Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Concise Asymmetric Synthesis of (1*R*,2*S*)-1-Amino-2-Vinylcyclopropanecarboxylic Acid-Derived Sulfonamide and Ethyl Ester

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Supporting Information

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acqus_SOLVENT	<DMSO>	acqus_PULPROG	<zg30>	acqus_PROBHD	<5 mm PABBO BB/19F-1H/D XYZ-GRD Z555401/0002 >	acqus_SFO1	500.133083507479
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XPoints	32768	ObservFreq	500.13	Date	16 Apr 2012 16:56:32			ObservNuc	1H
Temperature	26.7	NumberofScans	16	BMSSolvent	DMSO-d6	PulseSequence	zg30		
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Original Points Count	32768	Owner	prd	Points Count	32768	Pulse Sequence	zg30
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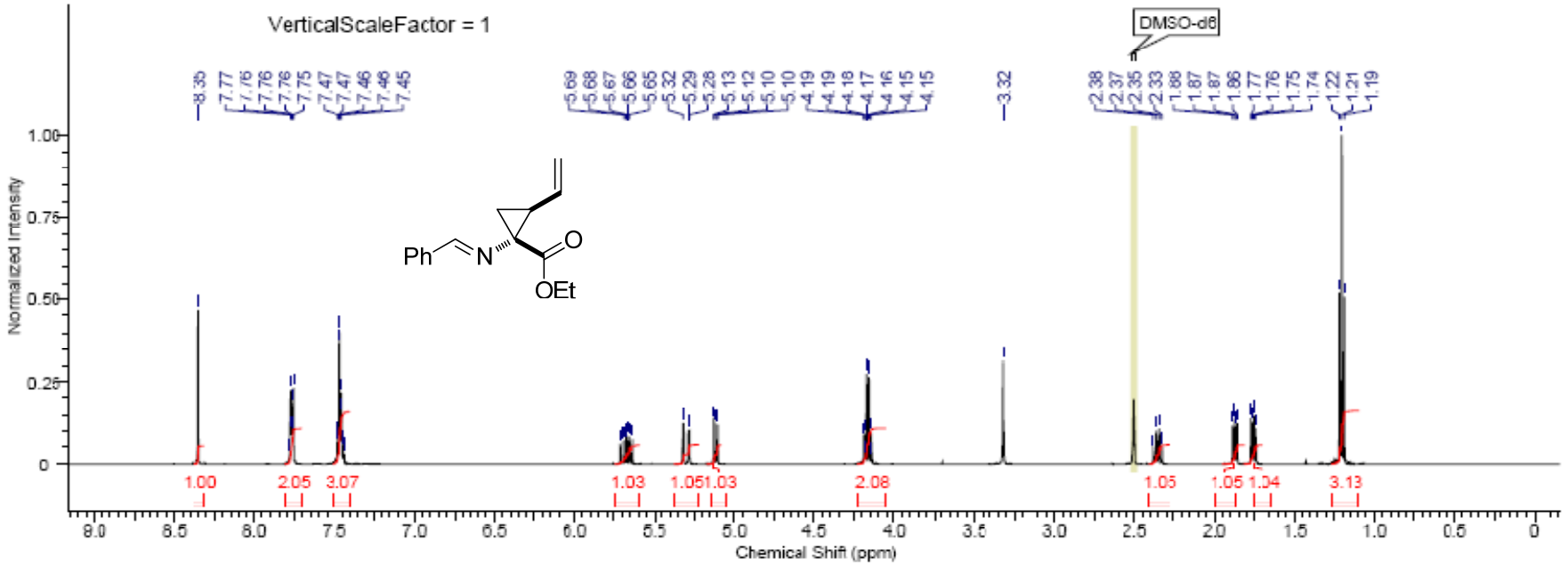
Spectrum Type	STANDARD	Sweep Width (Hz)	10330.26	Temperature (degree C)	26.700		



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NMRVendor	Bruker	BMSComment	ethyl ester	InstrumentField	spect	BMSUser	prd	XPoints	32768
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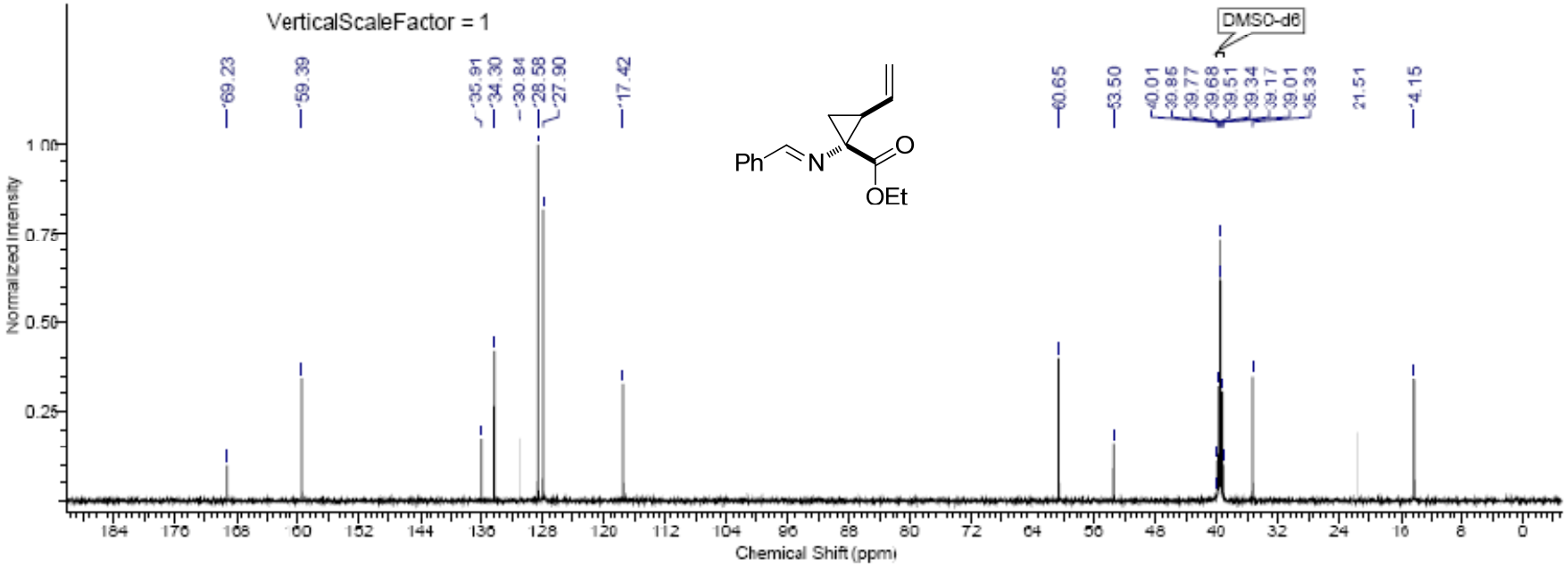

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procs_ORIGIN	Bruker BioSpin GmbH			*procs_OWNER*	prd	*NMRVendor*	Bruker	*BMSComment*	amide
InstrumentField	spect	*BMSUser*	prd	*XPoints*	32768	*ObservFreq*	500.13	*Date*	16 Apr 2012 17:05:04
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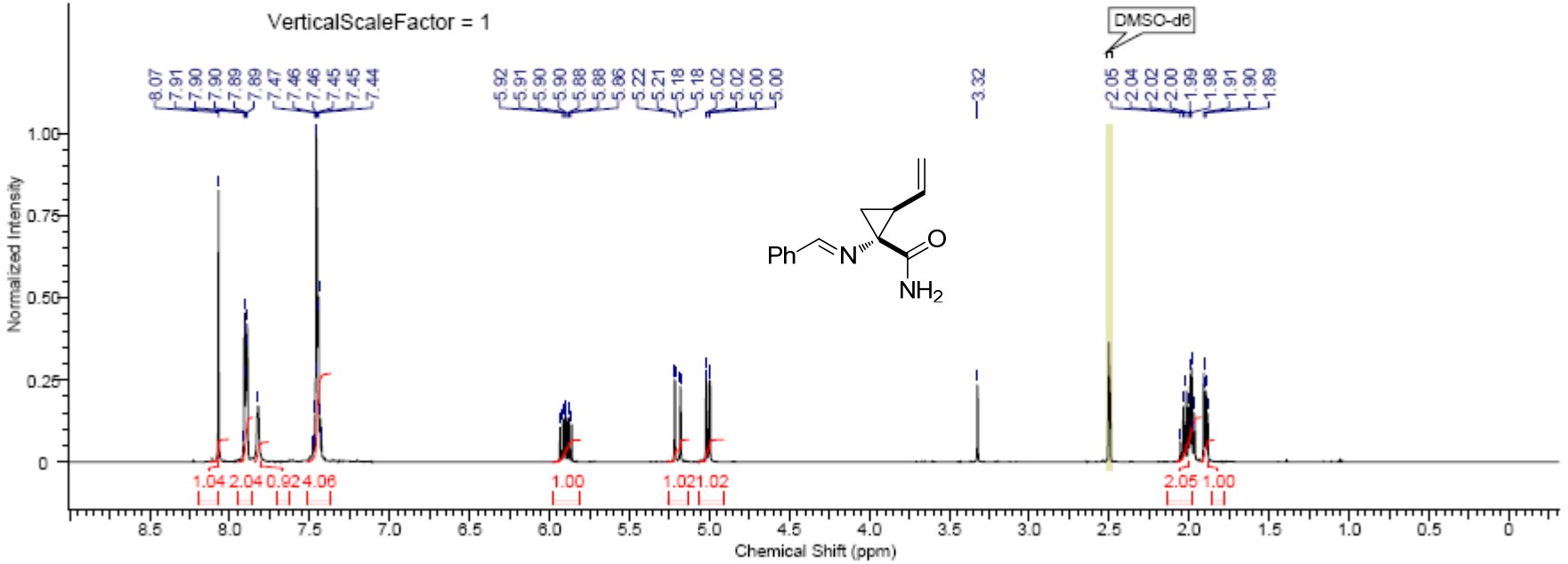

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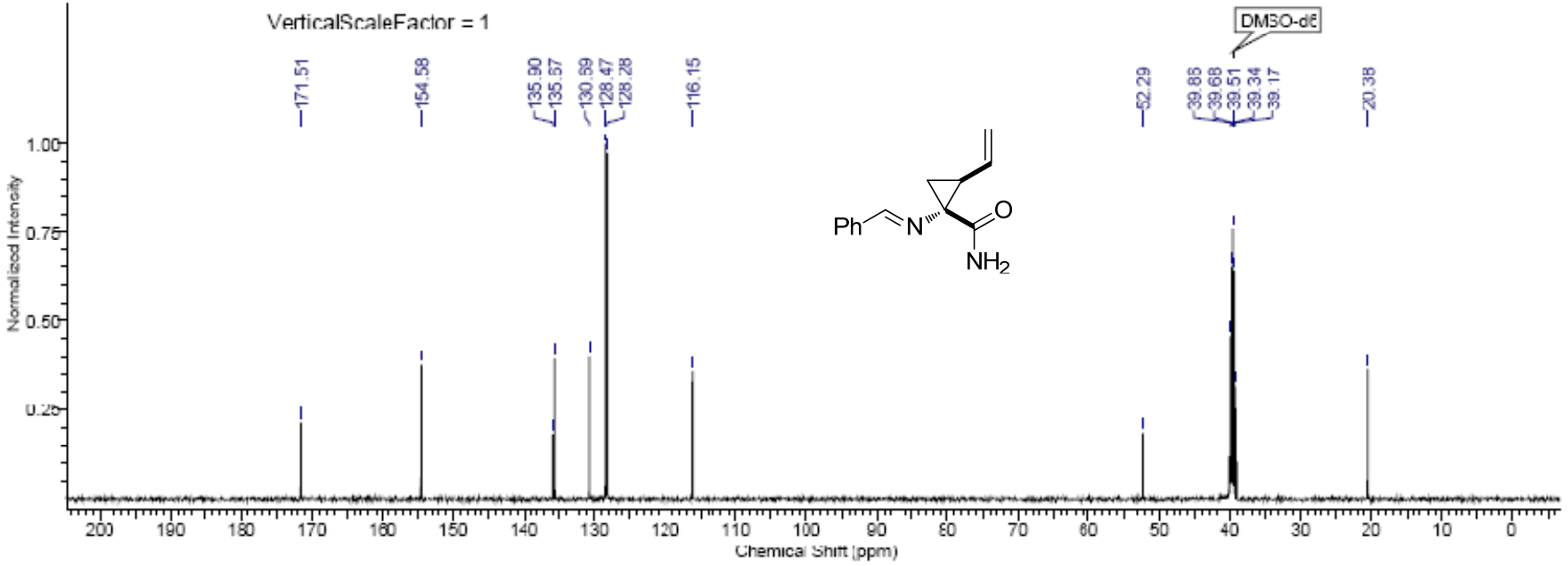

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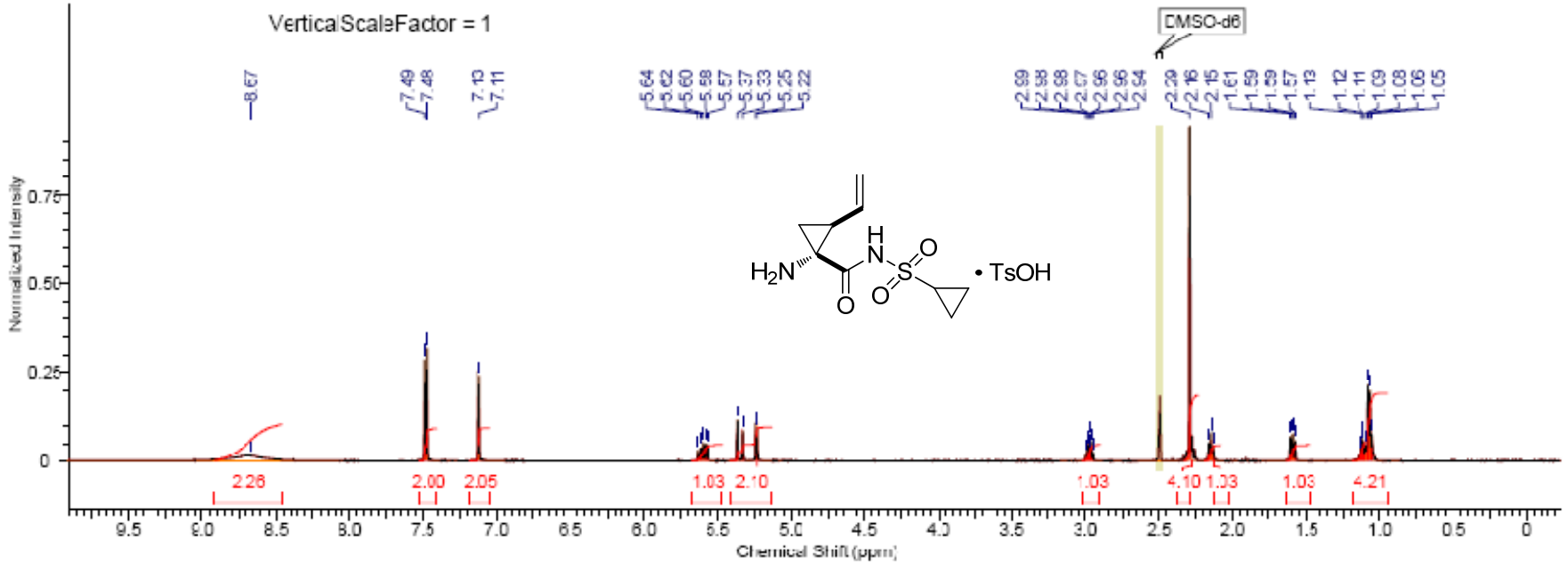

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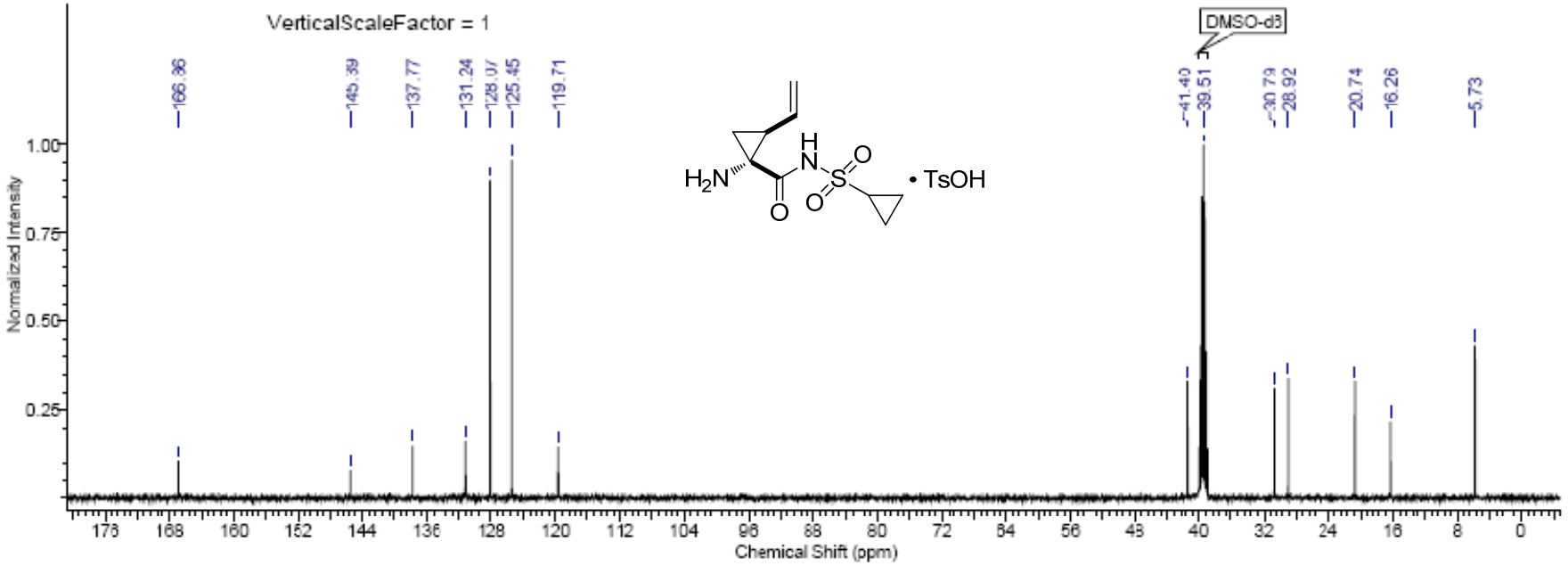

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procs_OWNER	prd	*NMRVendor*	Bruker	*BMSComment*	Tartrate salt	*InstrumentField*	spect	*BMSUser*	prd
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Temperature	26.5	*NumberofScans*	16	*BMSSolvent*	DMSO-d6	*PulseSequence*	zg30		
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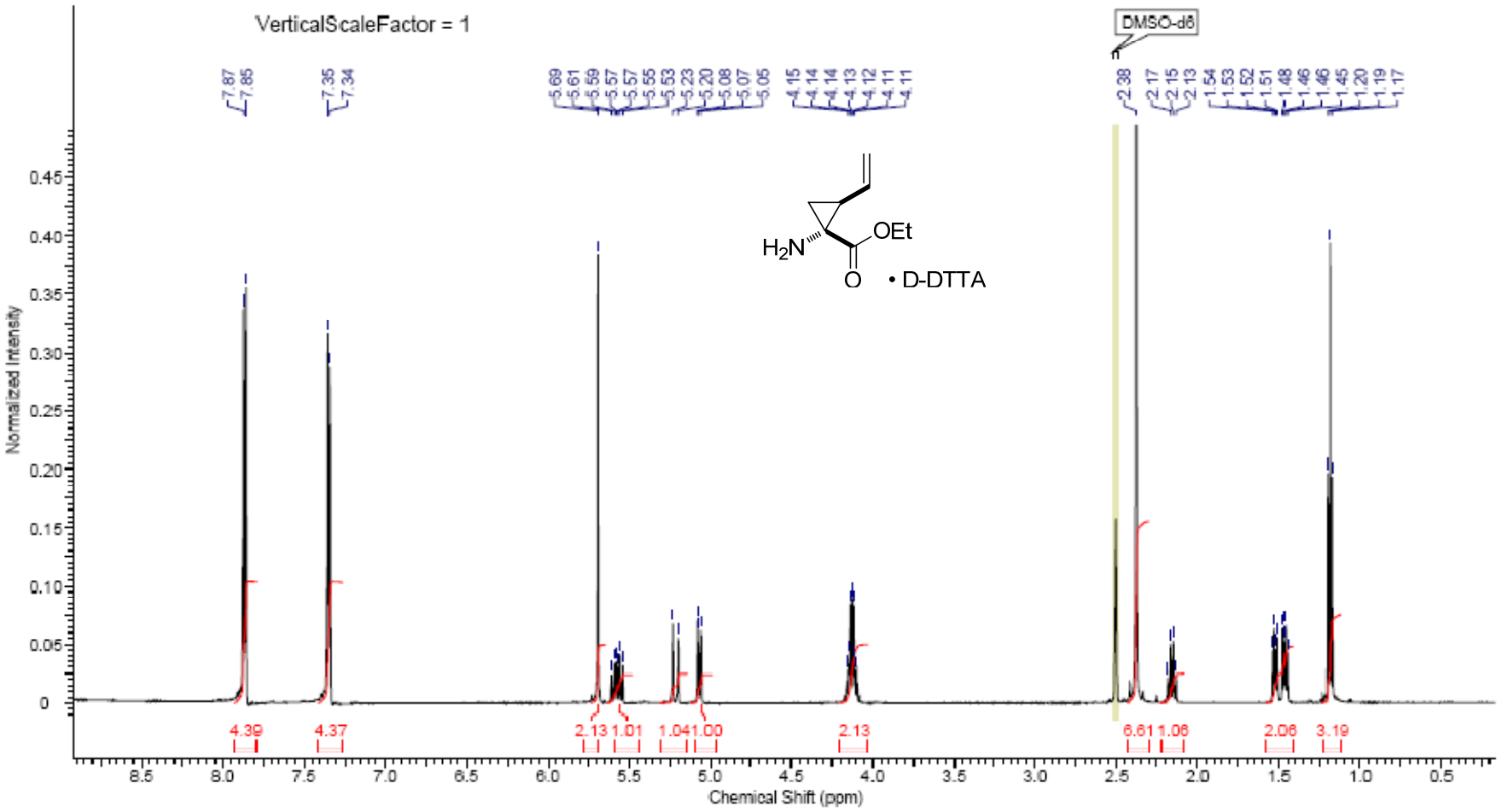
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	prd	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	181.00	*SW(cyclical) (Hz)*	10330.58	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	3083.7441
Spectrum Type	STANDARD	*Sweep Width (Hz)*	10330.26	*Temperature (degree C)*	26.500		



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acqus_TE	300.5	acqus_SW_h	30030.03003003	procs_ORIGIN	Bruker BioSpin GmbH	procs_OWNER	prd
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NumberofScans	2200	BMSSolvent	DMSO-d6	PulseSequence	zgpg30				
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Acquisition Time (sec)	1.0912	Comment	Tartrate salt	Date	08 May 2012 22:10:08		
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Frequency (MHz)	125.76	Nucleus	13C	Number of Transients	2200	Origin	spect
Original Points Count	32768	Owner	prd	Points Count	32768	Pulse Sequence	zgpg30
Receiver Gain	9195.20	SW(cyclical) (Hz)	30030.03	Solvent	DMSO-d6	Spectrum Offset (Hz)	12512.3994
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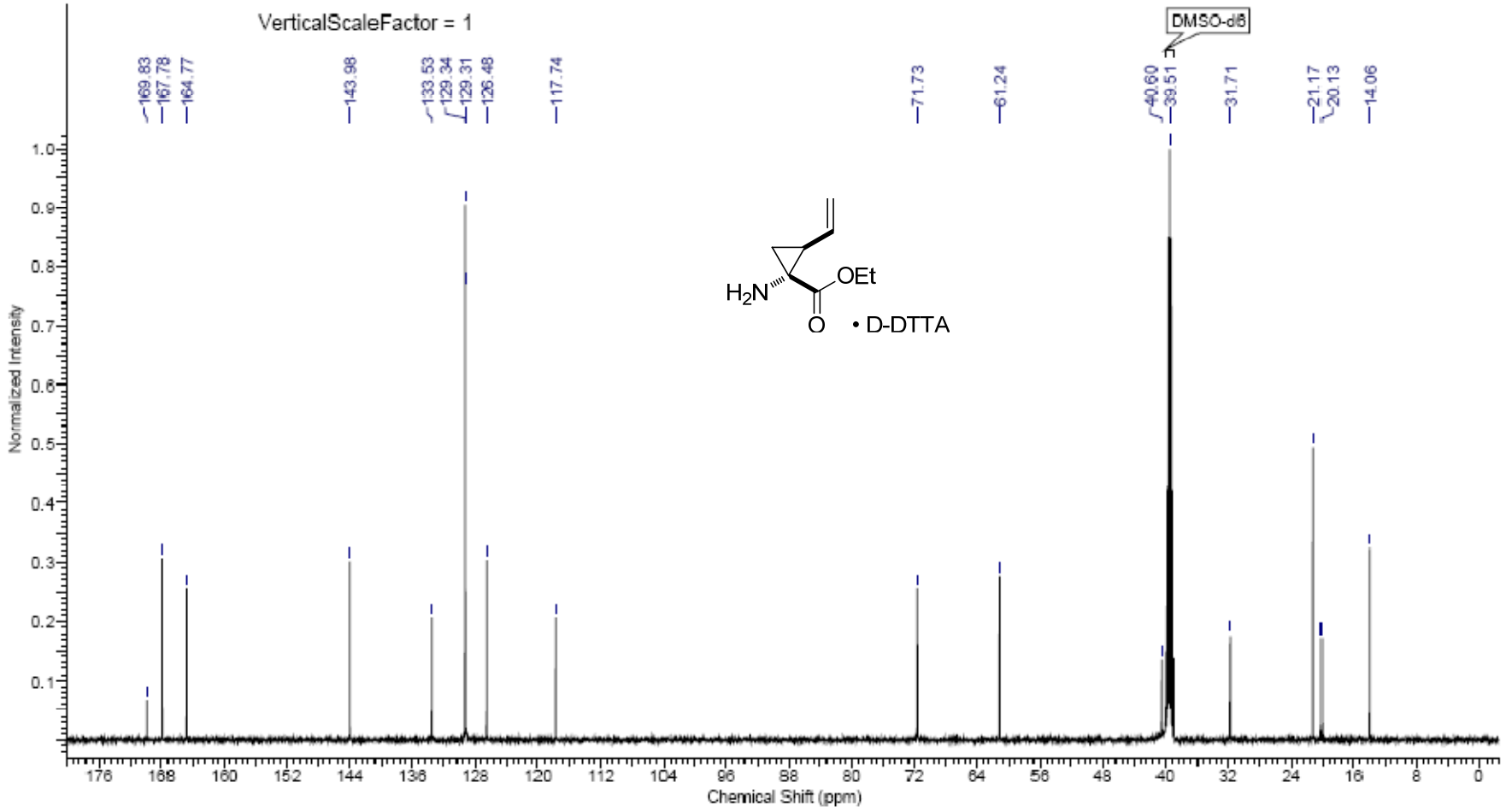
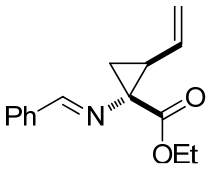
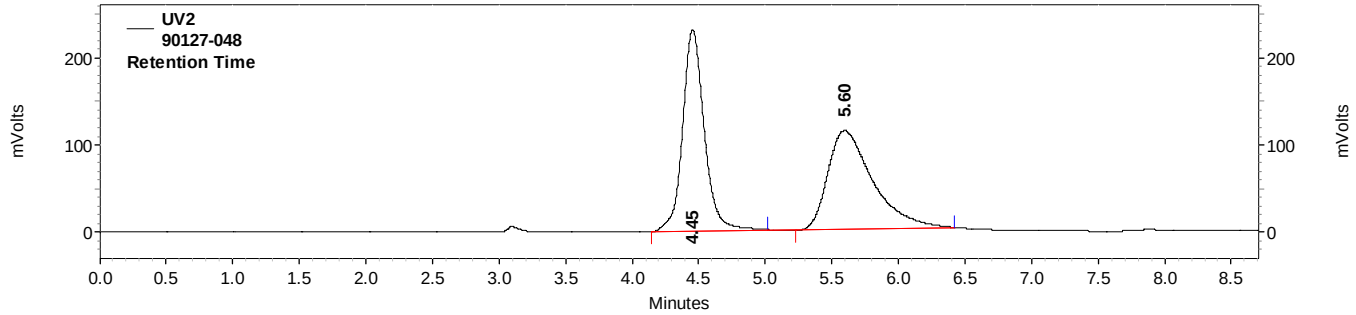


Chiral HPLC Methods and Chromtagrams (racemic and enantioenriched)

Method Description:

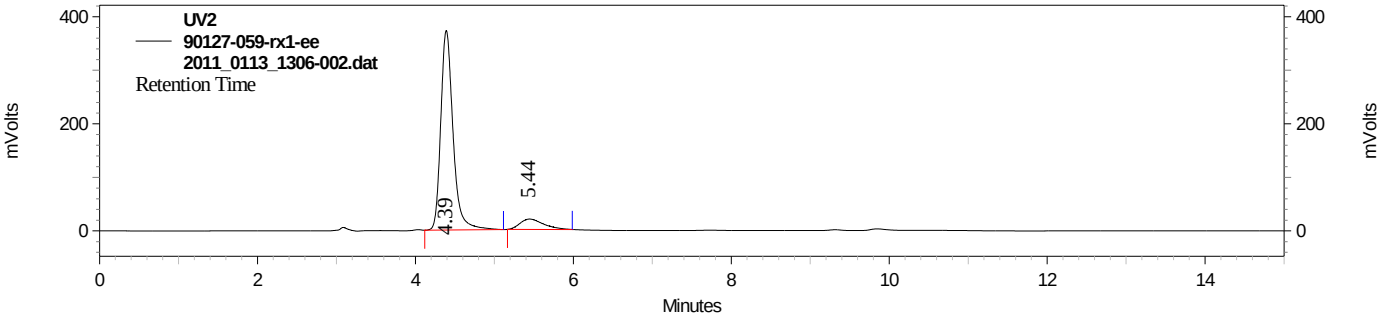
Vial = 19 Inj. Vol. = 5 uL
Percent B = 2% Isocratic
Flow Rate = .7 ml/min
Wavelength1 = 254
Wavelength2 = 280
Solvent Pair = Heptane/IPA/0.05%DEA
Solvent A = 0.05%DEA in Heptane
Solvent B = 0.05%DEA in IPA
Column 2 : Chiralpak AS-H (DEA ONLY) 5 um 4.6 x 150 mm SN ASH0CD-EI011





UV2 Results

Pk #	Retention Time	Area	Area Percent
1	4.455	2620726	49.885
2	5.596	2632846	50.115
Totals		5253572	100.000

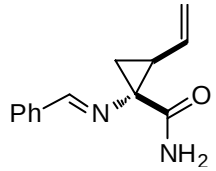


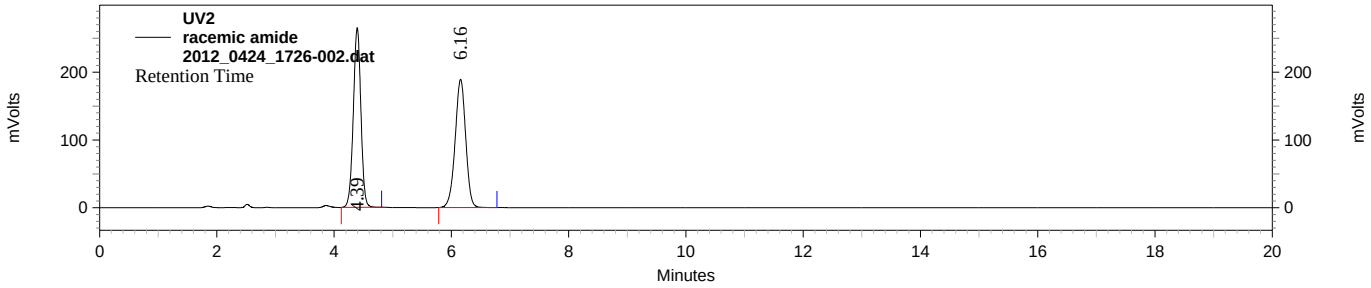
UV2 Results

Pk #	Retention Time	Area	Area Percent
1	4.390	4025261	90.905
2	5.443	402734	9.095
Totals		4427995	100.000

Method Description:

Well = 96 Inj. Vol. = 10 uL
Percent B = 15% Isocratic
Flow Rate = 1 ml/min
Wavelength1 = 254
Wavelength2 = 280
Solvent Pair = Heptane/IPA
Solvent A = Heptane
Solvent B = IPA
Column 1 : Chiralpak AD-H (DEA ONLY) 5 um 4.6 x 150 mm SN ADH0CD-EK023





UV2 Results

Pk #	Retention Time	Area	Area Percent
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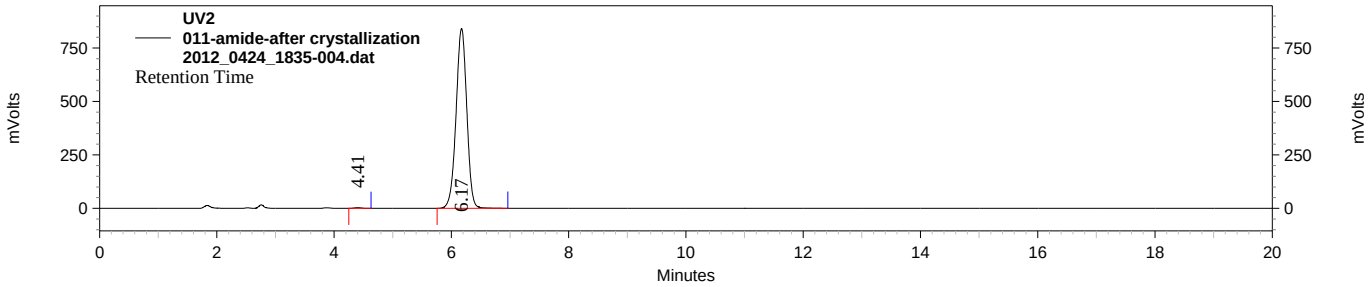
2	6.156	2368165	49.948
Totals		4741266	100.000

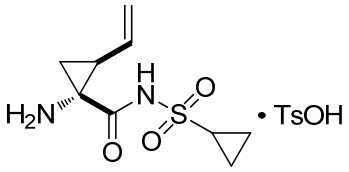


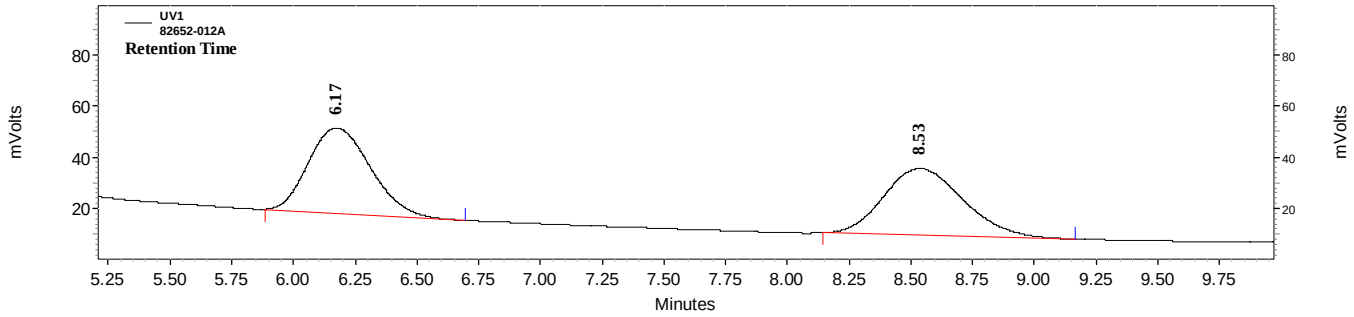
UV2 Results

Pk #	Retention Time	Area	Area Percent
1	4.406	26534	0.247
2	6.173	10697125	99.753
Totals		10723659	100.000

Method Description:

Vial = 20 Inj. Vol. = 30 uL
Percent B = 20% Isocratic
Flow Rate = 1 ml/min
Wavelength1 = 215
Wavelength2 = 250
Solvent Pair = TFA/Heptane/EtOH
Solvent A = A2=0.1% TFA in Heptane
Solvent B = B2=0.1% TFA in Ethanol
Column 5 : 5: Chiralcel OJ-H (TFA ONLY) 5 um 4.6 x 150 mm SN OJH0CD-DG005





UV1 Results

Pk #	Retention Time	Area	Area Percent
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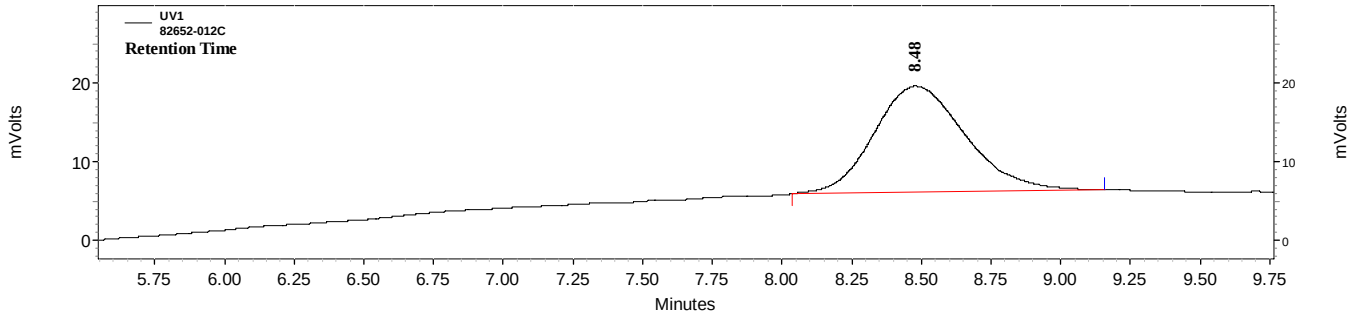
2	8.534	584191	49.980

Totals		1168850	100.000



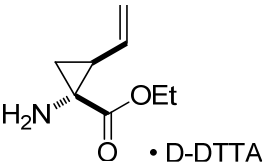
UV1 Results

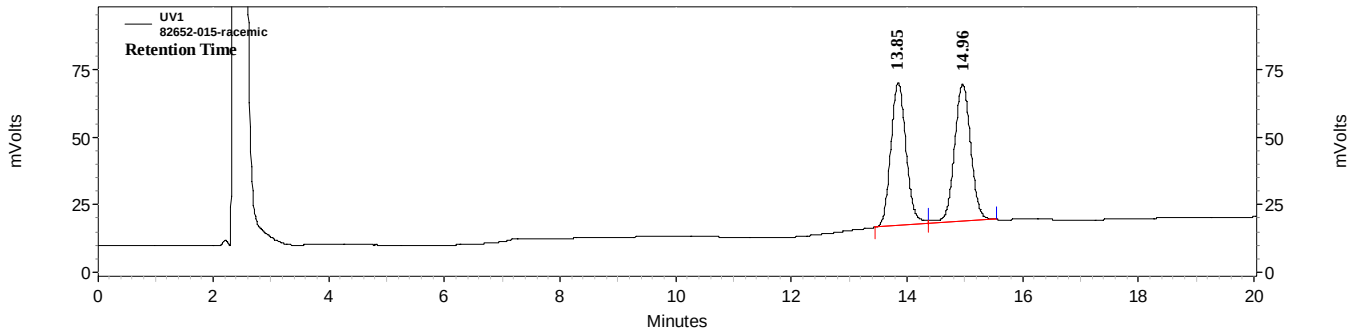
Pk #	Retention Time	Area	Area Percent
1	8.479	307280	100.000

Totals		307280	100.000

Method Description:

Vial = 48 Inj. Vol. = 10 uL
Start % B = 0
10 Min. 25%
20 Min. 35%
25 Min. 100%
Flow Rate = .8 ml/min
Wavelength1 = 220
Wavelength2 = 254
Solvent Pair = MeDuSA NH4OAc S160A/B
Solvent A = A2=0.01 M NH4OAc in MeOH:Water (20:80) S160A
Solvent B = B2=0.01 M NH4OAc in MeOH:Water:CH3CN (20:5:75) S160B
Column 1 : 1: Chiralpak AD-3R 3 um 4.6 x 150 mm SN AD3RCD-MK002





UV1 Results

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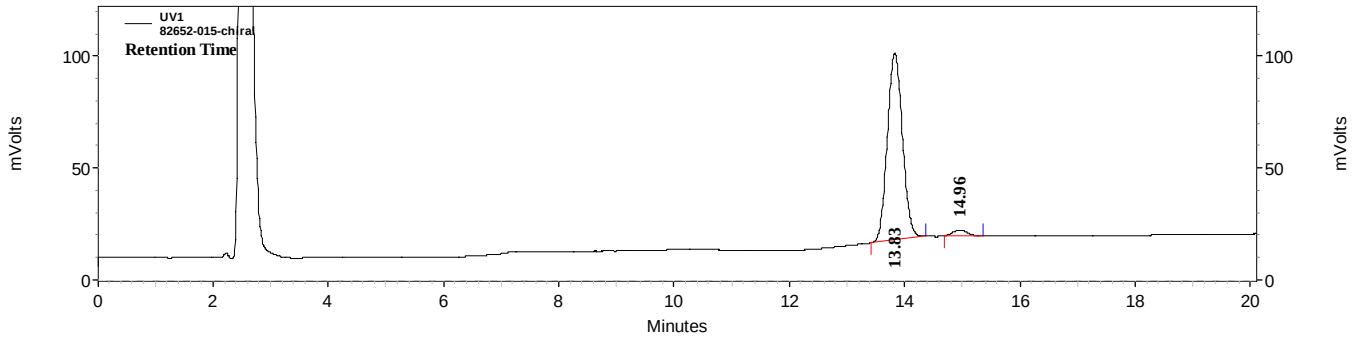
Totals		1985556	100.000

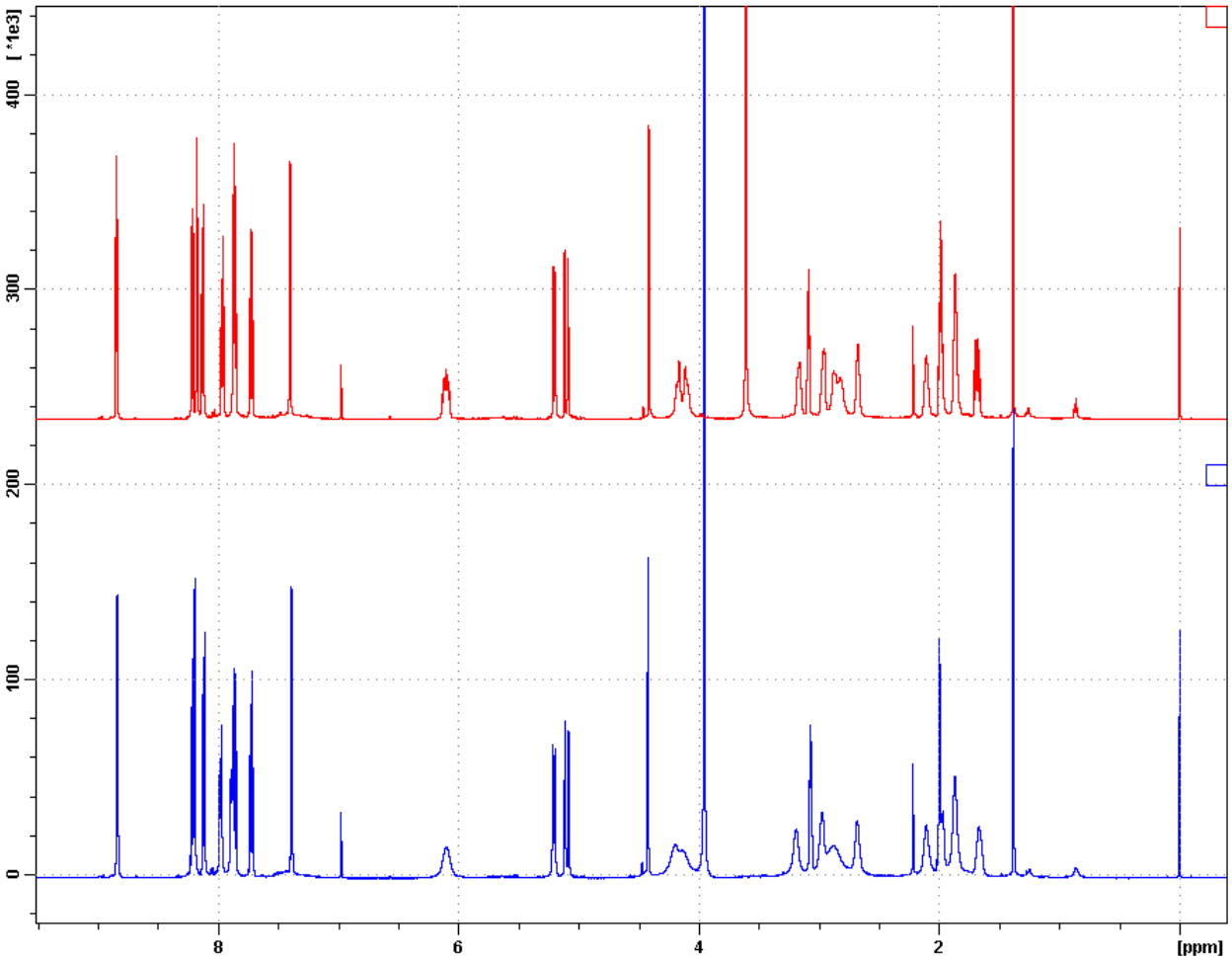


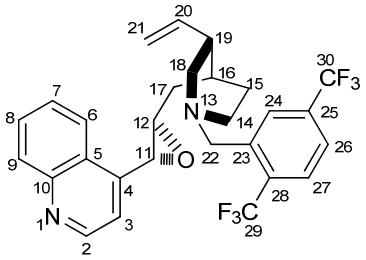
UV1 Results

Pk #	Retention Time	Area	Area Percent
1	13.827	1528696	97.095
2	14.956	45735	2.905
Totals		1574431	100.000

^{1}H NMR of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 25 (bottom) and 55 (top) °C

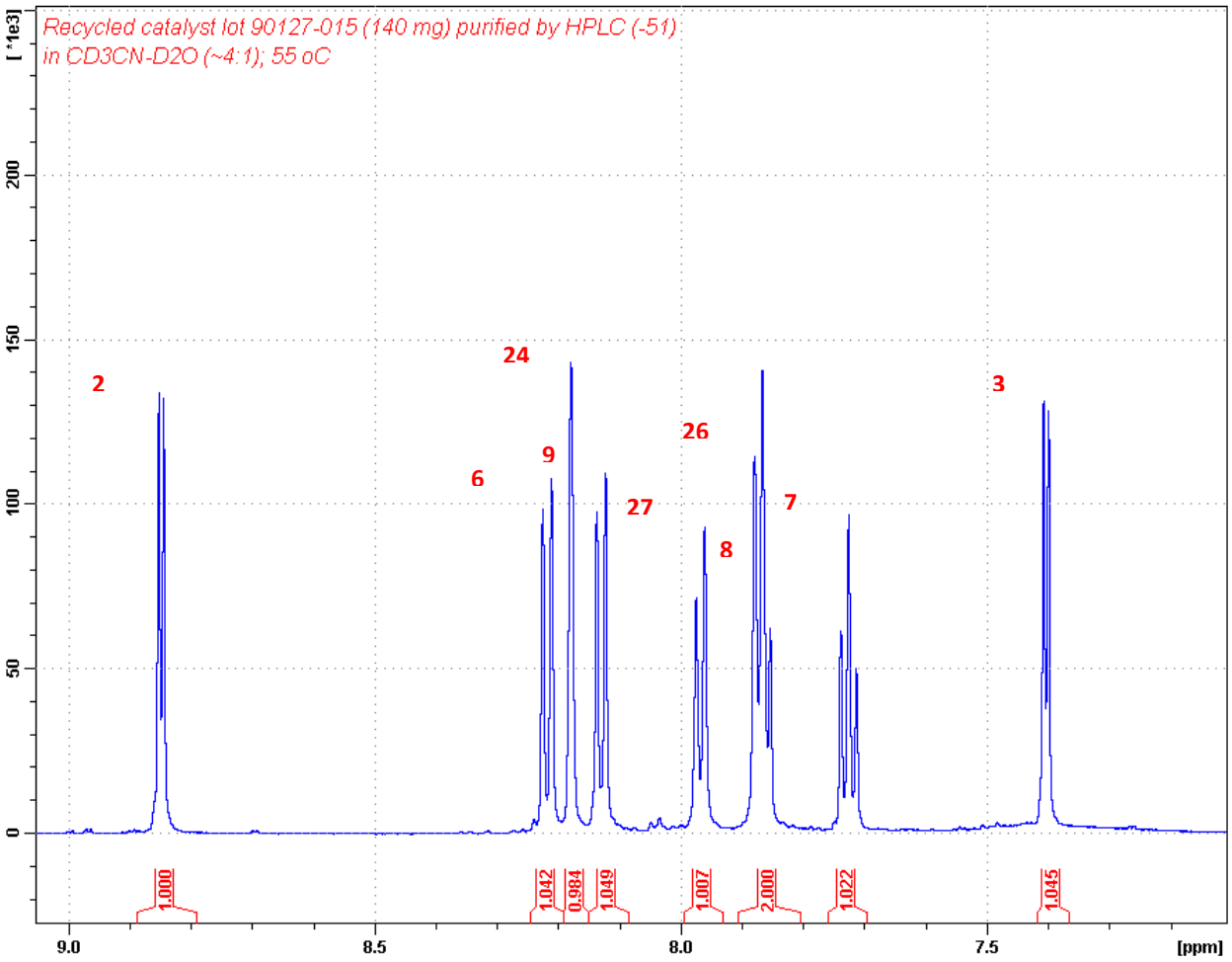


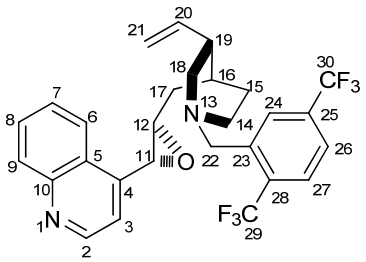


8

Partial ^{1}H NMR of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C

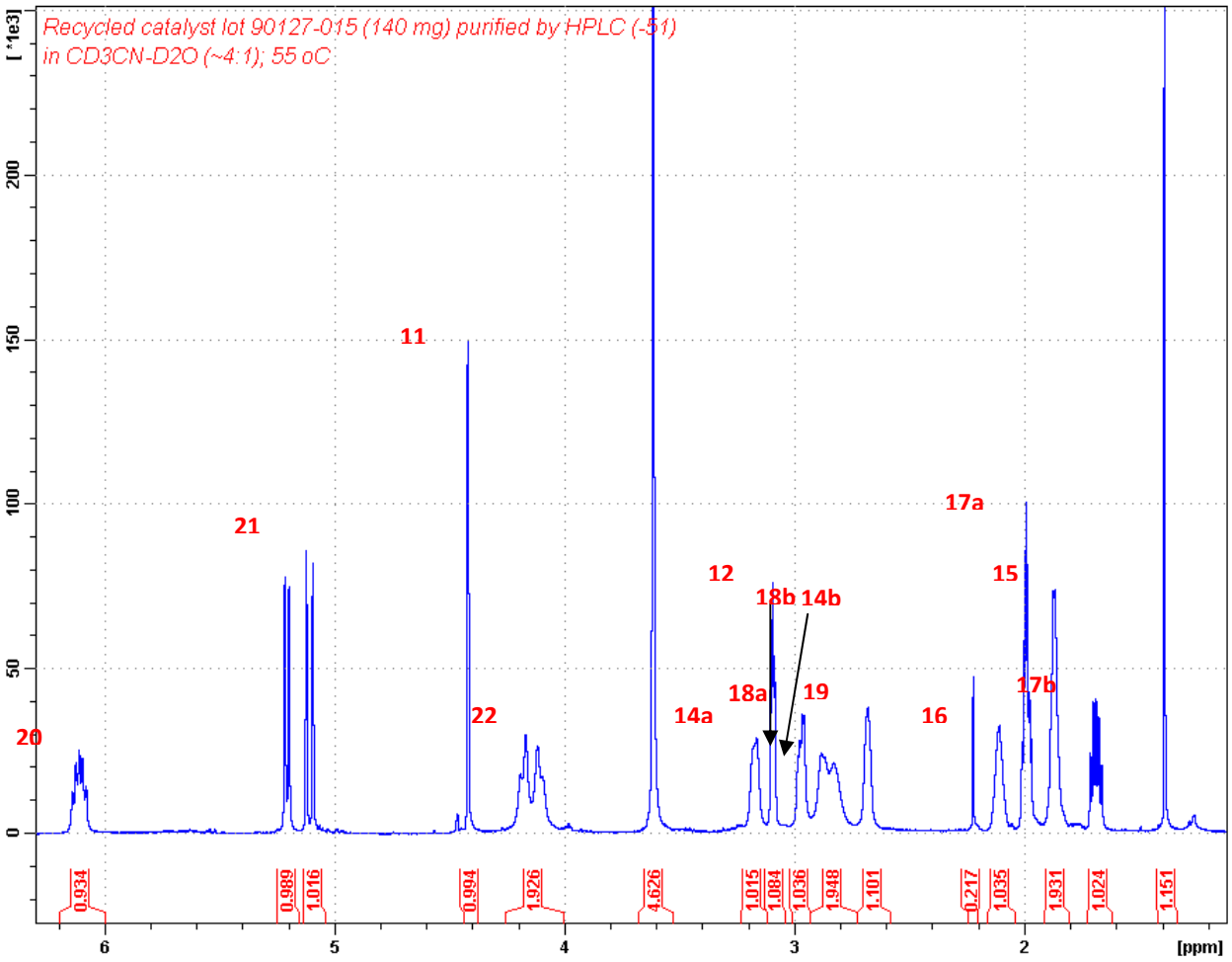


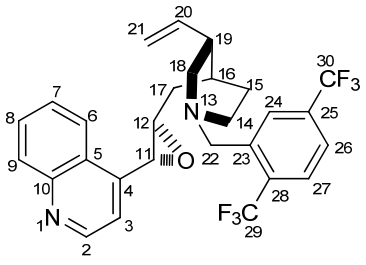


8

Partial ^{1}H NMR of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C

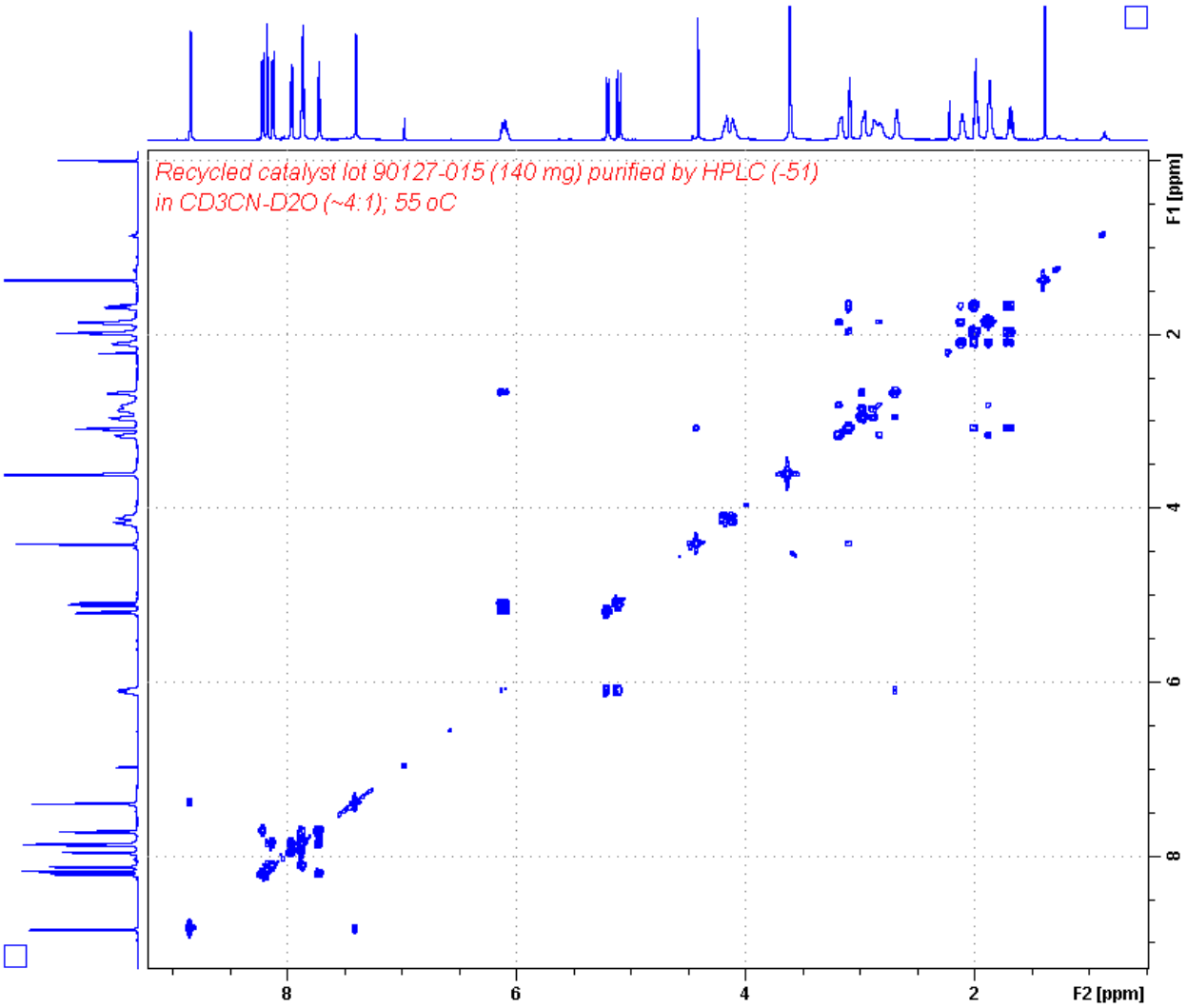


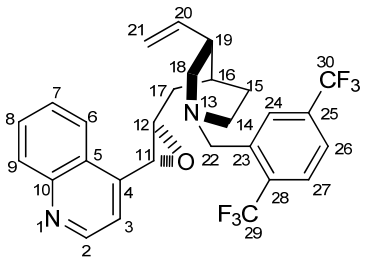


8

COSY of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C

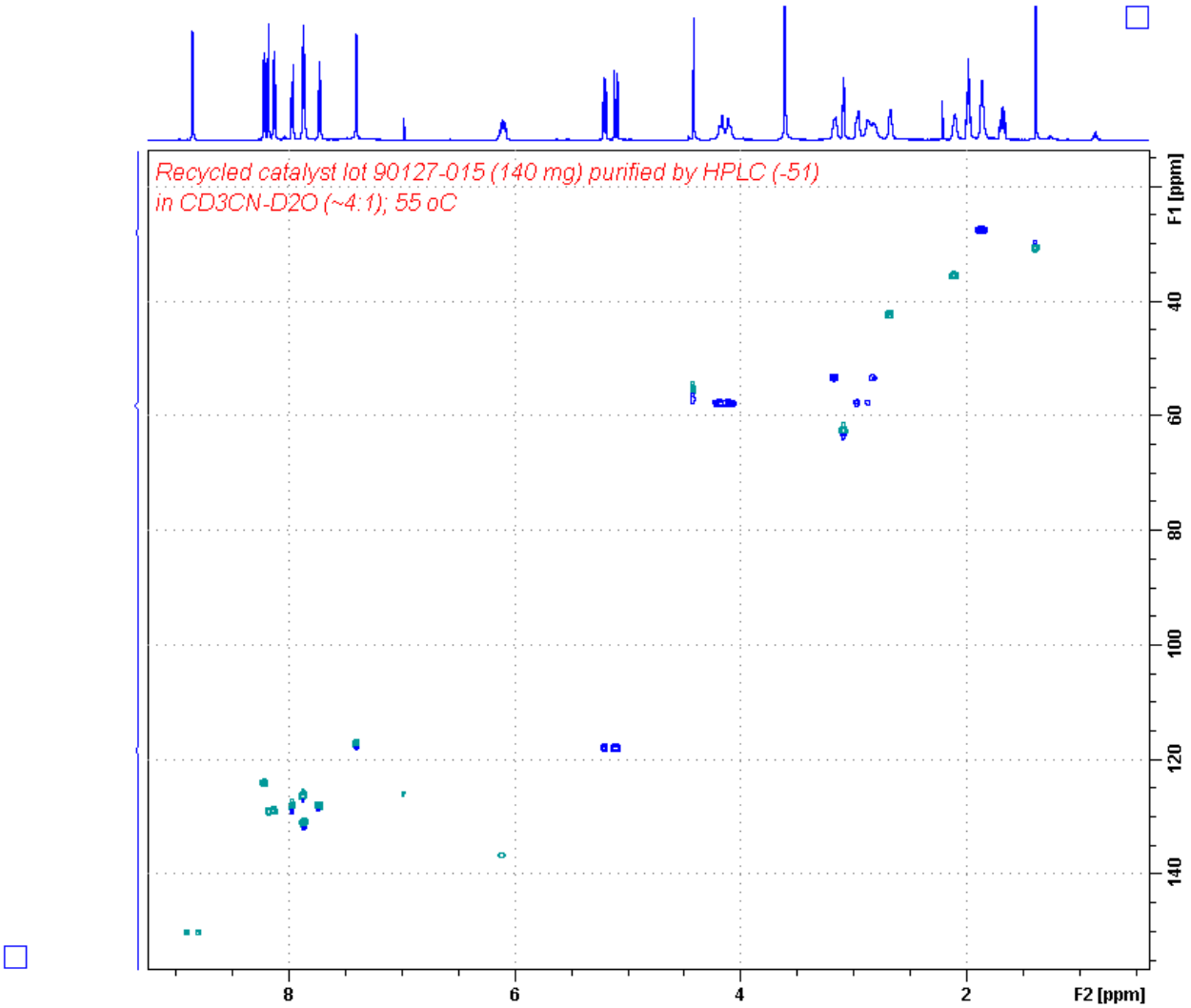


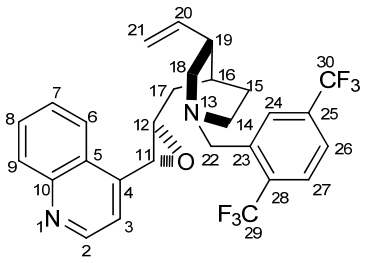


8

Edited HSQC of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C

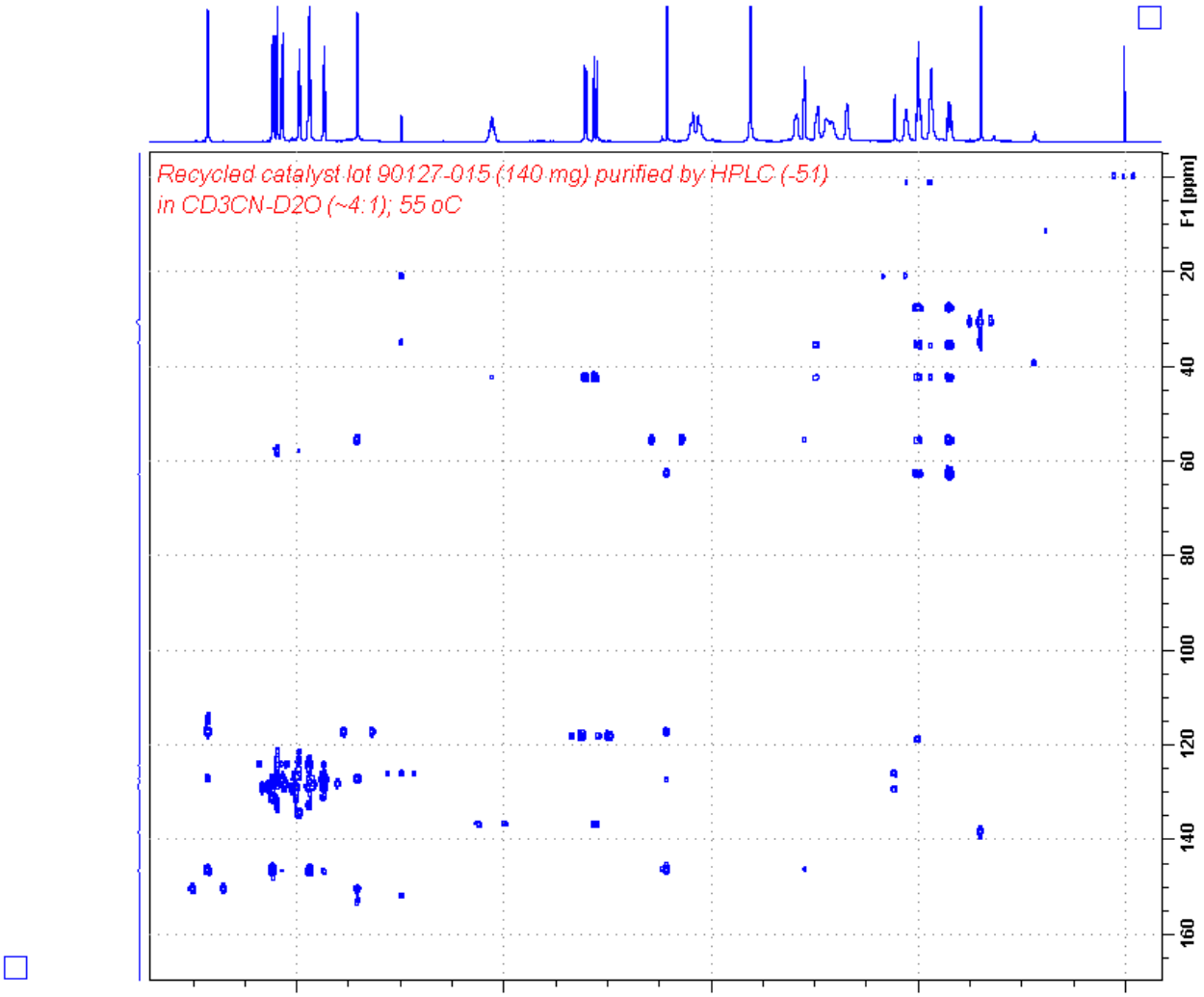


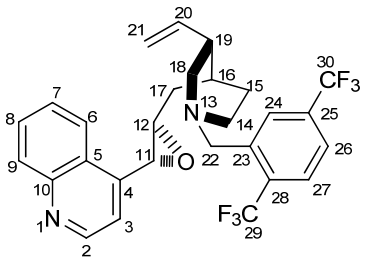


8

^{1}H-^{13}C HMBC of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C

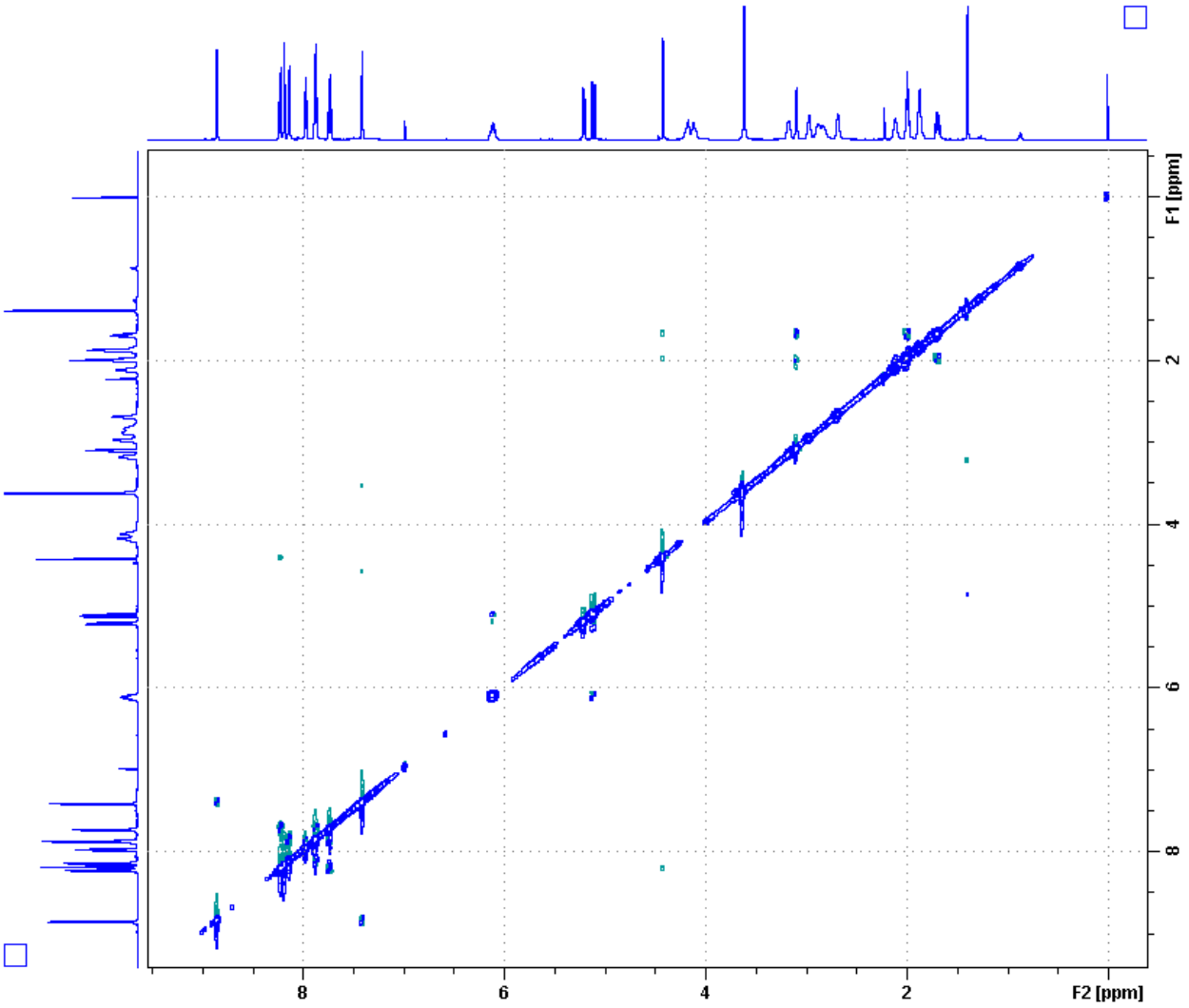


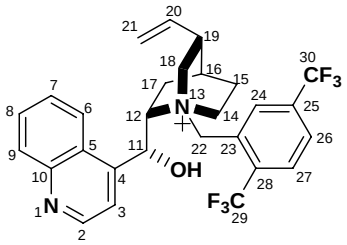


8

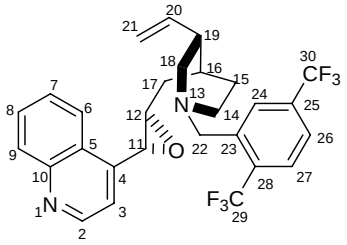
ROESY of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C





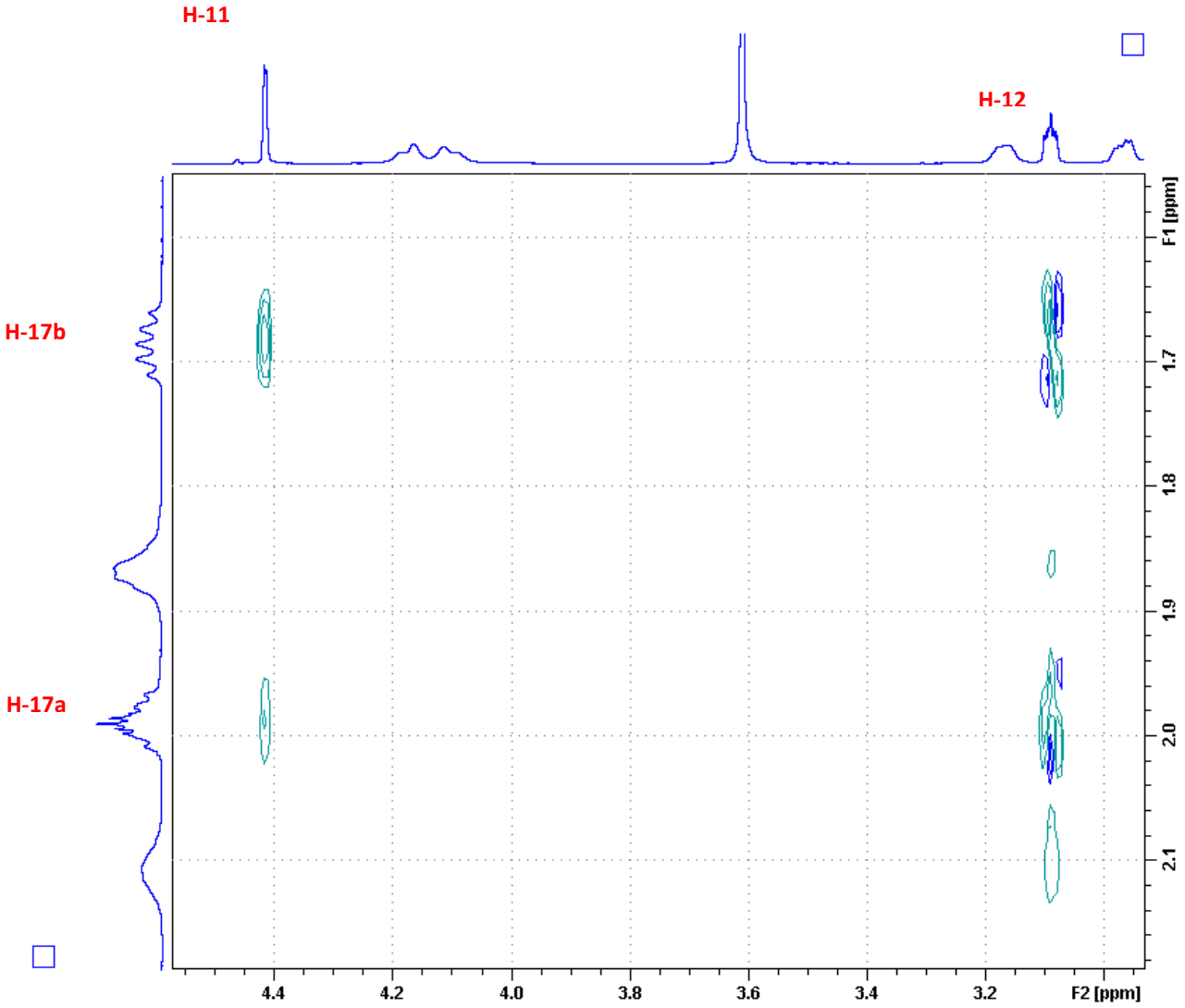
Chemical Formula: $C_{28}H_{27}F_6N_2O^+$
Exact Mass: 521.2022
Catalyst

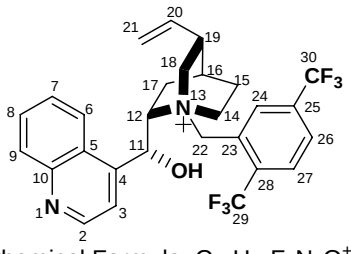


Chemical Formula: $C_{28}H_{26}F_6N_2O$
Exact Mass: 520.1949
Structure determined for the recycled catalyst

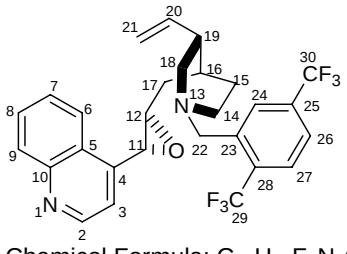
Partial ROESY of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C





Chemical Formula: $C_{28}H_{27}F_6N_2O^+$
Exact Mass: 521.2022
Catalyst

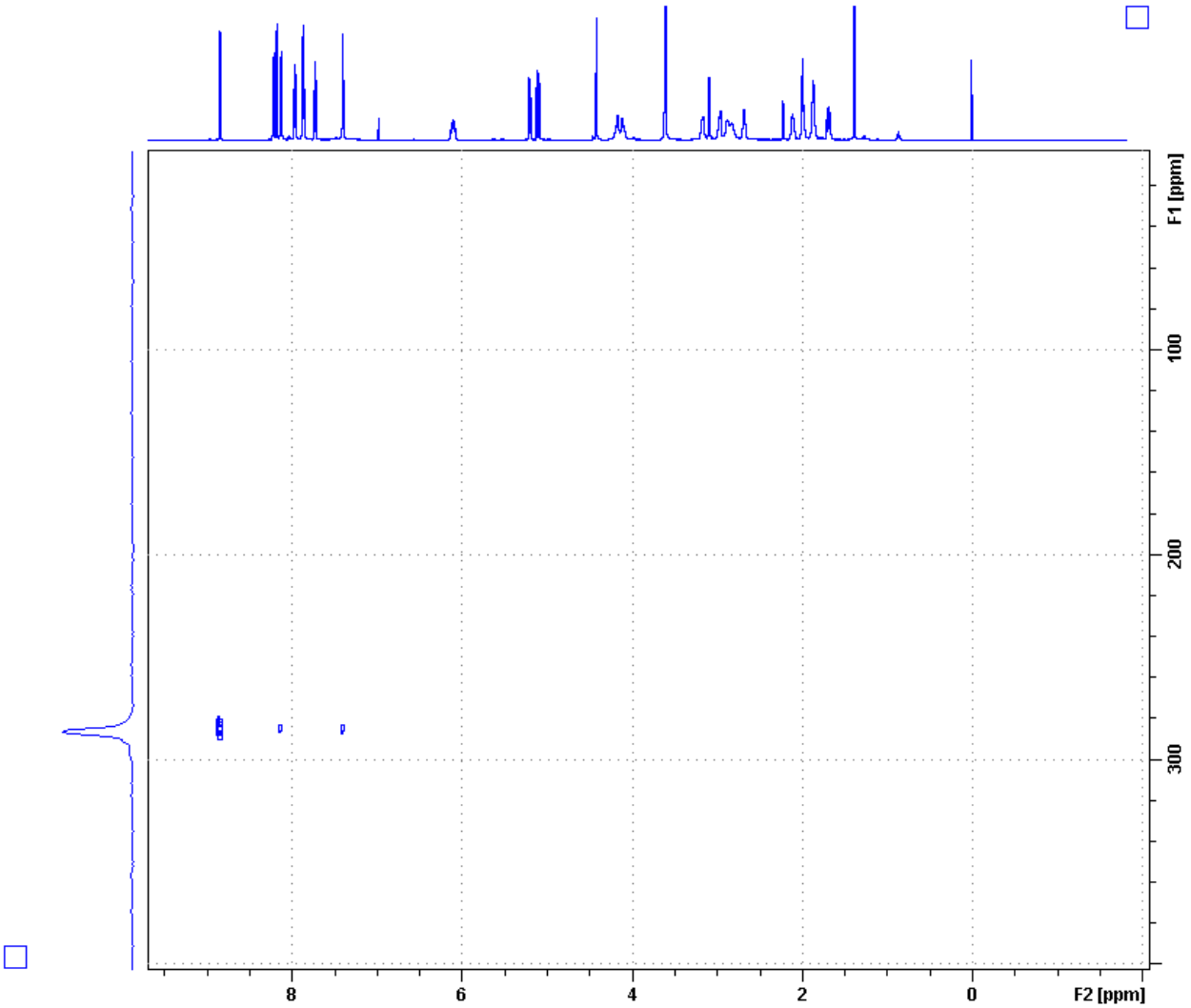


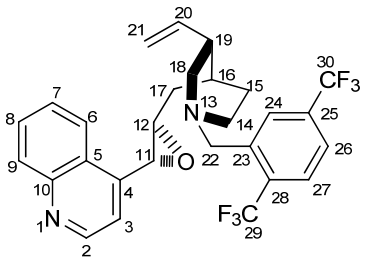
Chemical Formula: $C_{28}H_{26}F_6N_2O$
Exact Mass: 520.1949
Structure determined for the recycled catalyst

Note: The above key ROESY correlations determined the epoxy is in an orientation shown as above.

^{1}H-^{15}N HMBC of recycled catalyst isolated by HPLC (lot 86376-051-01)

in CD_3CN-D_2O (~4:1) at 55 °C





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