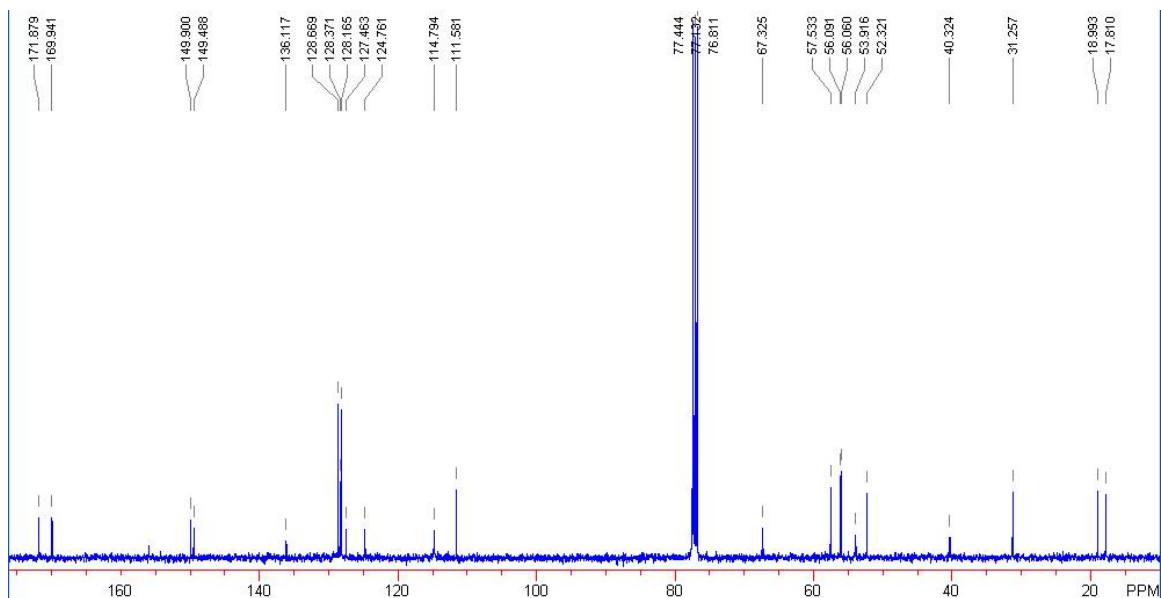
Compound **3k**. 1H NMR (400 MHz, $CDCl_3$) δ 0.90 (m, 6H), 2.15 (m, 1H), 3.06 (dd, 1H, $J=6.8, 14.1$ Hz), 3.22 (dd, 1H, $J=5.3, 13.7$ Hz), 3.75 (s, 3H), 3.88 (s, 3H), 3.90 (s, 3H), 4.51 (m, 1H), 4.57 (m, 1H), 5.09-5.18 (m, 2H), 5.61 (m, 1H), 6.70 (d, 1H, $J=7.4$ Hz), 6.82 (d, 1H, $J=8.3$ Hz), 7.19 (m, 2H), 7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.81, 18.99, 31.26, 40.32, 52.32, 53.92, 56.06, 56.09, 57.53, 67.32, 111.58, 114.79, 124.76, 127.46, 128.16, 128.37, 128.67, 136.12, 149.49, 149.90, 169.94, 171.88. M^+ predicted for $C_{25}H_{32}N_2O_7S_2$: 536.1651, found: 536.1641.

27 Mar 2006

Acquisition Time (sec)	2.0447	Comment	Imported from UXMNR.	Date	25 Mar 2006 23:13:04
File Name	\\\atlantis\instruments\2006Q1\NMR\data\SUNESIS-tshiau\nmr\tps524-172\tps524-172_001000.fid			Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	64	Original Points Count	16384
Pulse Sequence	zg30	Solvent	CHLOROFORM-D	Points Count	16384
Temperature (degree C)	27.000			Sweep Width (Hz)	8012.82

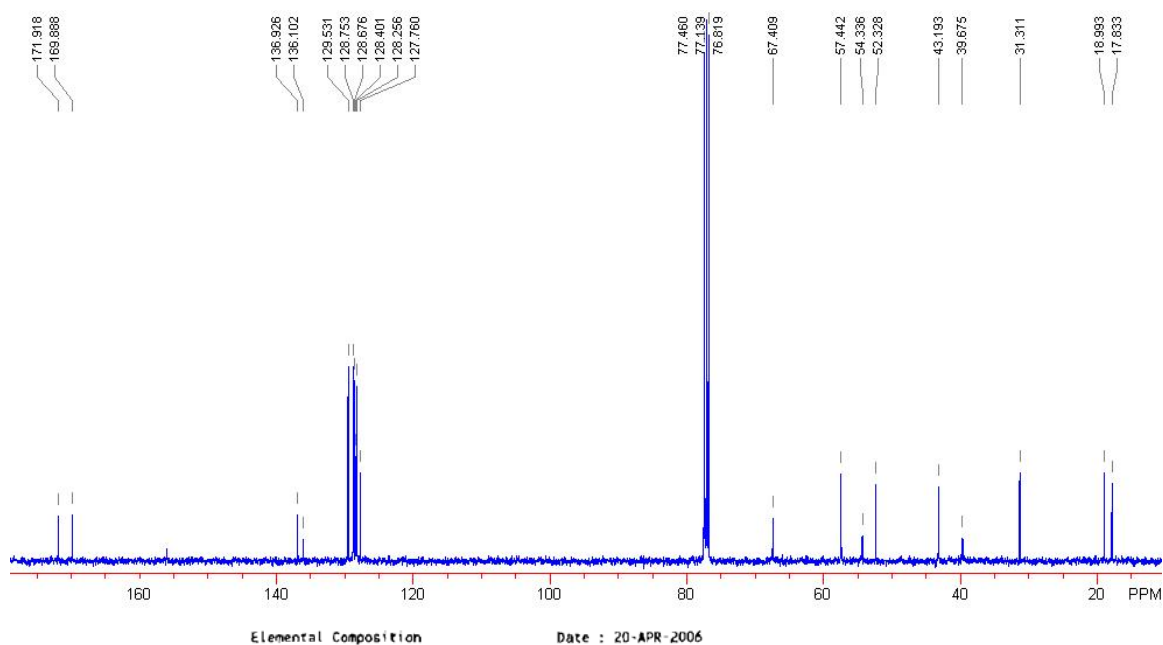


No.	(ppm)	Value	Absolute Value	No.	(ppm)	Value	Absolute Value
1	[0.72 .. 0.99]	6.387	3.66841e+9	9	[4.54 .. 4.64]	0.871	5.00506e+8
2	[2.05 .. 2.21]	1.110	6.37821e+8	10	[4.99 .. 5.22]	2.000	1.14876e+9
3	[2.97 .. 3.14]	1.045	6.00303e+8	11	[5.46 .. 5.68]	0.951	5.46421e+8
4	[3.14 .. 3.29]	0.969	5.56518e+8	12	[6.61 .. 6.77]	0.884	5.07680e+8
5	[3.71 .. 3.77]	2.690	1.54528e+9	13	[6.77 .. 6.89]	0.965	5.54545e+8
6	[3.86 .. 3.89]	3.069	1.76290e+9	14	[7.09 .. 7.26]	1.882	1.08089e+9
7	[3.89 .. 3.93]	2.552	1.46598e+9	15	[7.31 .. 7.45]	4.494	2.58153e+9
8	[4.43 .. 4.54]	1.055	6.06031e+8				



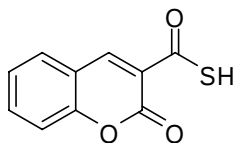
Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

Mass	PPM	mDa	Calc. Mass	DBE	C	H	N	O	S
536.164060	-0.6	-0.3	536.163753	11.5	23	30	5	6	2
	0.6	0.3	536.164403	20.5	31	26	3	4	1
	-0.7	-0.3	536.163711	30.0	37	20	4	1	
	-1.5	-0.8	536.163245	24.0	37	28			2
	1.9	1.0	536.165054	29.5	39	22	1	2	
	-1.9	-1.0	536.163061	21.0	29	24	6	3	1
	1.9	1.0	536.165095	11.0	25	32	2	7	2
	2.8	1.5	536.165562	17.0	25	24	6	8	
	-3.1	-1.7	536.162374	25.0	36	24		5	
	3.1	1.7	536.165746	20.0	33	28		5	1
	-4.4	-2.3	536.161723	16.0	28	28	2	7	1
	4.4	2.4	536.166433	16.0	26	28	6	3	2
	5.6	3.0	536.167083	25.0	34	24	4	1	1
	-5.6	-3.0	536.161031	25.5	34	22	3	4	
	-6.9	-3.7	536.160381	16.5	26	26	5	6	1
	6.9	3.7	536.167775	15.5	28	30	3	4	2
	-7.8	-4.2	536.159873	29.0	40	24			1
	8.1	4.4	536.168426	24.5	36	26	1	2	1
	-8.2	-4.4	536.159689	26.0	32	20	6	3	
	-9.0	-4.8	536.159222	20.0	32	28	2	2	2
	9.1	4.9	536.168934	12.0	22	28	6	8	1
	9.4	5.1	536.169118	15.0	30	32		5	2
	10.3	5.5	536.169585	21.0	30	24	4	6	
	-10.6	-5.7	536.158351	21.0	31	24	2	7	
	-11.5	-6.2	536.157879	20.5	30	26	5	1	2
	11.9	6.4	536.170455	20.0	31	28	4	1	2
	12.8	6.9	536.170928	20.5	32	26	1	7	
	-13.2	-7.1	536.157009	21.5	29	22	5	6	
	-14.0	-7.5	536.156542	15.5	29	30	1	5	2
	-14.1	-7.6	536.156501	34.0	43	20			
	14.4	7.7	536.171798	19.5	33	30	1	2	2
	15.3	8.2	536.172265	25.5	33	22	5	3	
	-15.3	-8.2	536.155850	25.0	35	24	2	2	1
	15.4	8.2	536.172306	7.0	19	32	6	8	2
	-16.5	-8.9	536.155199	16.0	27	28	4	4	2
	16.6	8.9	536.172957	16.0	27	28	4	6	1
	17.8	9.5	536.173608	25.0	35	24	2	4	
	-17.8	-9.6	536.154507	25.5	33	22	5	1	1



Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

Mass	PPM	mda	Calc. Mass	DBE	C	H	N	O	S
491.166770	0.0	0.0	491.166749	20.0	30	25	3	2	1
	1.3	0.6	491.167400	29.0	38	21	1		
	1.4	0.7	491.167441	10.5	24	31	2	5	2
	-1.4	-0.7	491.166098	11.0	22	29	5	4	2
	2.3	1.1	491.167908	16.5	24	23	6	6	
	2.7	1.3	491.168092	19.5	32	27		3	1
	-2.8	-1.4	491.165406	20.5	28	23	6	1	1
	4.1	2.0	491.168778	15.5	25	27	6	1	2
	-4.1	-2.0	491.164761	6.0	21	33	1	8	2
	-4.2	-2.1	491.164720	24.5	35	23		3	
	5.1	2.5	491.169251	16.0	26	25	3	7	
	-5.5	-2.7	491.164069	15.5	27	27	2	5	1
	6.8	3.4	491.170121	15.0	27	29	3	2	2
	-6.8	-3.4	491.163418	6.5	19	31	4	7	2
	-6.9	-3.4	491.163377	25.0	33	21	3	2	
	7.8	3.8	491.170593	15.5	28	27		8	
	8.1	4.0	491.170772	24.0	35	25	1		1
	-8.2	-4.0	491.162726	16.0	25	25	5	4	1
	9.2	4.5	491.171280	11.5	21	27	6	6	1
	9.6	4.7	491.171464	14.5	29	31		3	2
	-9.6	-4.7	491.162034	25.5	31	19	6	1	
	10.5	5.2	491.171931	20.5	29	23	4	4	
	-10.6	-5.2	491.161568	19.5	31	27	2		2
	-11.0	-5.4	491.161389	11.0	24	29	1	8	1
	11.9	5.9	491.172622	11.0	23	29	3	7	1
	-12.4	-6.1	491.160697	20.5	30	23	2	5	
	13.2	6.5	491.173273	20.0	31	25	1	5	
	-13.7	-6.7	491.160046	11.5	22	27	4	7	1
	14.6	7.2	491.173965	10.5	25	31		8	1
	15.0	7.4	491.174144	19.0	32	29	1		2
	-15.1	-7.4	491.159354	21.0	28	21	5	4	
	16.0	7.8	491.174611	25.0	32	21	5	1	
	16.0	7.9	491.174652	6.5	18	31	6	6	2
	-16.0	-7.9	491.158888	15.0	28	29	1	3	2
	17.4	8.5	491.175302	15.5	26	27	4	4	1
	-17.5	-8.6	491.158196	24.5	34	23	2		1
	-17.8	-8.8	491.158017	16.0	27	25	1	8	
	18.7	9.2	491.175953	24.5	34	23	2	2	
	18.8	9.2	491.175994	6.0	20	33	3	7	2
	-18.8	-9.2	491.157545	15.5	26	27	4	2	2
	20.1	9.9	491.176645	15.0	28	29	1	5	1



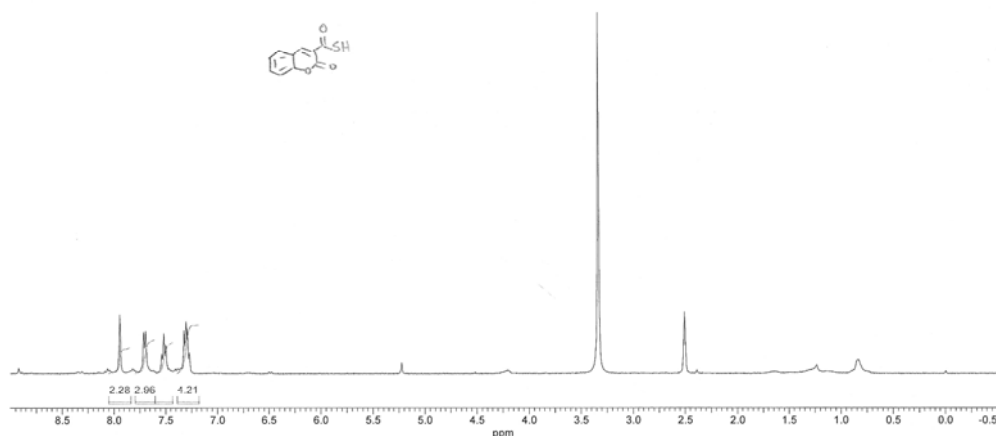
Compound 5

Chemical Formula: C₁₀H₆O₃S

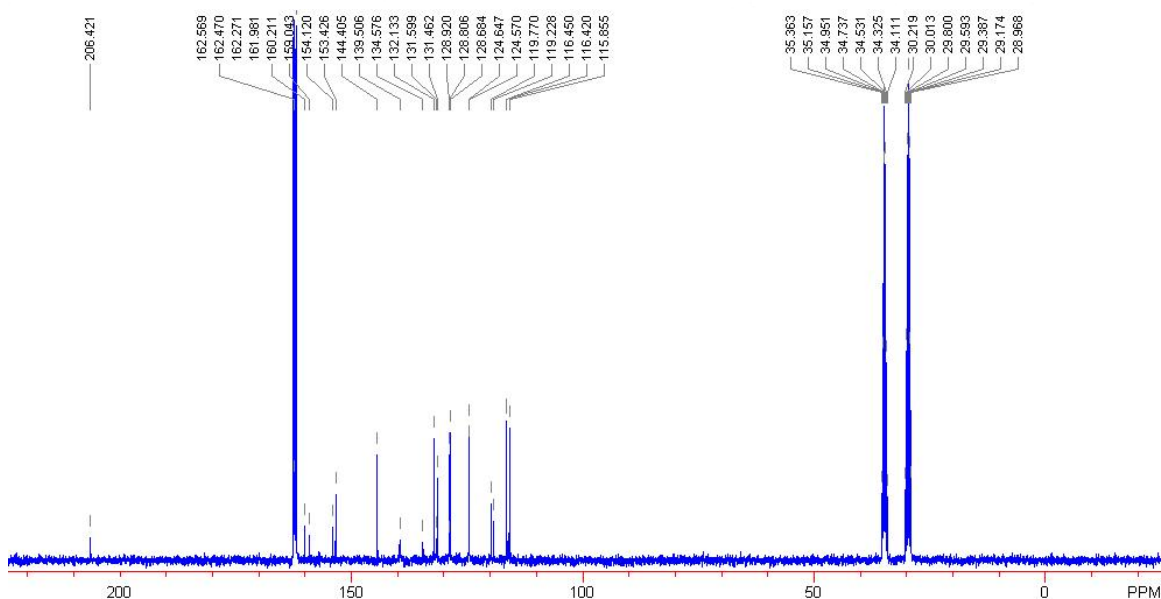
Exact Mass: 206.0038

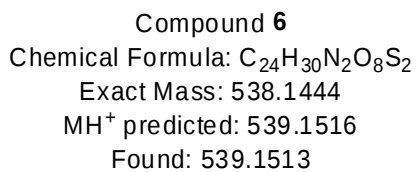
Compound 5. ¹HNMR (400 MHz, d₆-DMSO) δ 7.27-7.32 (m, 2H), 7.52 (m, 1H), 7.70 (d, 1H, J=7.4 Hz), 7.94 (s, 1H). ¹³CNMR (100 MHz, d₇-DMF, partially hydrolysed) δ 115.86, 116.42, 116.45, 119.23, 119.77, 124.57, 124.65, 128.68, 128.81, 128.92, 131.46, 131.60, 132.13, 134.58, 139.51, 144.41, 153.43, 154.12, 159.4, 160.21, 206.42.

Acquisition Time (sec)	2.0447	Comment	Imported from UXNMR	Date	31 Mar 2006 20:09:36
File Name	\Atlas\instruments\2006Q1\NMR\data\SUNESIS-tshiau\nmr\tps524-122\tps524-122_002000.fid			Frequency (MHz)	400.13
Nucleus	¹ H	Number of Transients	16	Original Points Count	16384
Pulse Sequence	zg30	Solvent	DMSO-D6	Sweep Width (Hz)	8012.82
				Points Count	16384
				Temperature (degree C)	27.000



No.	(ppm)	Value	Absolute Value
1	[7.18 .. 7.39]	4.214	6.92772e+8
2	[7.43 .. 7.60]	2.684	4.41282e+8
3	[7.60 .. 7.79]	2.955	4.85612e+8
4	[7.84 .. 8.05]	2.276	3.74136e+8

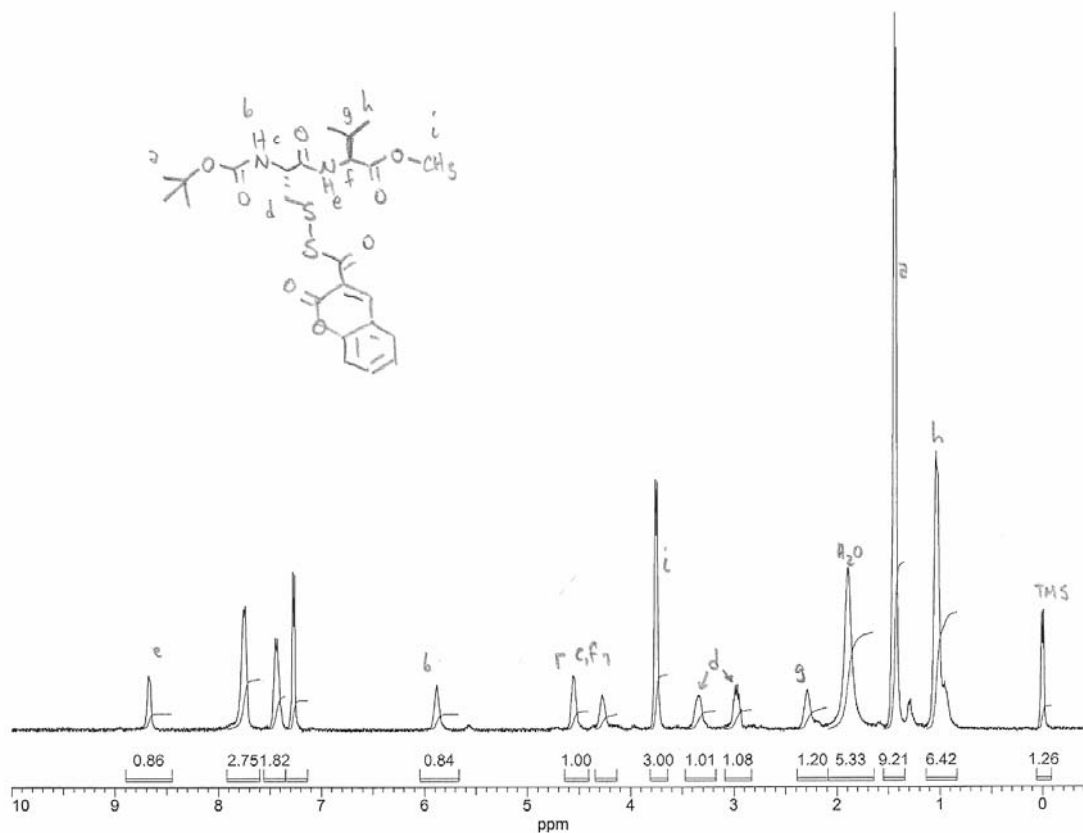




Selective Reduction of Peptide Isothiazolidin-3-ones Supporting Information Page 32

14 Jun 2004

Acquisition Time (sec)	2.0447	Comment	Imported from UxNMR.	
Date	14 Jun 2004 22:58:08			
File Name	\\atlas\instruments\2004Q2\NMR\data\SUNESIS-Ishiau\nmr\tps-524-123\tps-524-123_001000fid			
Frequency (MHz)	400.13	Nucleus	1H	Number of Transients 16
Original Points Count	16384	Points Count	16384	Pulse Sequence zg30
Solvent	CHLOROFORM-D		Sweep Width (Hz)	8012.82
Temperature (degree C)	27.000			



No.	(ppm)	Value	Absolute Value
1	[-0.09 .. 0.06]	1.264	2.11449e+8
2	[0.83 .. 1.13]	6.418	1.07402e+9
3	[1.34 .. 1.55]	9.206	1.54054e+9
4	[1.64 .. 2.09]	5.326	8.91176e+8
5	[2.09 .. 2.39]	1.195	1.99990e+8
6	[2.83 .. 3.09]	1.078	1.80322e+8
7	[3.18 .. 3.47]	1.013	1.69433e+8
8	[3.64 .. 3.81]	3.000	5.02010e+8
9	[4.13 .. 4.35]	0.830	1.38936e+8
10	[4.41 .. 4.64]	1.002	1.67707e+8
11	[5.67 .. 6.05]	0.838	1.40266e+8
12	[7.13 .. 7.35]	1.578	2.64013e+8
13	[7.35 .. 7.56]	1.825	3.05375e+8
14	[7.60 .. 7.92]	2.745	4.59342e+8
15	[8.45 .. 8.90]	0.860	1.43829e+8

Elemental Composition

Date : 21-APR-2006

Heteroatom Max: 20 Ion: Both Even and Odd
Limits:

539.151250	10.0			-0.5	0	0	0	0	0
				40.0	200	400	6	8	2
Mass	PPM	mDa	Calc. Mass	OBE	C	H	N	O	S
539.151250	0.5	0.2	539.151493	20.0	30	25	3	5	1
	-0.8	-0.4	539.150842	11.0	22	29	5	7	2
	-0.8	-0.4	539.150801	29.5	36	19	4	2	
	1.7	0.9	539.152144	29.0	38	21	1	3	
	-1.7	-0.9	539.150334	23.5	36	27		1	2
	1.7	0.9	539.152185	10.5	24	31	2	8	2
	-2.0	-1.1	539.150150	20.5	28	23	6	4	1
	2.9	1.6	539.152836	19.5	32	27		6	1
	-3.3	-1.8	539.149464	24.5	35	23		6	
	-4.2	-2.3	539.148992	24.0	34	25	3		2
	4.2	2.3	539.153522	15.5	25	27	6	4	2
	-4.5	-2.4	539.148813	15.5	27	27	2	8	1
	5.4	2.9	539.154173	24.5	33	23	4	2	1
	-5.8	-3.1	539.148121	25.0	33	21	3	5	
	6.6	3.6	539.154824	33.5	41	19	2		
	6.7	3.6	539.154865	15.0	27	29	3	5	2
	-7.0	-3.8	539.147470	16.0	25	25	5	7	1
	7.9	4.3	539.155516	24.0	35	25	1	3	1
	-8.0	-4.3	539.146962	28.5	39	23		1	1
	-8.3	-4.5	539.146778	25.5	31	19	6	4	
	-9.2	-4.9	539.146312	19.5	31	27	2	3	2
	9.2	5.0	539.156208	14.5	29	31		6	2
	10.1	5.4	539.156674	20.5	29	23	4	7	
	-10.4	-5.6	539.145620	29.0	37	21	3		1
	-10.8	-5.8	539.145441	20.5	30	23	2	8	
	-11.6	-6.3	539.144969	20.0	29	25	5	2	2
	11.7	6.3	539.157545	19.5	30	27	4	2	2
	12.6	6.8	539.158017	20.0	31	25	1	8	
	12.9	6.9	539.158196	28.5	38	23	2		1
	-13.3	-7.2	539.144098	21.0	28	21	5	7	
	-14.1	-7.6	539.143632	15.0	28	29	1	6	2
	14.2	7.6	539.158888	19.0	32	29	1	3	2
	-14.2	-7.7	539.143590	33.5	42	19		1	
	15.0	8.1	539.159354	25.0	32	21	5	4	
	-15.4	-8.3	539.142940	24.5	34	23	2	3	1
	16.3	8.8	539.160046	15.5	26	27	4	7	1
	-16.6	-9.0	539.142289	15.5	26	27	4	5	2
	-16.7	-9.0	539.142248	34.0	40	17	3		
	17.5	9.4	539.160697	24.5	34	23	2	5	
	-17.9	-9.7	539.141597	25.0	32	21	5	2	1