

SUPPORTING INFORMATION

Intramolecular C–N Bond Formation Reactions Catalyzed by Ruthenium Porphyrins: Amidation of Sulfamate Esters and Aziridination of Unsaturated Sulfonamides

Jiang-Lin Liang, Shi-Xue Yuan, Jie-Sheng Huang, and Chi-Ming Che*

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General Experimental Methods

PhI(OAc)₂, NH₂SO₂-*p*-C₆H₄NO₂, fluorene, and europium tris(3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorate) were used as received. Al₂O₃ (pH = 7.4) was dried to constant weight at 250 °C for 12 h before use. Solvents were purified according to standard procedures. 9,10-Dihydro-anthracene was recrystallized from absolute ethanol. Cyclohexene, cumene, ethylbenzene, and toluene were purified by passing through a column of activated alumina. 2-(4-X-phenyl)ethanol (X = Cl, Me, MeO), 2-naphthalen-1-yl-ethanol, 2-naphthalen-2-yl-ethanol, 3-(4-X-phenyl)-propan-1-ol (X = F, MeO), 3-(3-methoxy-phenyl)-propan-1-ol, and 3-(2-methoxy-phenyl)-propan-1-ol were prepared by reduction of the respective carboxylic acids with LiAlH₄ in diethyl ether. Complexes [Ru(Por)(CO)] (Por = F₂₀-TPP,¹ D₄-Por*,^{2,3} TPP/TMP/OEP⁴), [M(F₂₀-TPP)Cl] (M = Fe, Mn),⁵ (IR,2R)-[Ru(Br₄salen)(PPh₃)₂],⁶ [Ru(pybox-ip)Cl₂(CH₂=CH₂)],⁷ sulfamate esters **1a-f,p**^{8a,b} CCl₃CH₂OSO₂NH₂,^{8c} and unsaturated sulfonamides **3a-h**,^{9a} **3i**^{9b} were prepared by literature methods. ¹H and ¹³C NMR spectra were recorded on a 400 or 300 MHz spectrometer and the chemical shifts are relative to tetramethylsilane. High resolution mass spectra were obtained by EI method.

References

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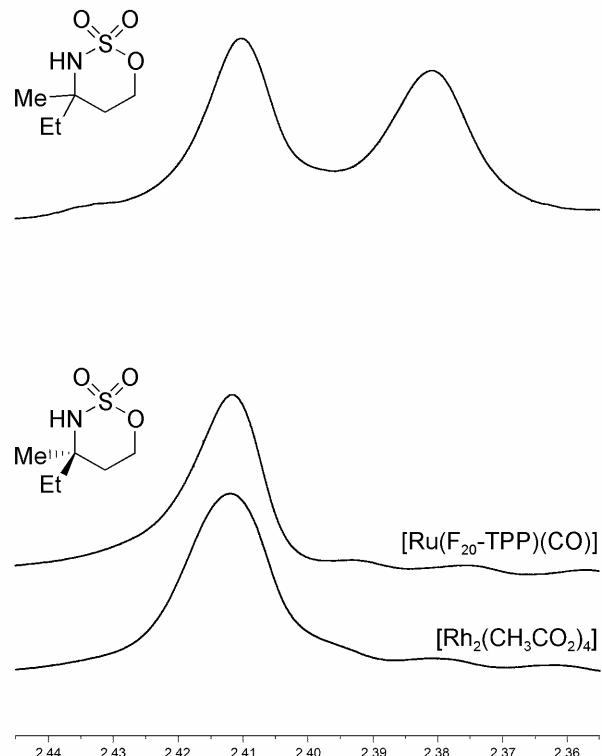
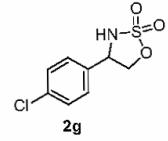
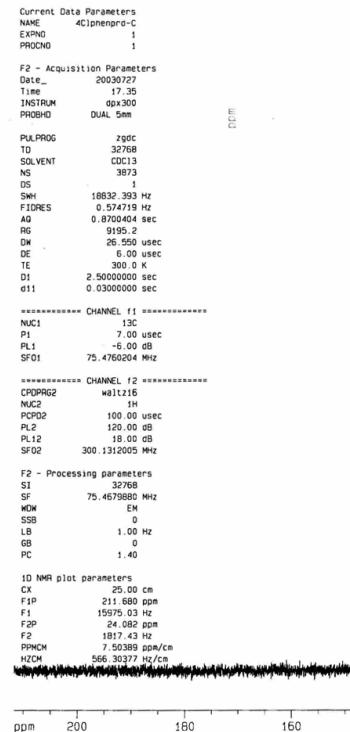
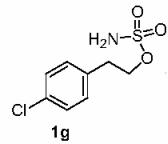
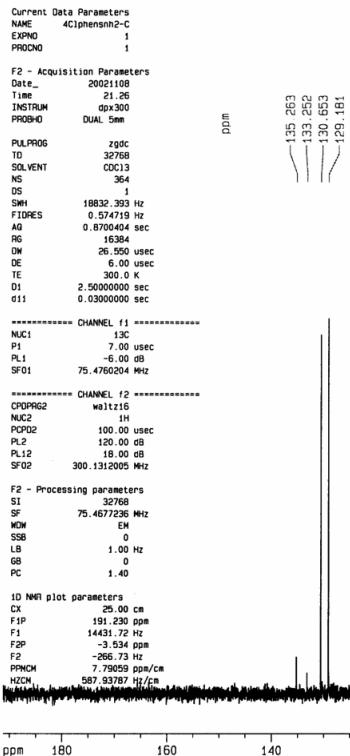
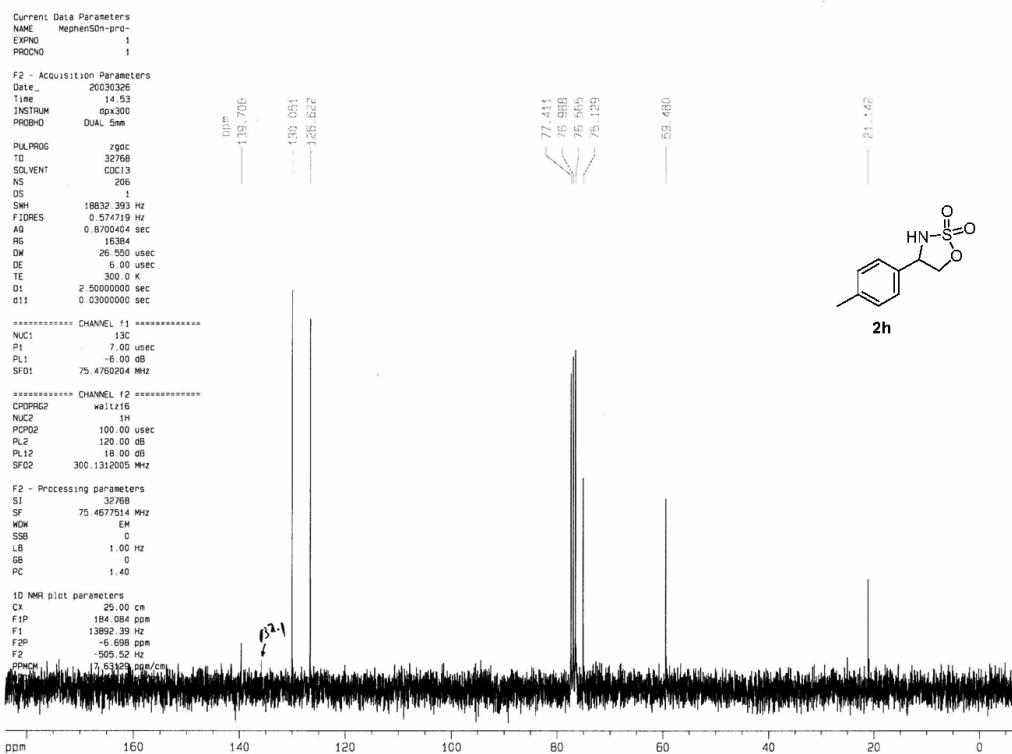
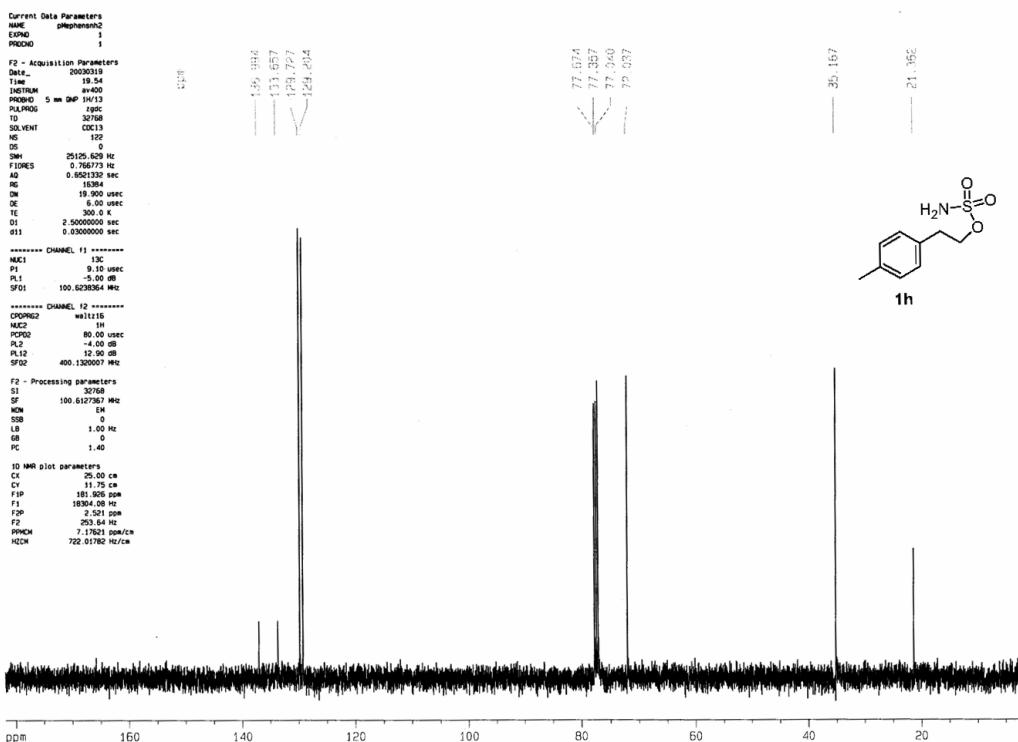
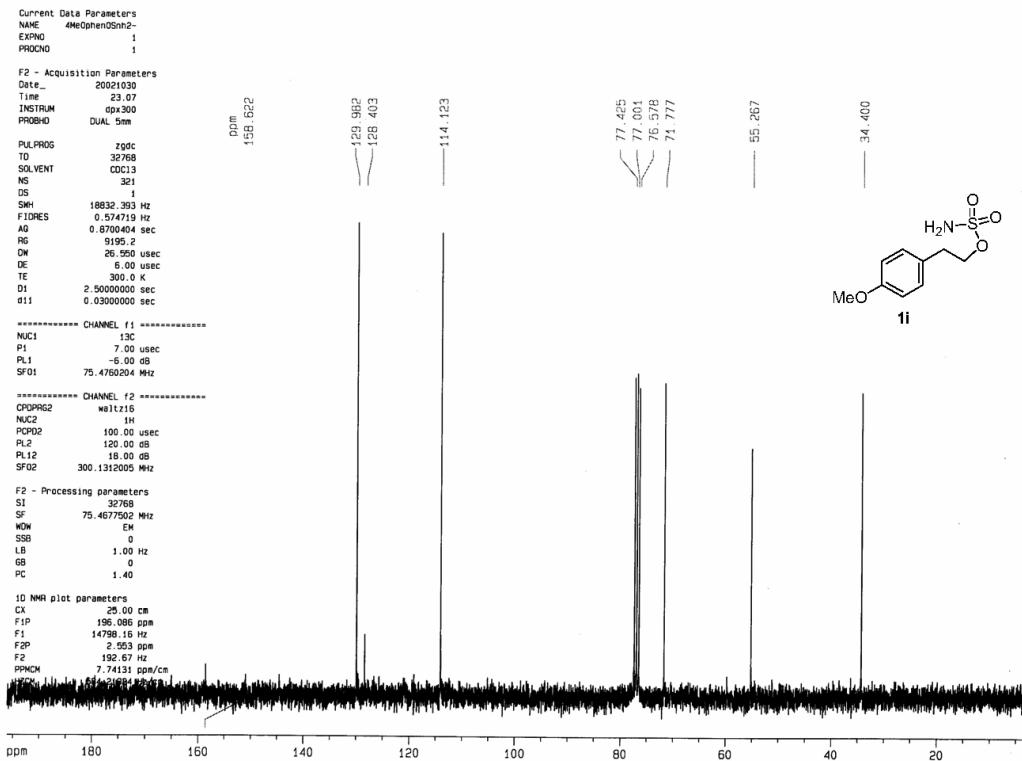
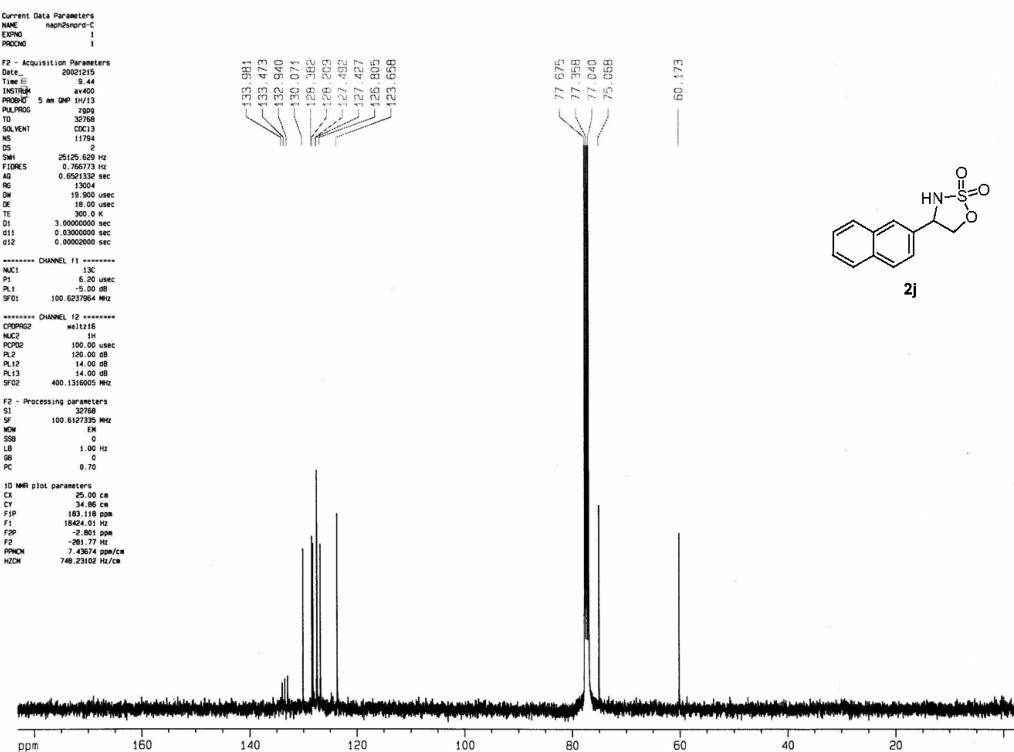
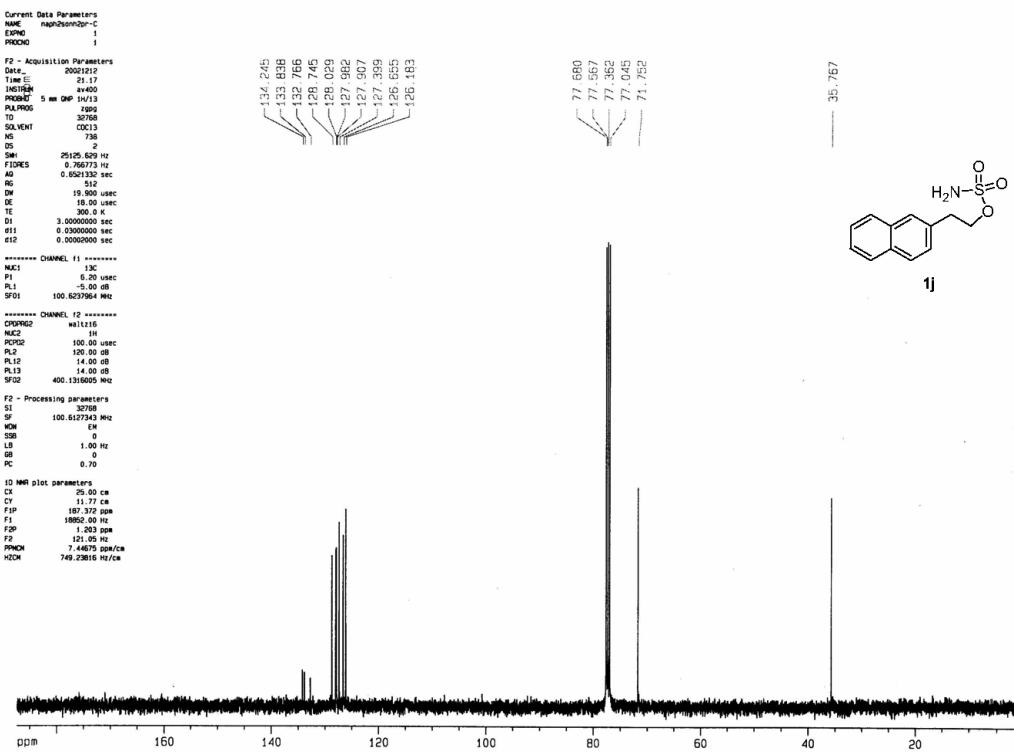


Figure S1. The Me signals in the ¹H NMR spectra of **2p** obtained from the PhI(OAc)₂-amidation of *rac*-**1p** catalyzed by $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{CO})]$ (upper) and from the PhI(OAc)₂-amidation of (*S*)-**1p** catalyzed by $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{CO})]$ and $[\text{Rh}_2(\text{CH}_3\text{CO}_2)_4]$ (lower) in the presence of nearly the same amount of an NMR shift reagent, europium tris(3-(heptafluoropropylhydroxymethylene)-(+)-camphorate). Some of the methylene signals (the weak peaks) also appear in the region of interest.









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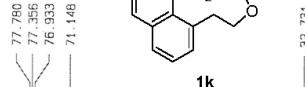
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ppm
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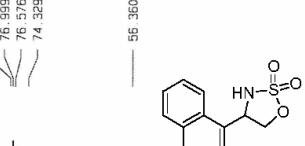
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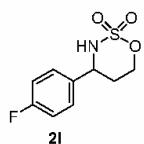
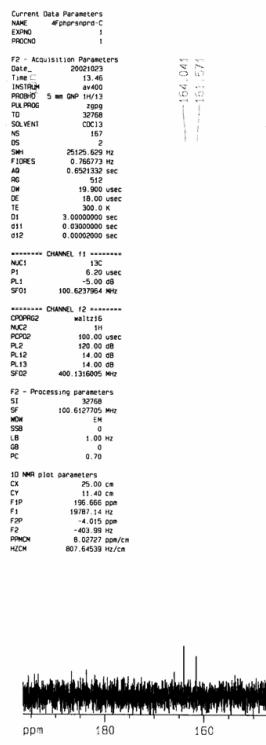
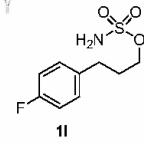
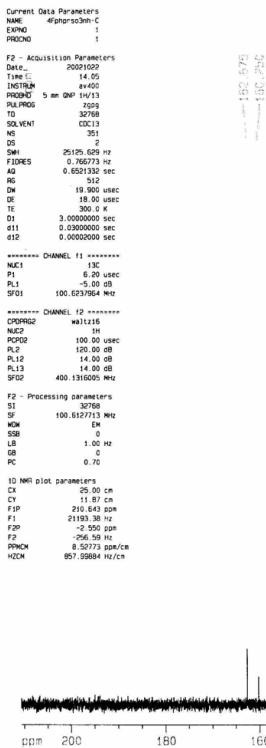
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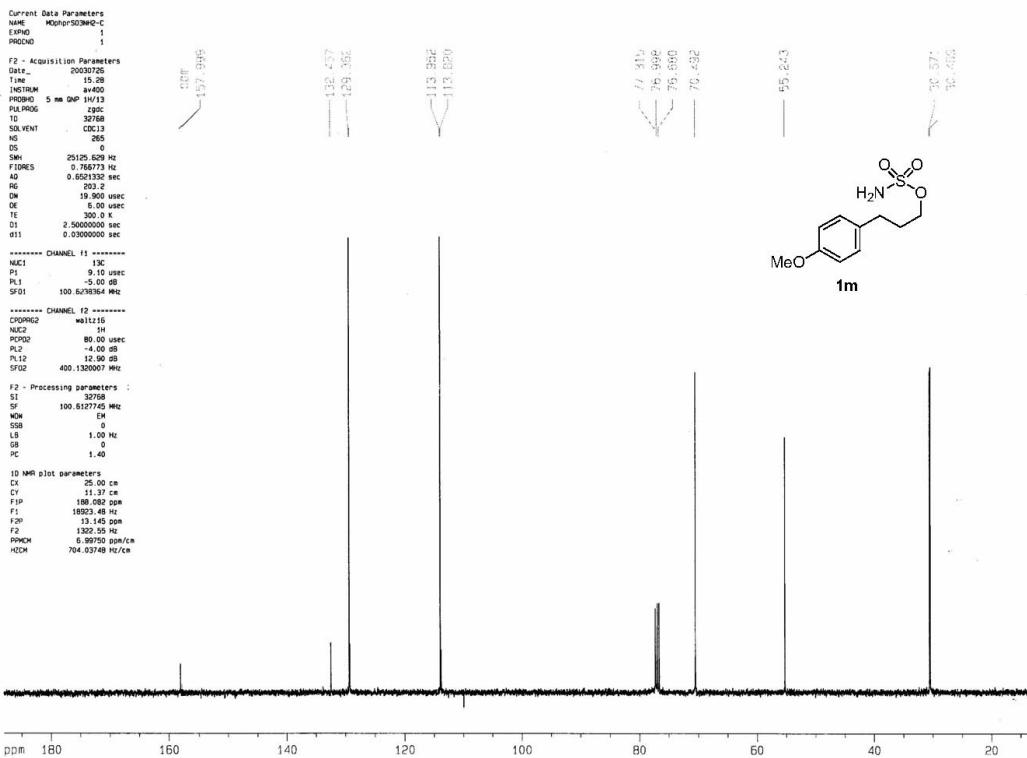


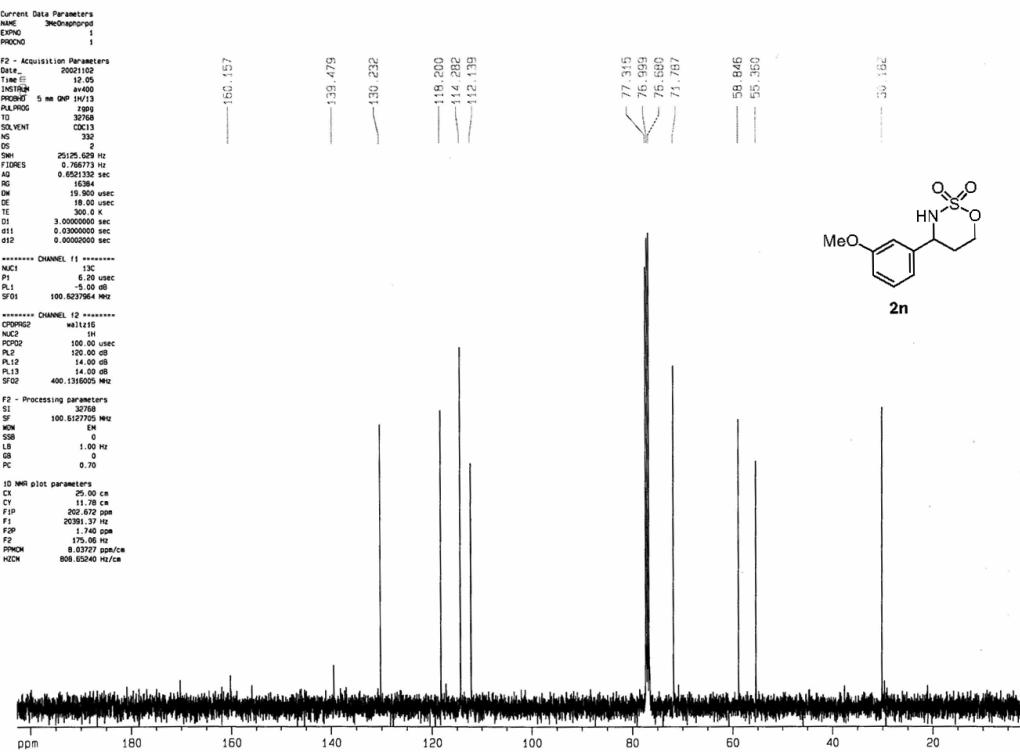
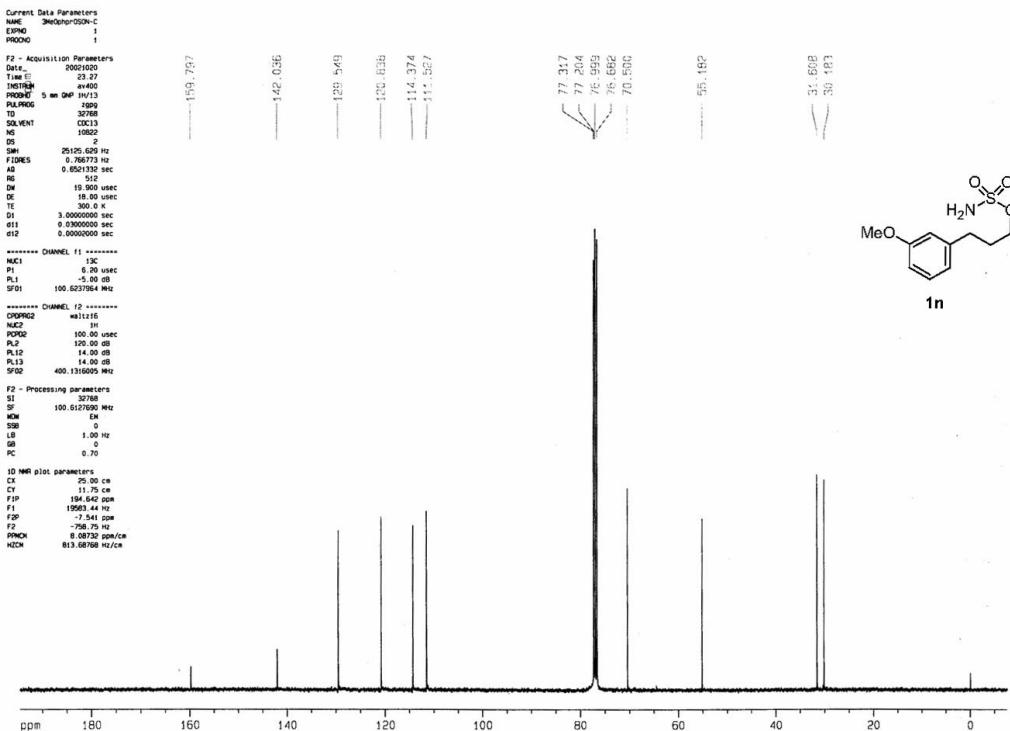
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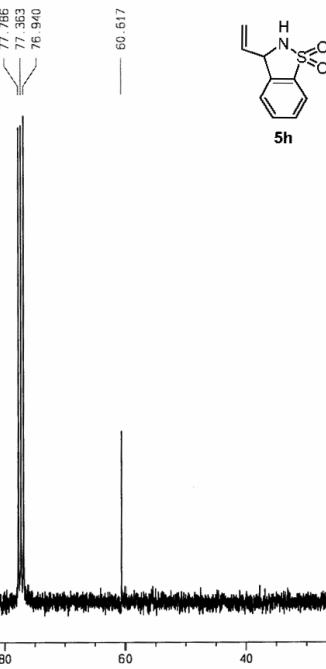
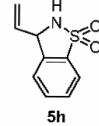
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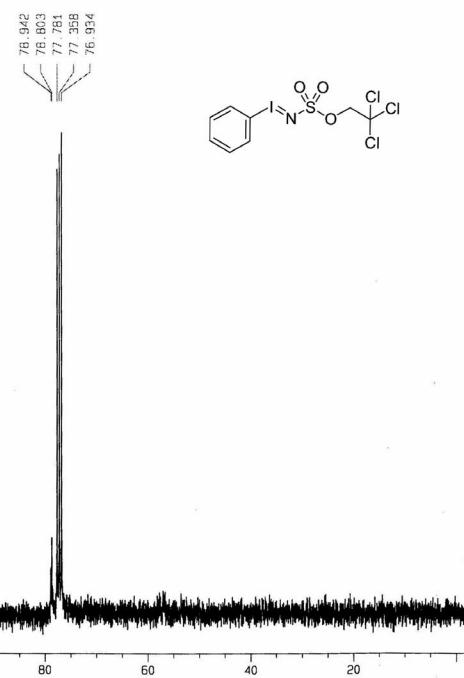
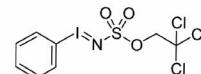
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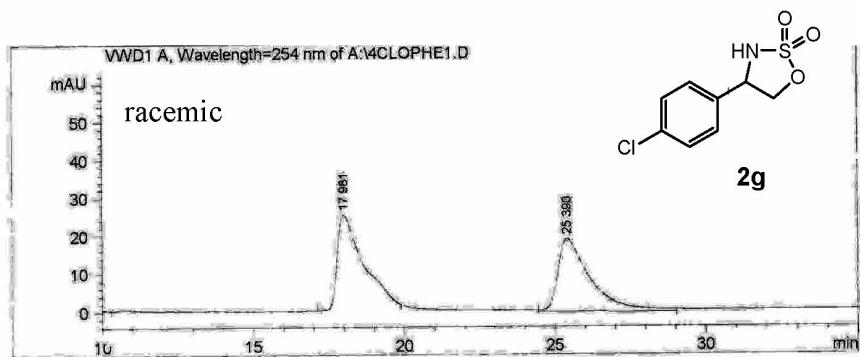
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 ED 1
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 25.00 cm
 F1P 197.086 ppm
 F1 14873.63 Hz
 F2P -1.699 ppm
 F2 -128.12 Hz
 PPMCH 7.95135 ppm/cm
 WPPMCH 547.0395 Hz/cm





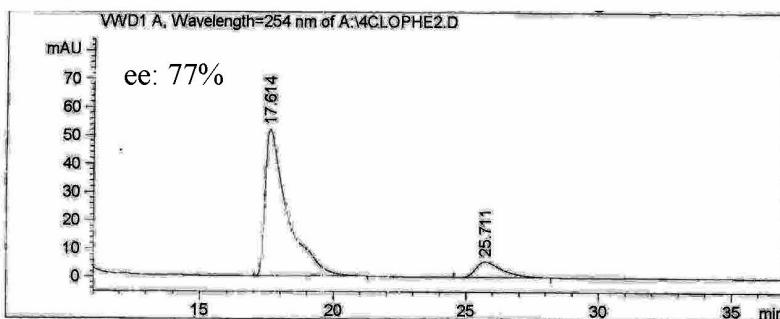
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.697	BV	0.336	206.36786	9.35329	5.3335
2	3.873	VV	0.235	197.06990	10.92132	5.0932
3	4.684	VV	0.347	235.85127	9.83729	6.0955
4	5.421	VV	0.649	197.20091	3.96422	5.0966
5	6.828	VB	0.450	95.53120	2.89944	2.4690
6	9.552	BB	0.350	33.16621	1.37367	0.8572
7	17.981	MM	0.987	1470.00061	24.81620	37.9919
8	25.390	MM	1.253	1434.06189	19.07464	37.0630



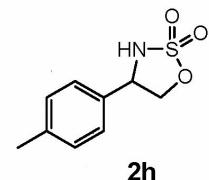
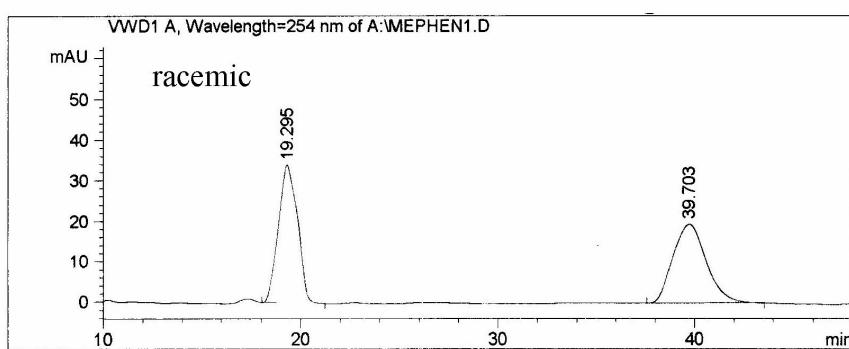
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.219	BV	0.608	3604.46655	79.77026	46.6792
2	5.337	VB	0.499	699.36847	18.60172	9.0571
3	17.614	BB	0.809	3028.50024	51.95335	39.2202
4	25.711	BB	1.018	389.44406	5.64511	5.0434



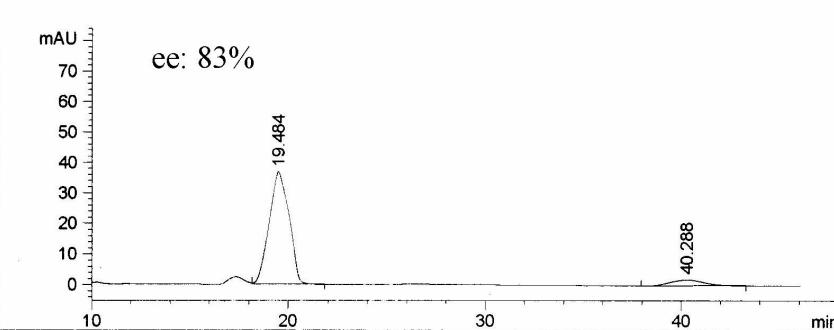
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.295	BB	0.947	2285.99683	34.10294	49.9690
2	39.703	BB	1.862	2288.82935	19.52537	50.0310



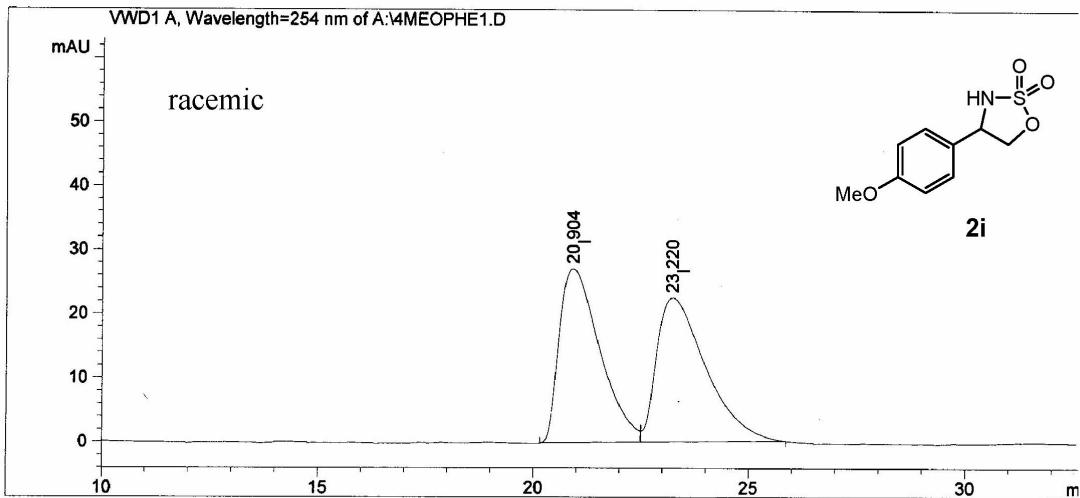
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.176	BB	0.536	7691.54785	225.86168	73.3380
2	19.484	VB	1.159	2564.74023	36.89394	24.4545
3	40.288	BB	1.939	231.51767	1.92368	2.2075



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Area Percent Report
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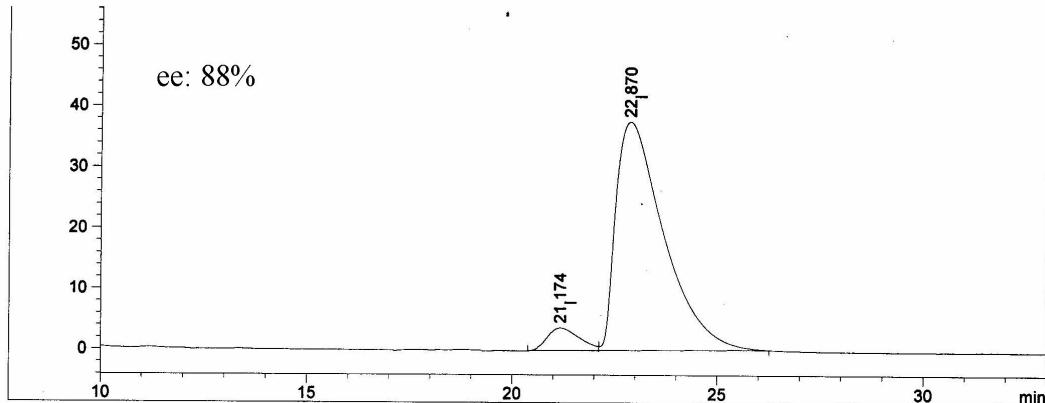
Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.904	BF	0.777	1788.34705	27.25665	49.8426
2	23.220	FB	0.947	1799.64465	22.60450	50.1574

ee: 88%



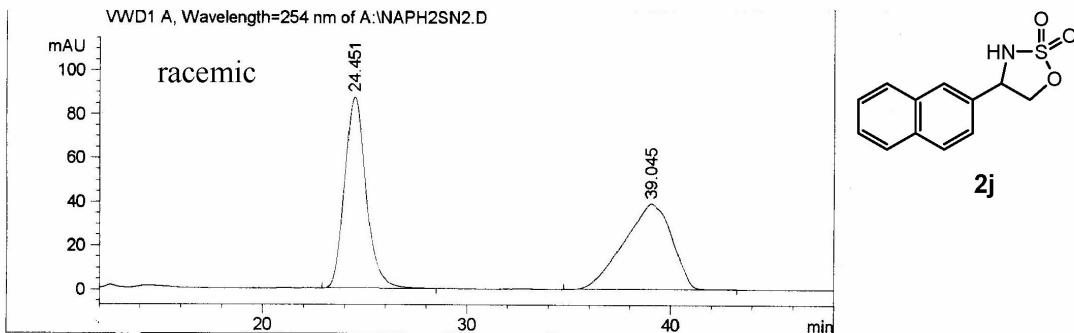
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.174	BF	0.669	204.37428	3.73441	6.2427
2	22.870	FB	1.120	3069.41528	37.61686	93.7573



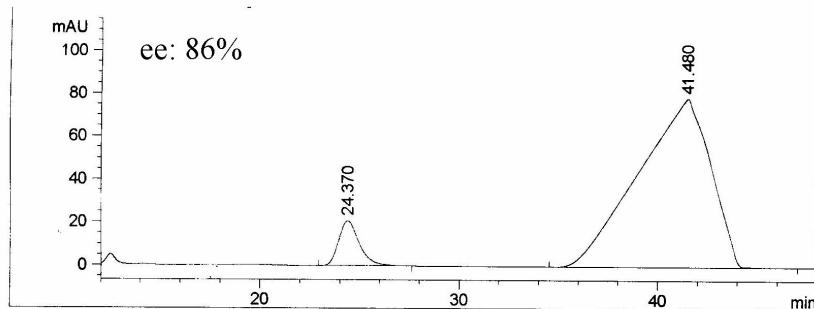
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.451	BB	1.124	6394.72510	87.23300	49.7916
2	39.045	BB	2.119	6448.24951	39.17011	50.2084



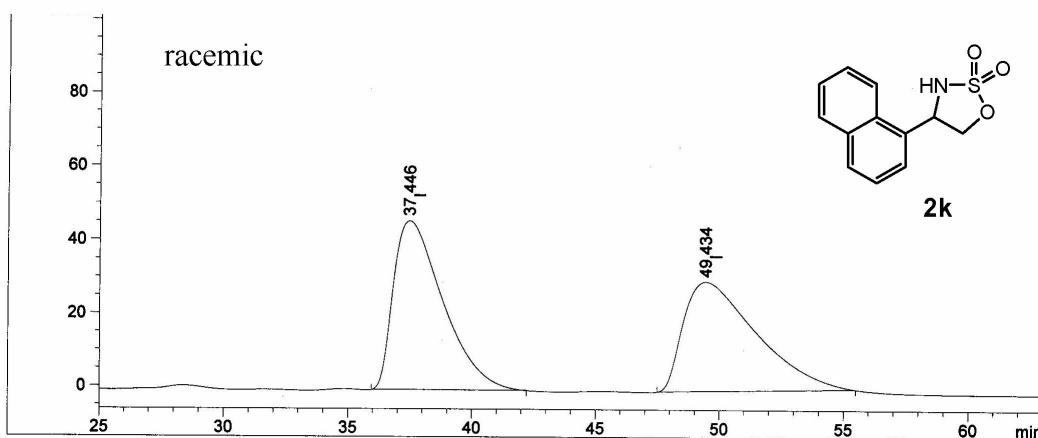
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.264	VV	0.478	2604.58667	78.32549	10.8569
2	24.370	BB	1.103	1503.19019	20.78739	6.2658
3	41.480	BB	3.136	19882.42773	78.51532	82.8773



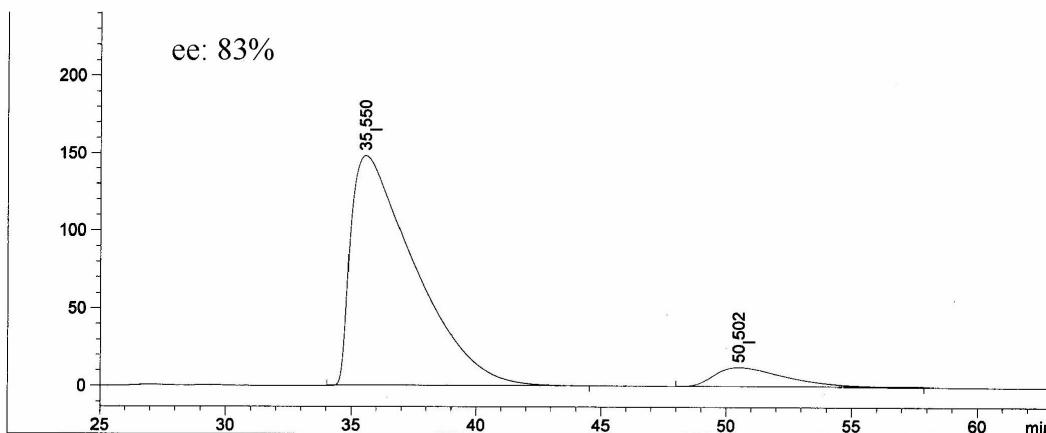
Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.446	BB	1.650	6447.01807	46.19490	51.0611
2	49.434	BB	2.453	6179.07471	30.09880	48.9389



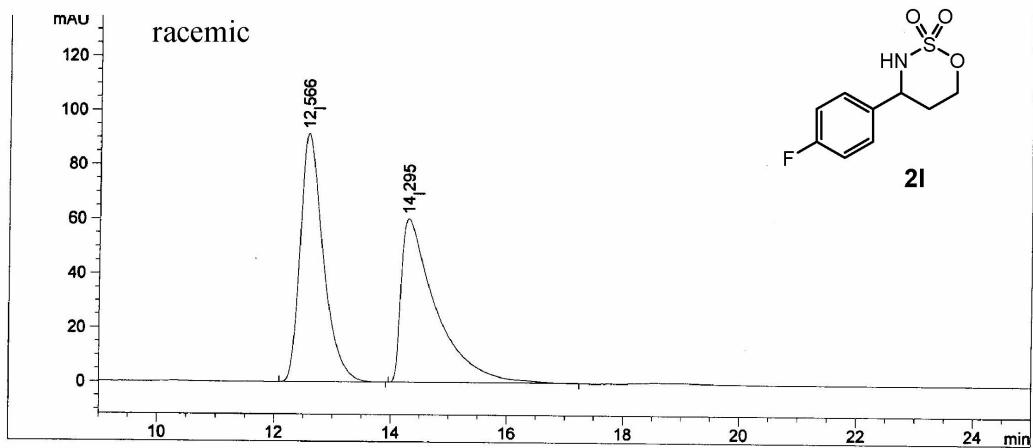
Area Percent Report

Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.550	BB	2.537	26479.71680	148.24733	91.4833
2	50.502	BB	2.968	2465.13208	12.41369	8.5167



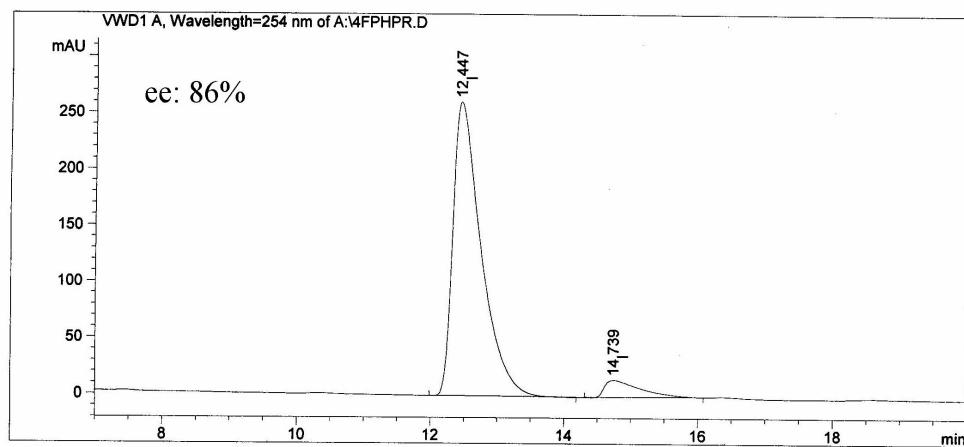
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.566	BB	0.412	2520.43164	91.48117	50.0180
2	14.295	BB	0.587	2518.61816	60.34896	49.9820



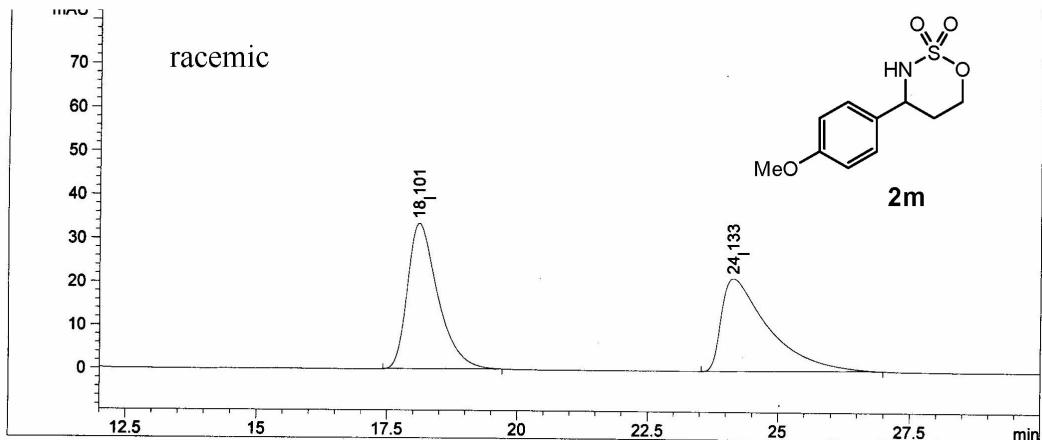
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Area Percent Report
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Sorted by Signal

Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.153	BV	0.476	7154.34033	204.21143	46.5269
2	12.447	BB	0.431	7653.42627	261.47845	49.7726
3	14.739	BV	0.542	569.00488	15.24636	3.7004

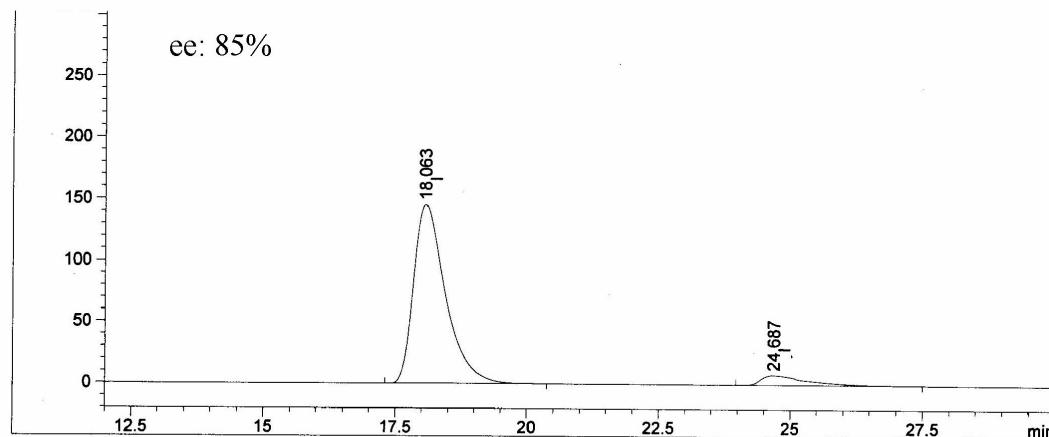


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Area Percent Report
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Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.101	BB	0.600	1363.94897	33.53594	50.3687
2	24.133	BB	0.873	1343.98328	21.40095	49.6314

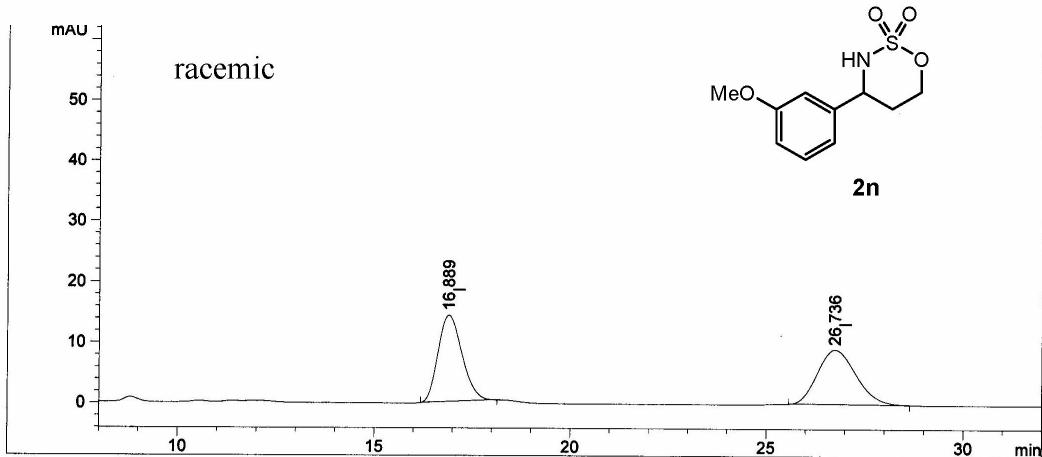


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Area Percent Report
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Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.063	BB	0.634	6132.49756	145.72507	92.5279
2	24.687	BB	0.921	495.22739	8.02328	7.4721

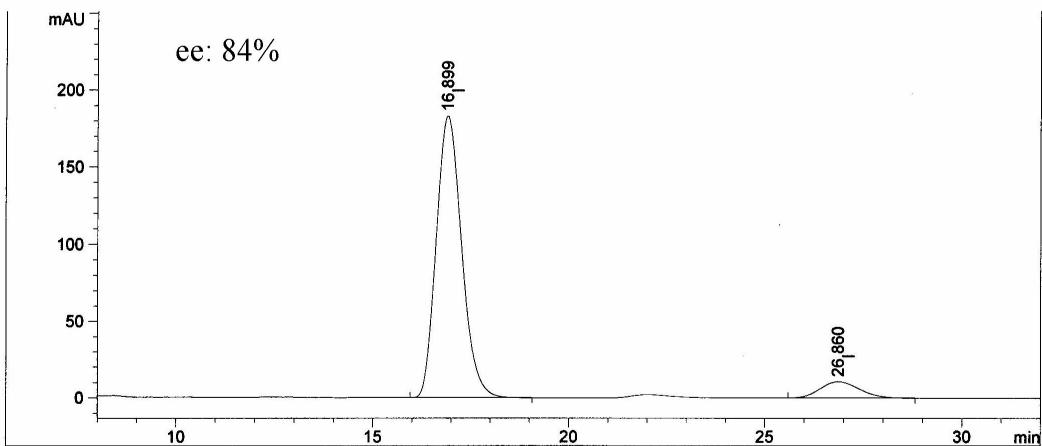


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Area Percent Report
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Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.889	BB	0.629	606.81854	14.27902	49.6323
2	26.736	BB	0.840	615.81067	9.05418	50.3677



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Area Percent Report
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Sorted by Signal
Multiplier : 1.000000
Dilution : 1.000000

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.899	BB	0.707	8285.23730	183.37740	91.8349
2	26.860	BB	1.006	736.64673	10.72161	8.1651