

Supporting Information

for

Recyclable fluororous cinchona alkaloid ester as a chiral promoter for asymmetric fluorination of β -ketoesters

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Email: Wen-Bin Yi - yiwenbin@mail.njust.edu.cn; Wei Zhang - wei2.zhang@umb.edu

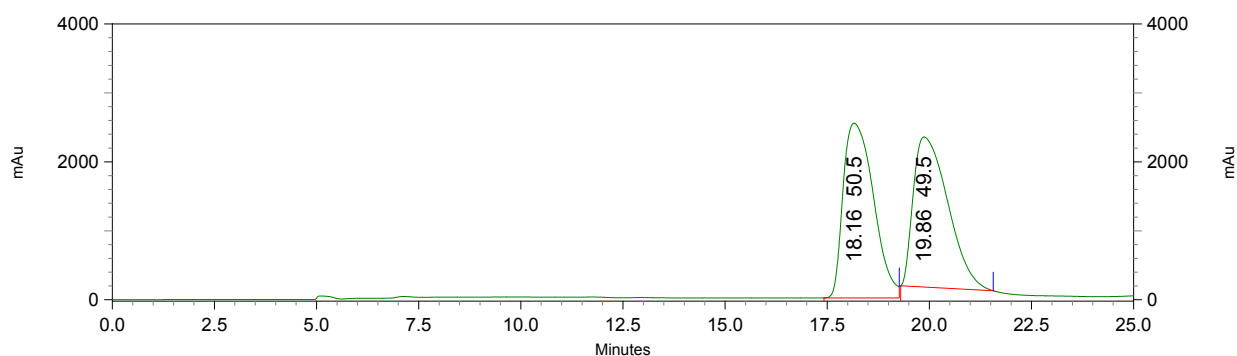
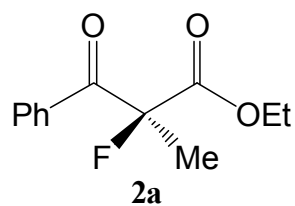
*Corresponding author

Chiral HPLC chromatograms for fluorination products 2a–i. LC–MS, NMR spectra for fluorination products 2a–i and cinchona alkaloid derivatives C-1, C-2, C-3 and C-6. LC–MS spectra for 2h and HRMS spectra for C-1.

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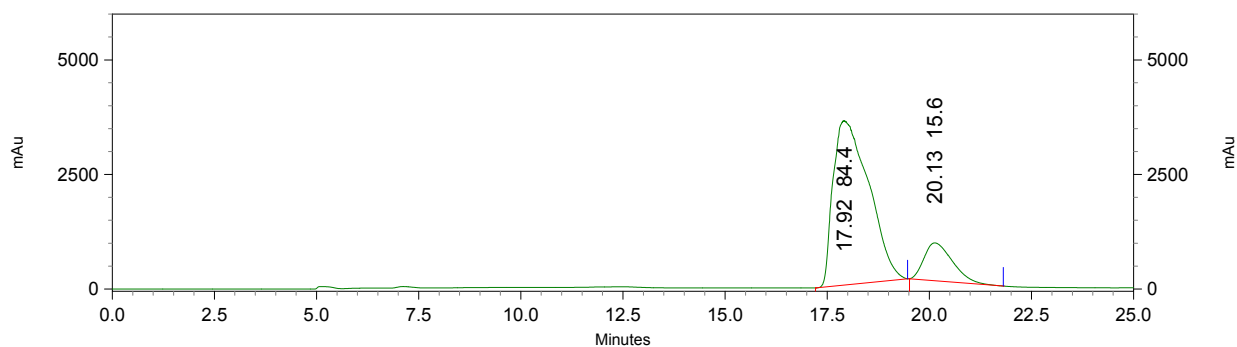
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4. NMR spectra of catalysts and fluorination products.....	S13

1. HPLC Chromatogram of Fluorination Products



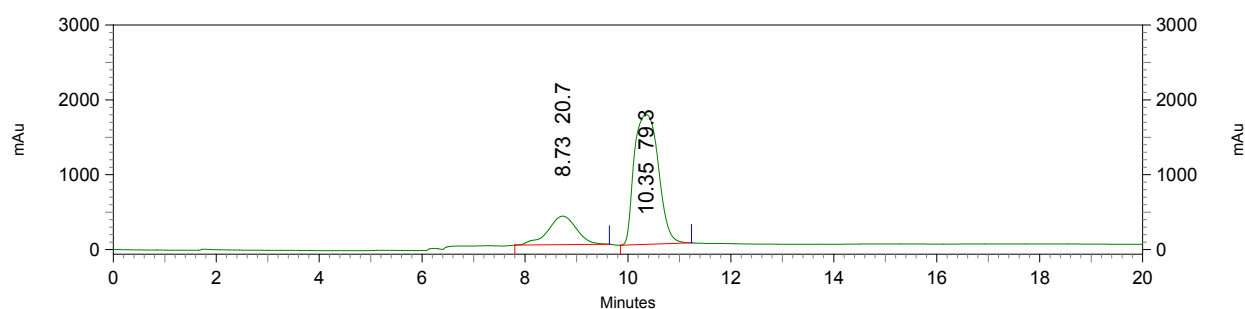
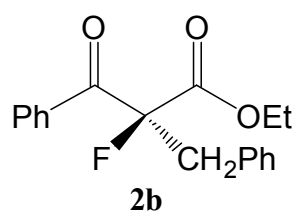
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19.864	128451886	49.53	2176088	46.19
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Racemic sample



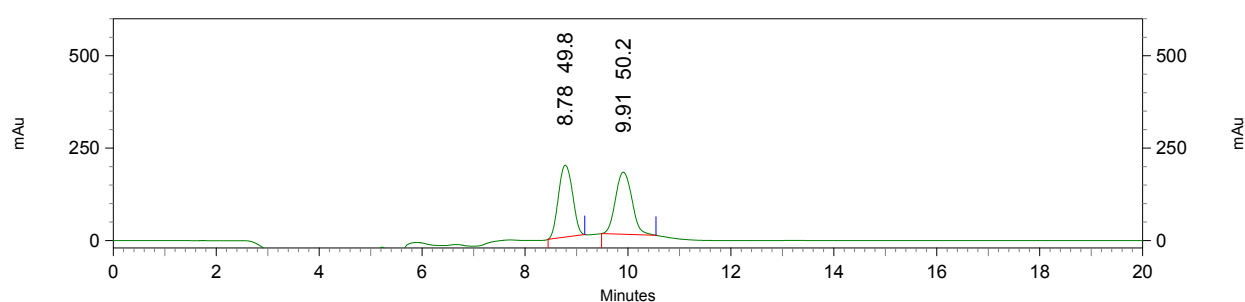
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17.924	217622833	84.43	3586151	81.27
20.132	40123778	15.57	826271	18.73
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Chiral sample



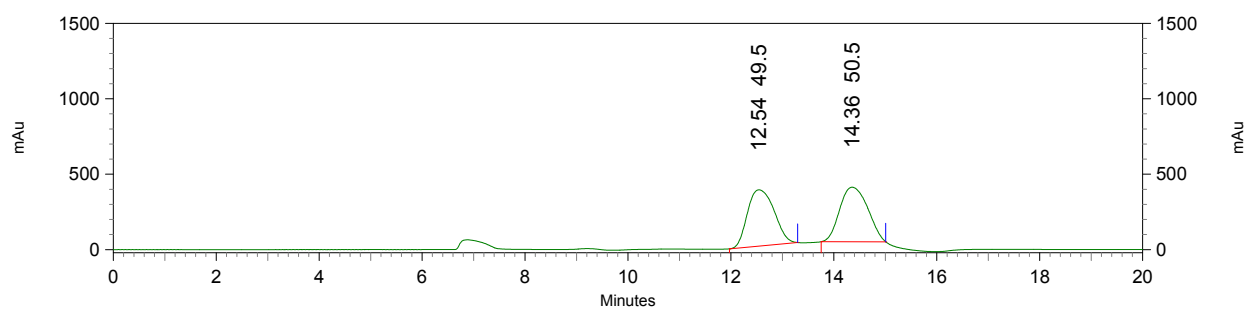
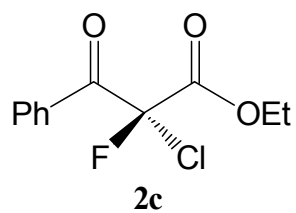
Retention Time	Area	Area %	Height	Height %
8.732	14775829	20.68	381327	18.03
10.352	56661484	79.32	1733272	81.97
Totals	71437313	100.00	2114599	100.00

Chiral sample



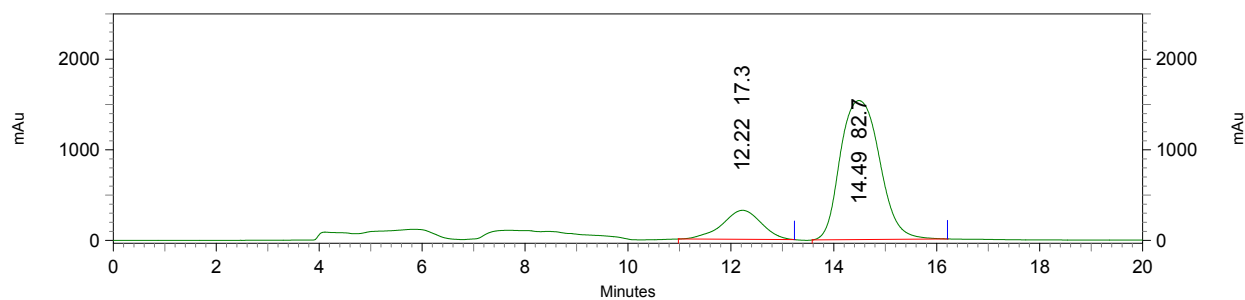
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9.912	3735561	50.25	168094	46.37
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Racemic sample



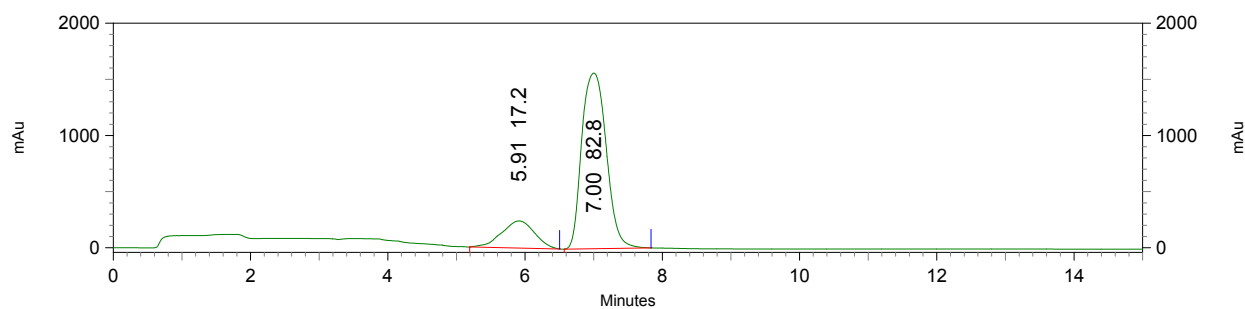
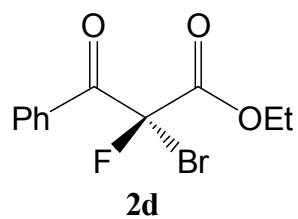
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12.544	13445373	49.54	373360	50.78
14.356	13692870	50.46	361825	49.22
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Racemic sample



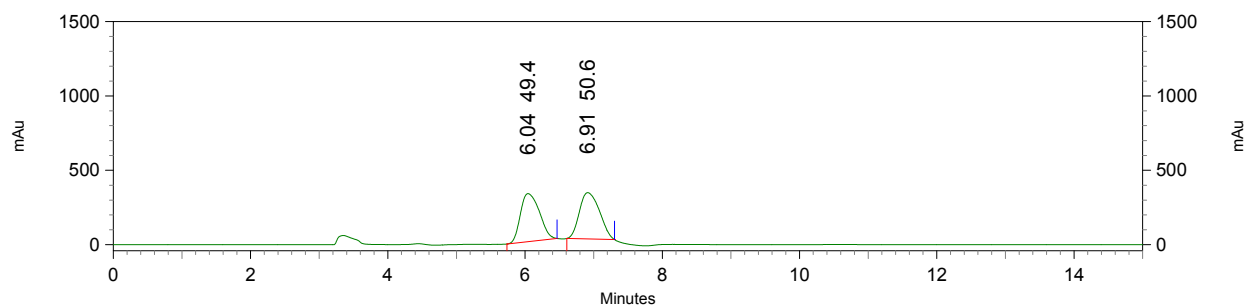
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14.492	81483764	82.73	1534387	82.72
Totals	98490813	100.00	1854812	100.00

Chiral sample



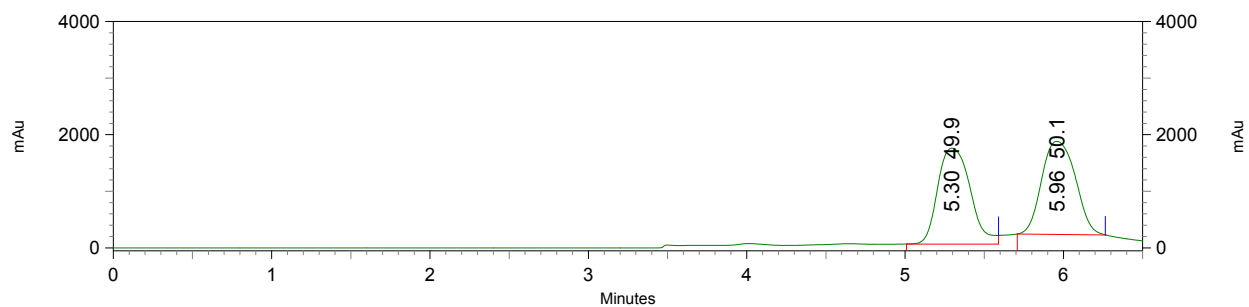
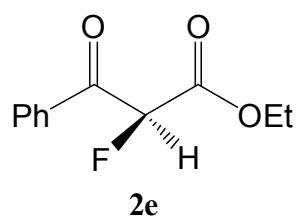
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5.912	8053638	17.15	241788	13.39
7.004	38894427	82.85	1563960	86.61
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Chiral sample



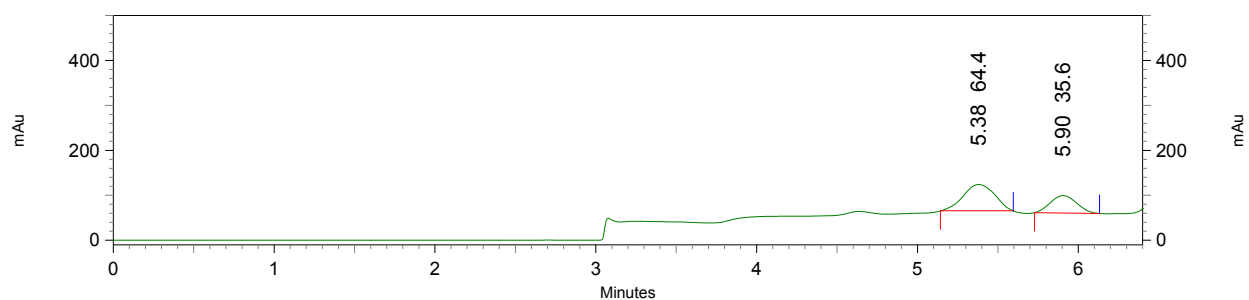
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6.044	6190037	49.40	323087	50.94
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Racemic sample



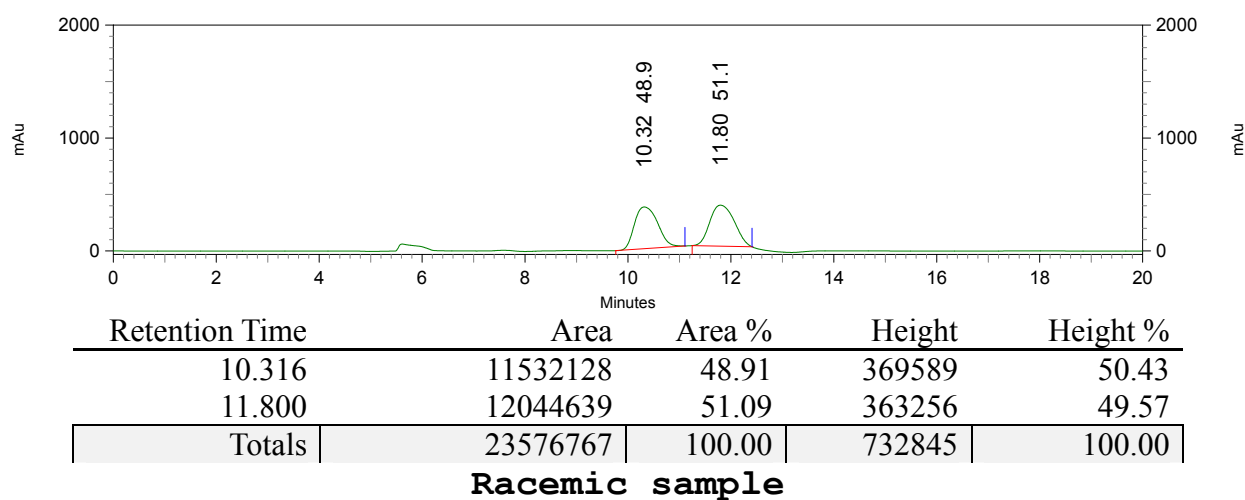
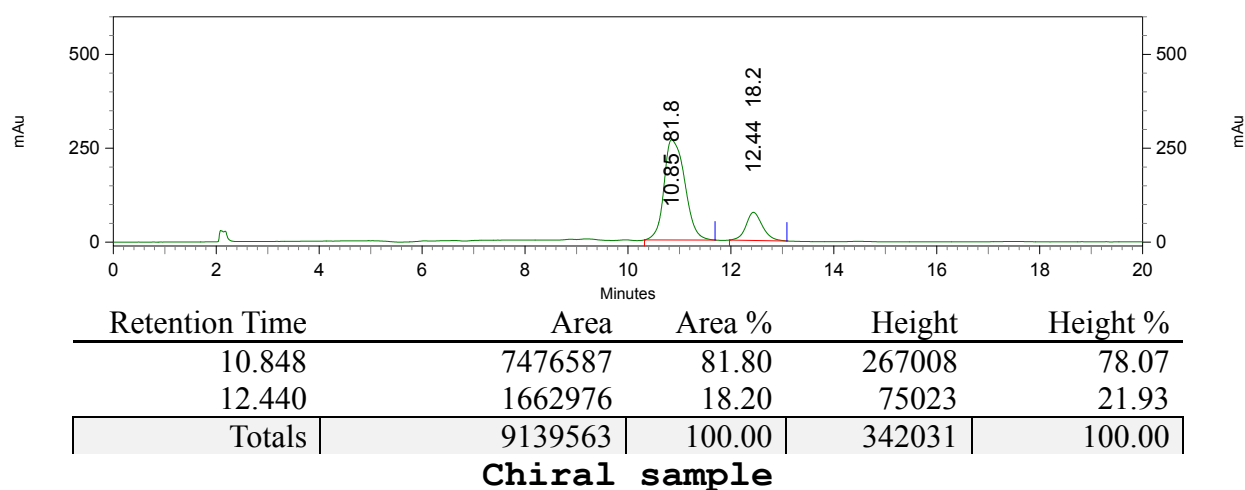
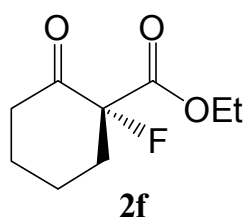
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5.296	24226523	49.93	1693699	50.77
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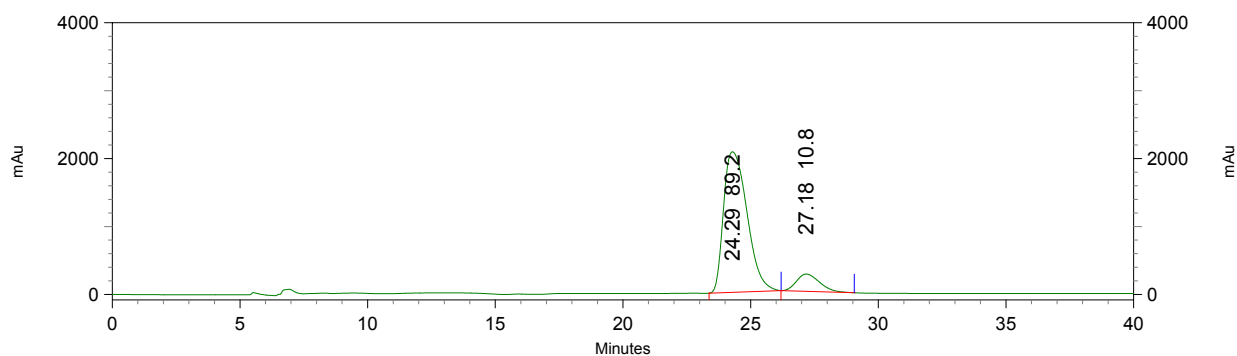
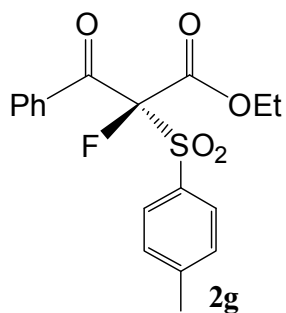
Racemic sample



Retention Time	Area	Area %	Height	Height %
5.380	797907	64.43	58574	60.19
5.904	440552	35.57	38740	39.81
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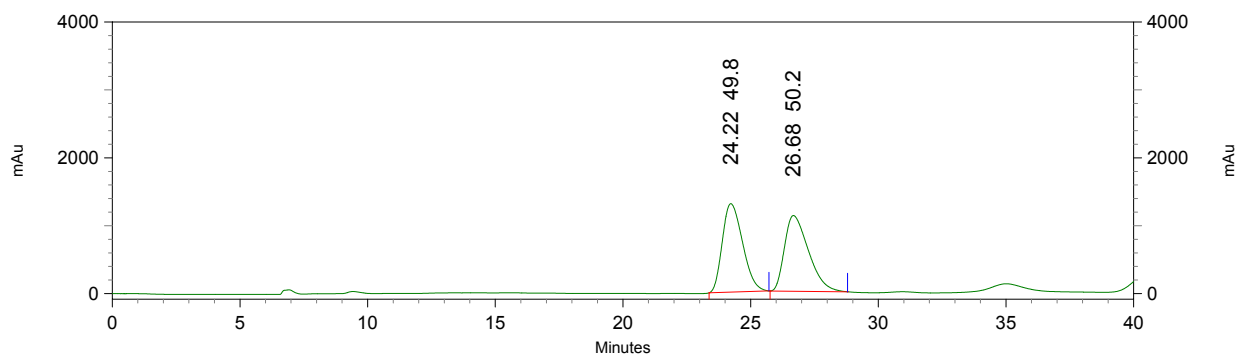
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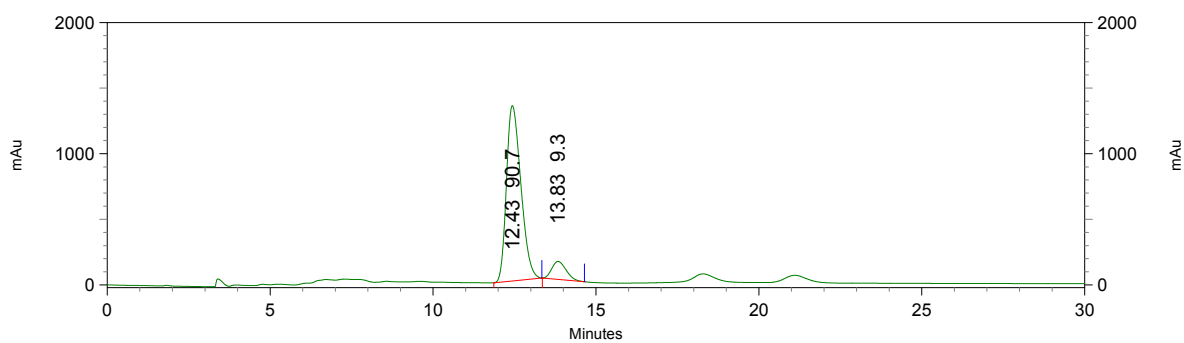
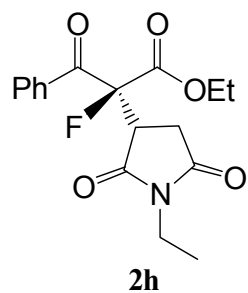
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24.288	132223497	89.19	2069101	89.03
27.176	16028095	10.81	254896	10.97
Totals	148251592	100.00	2323997	100.00

Chiral sample



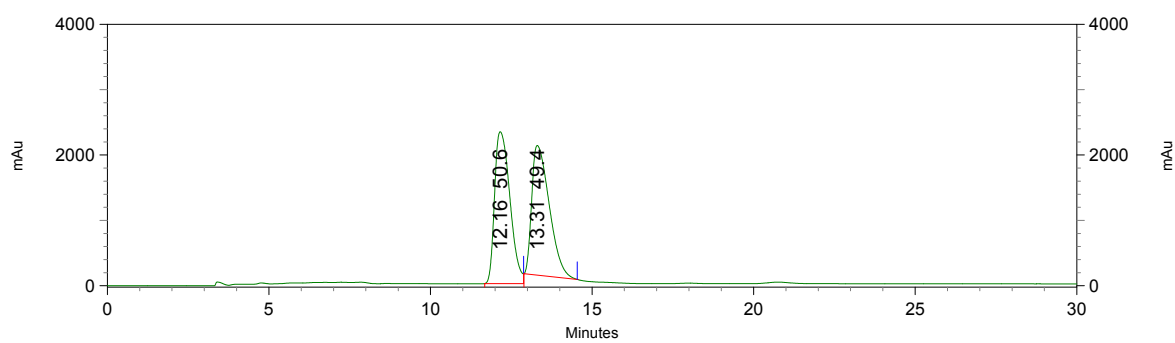
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24.224	71970053	49.76	1302776	53.90
26.676	72665895	50.24	1114459	46.10
Totals	144635948	100.00	2417235	100.00

Racemic sample



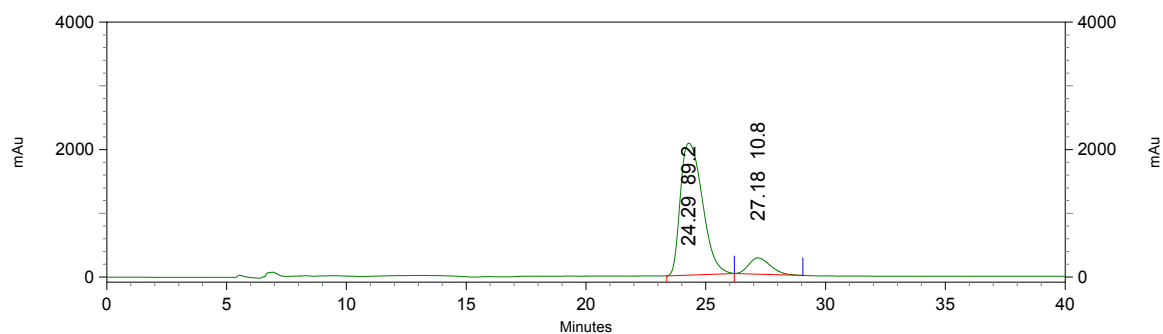
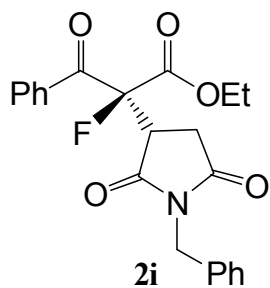
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13.832	4214965	9.30	138013	9.36
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Chiral sample



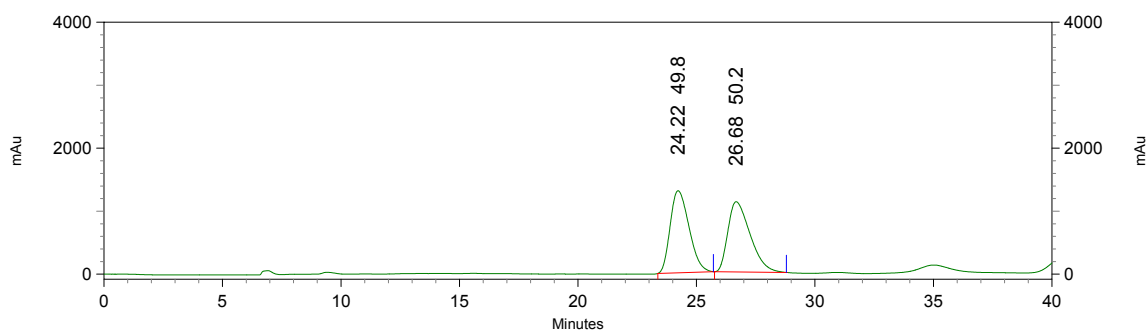
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13.308	74742615	49.44	1982343	46.06
Totals	151172090	100.00	4304190	100.00

Racemic sample



Retention Time	Area	Area %	Height	Height %
24.288	132223497	89.19	2069101	89.03
27.176	16028095	10.81	254896	10.97
Totals	148251592	100.00	2323997	100.00

Chiral sample



Retention Time	Area	Area %	Height	Height %
24.224	71970053	49.76	1302776	53.90
26.676	72665895	50.24	1114459	46.10
Totals	144635948	100.00	2417235	100.00

Racemic sample

2. HRMS of C-1

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 150.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

300 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-150 H: 0-200 N: 1-5 O: 1-5 F: 12-13

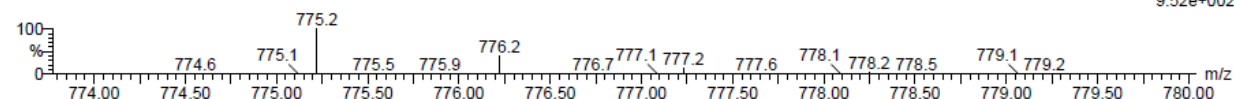
Kadam, Asha, (2)F-QN University of Illinois, SCS, Mass Spectrometry Lab

Qtof_38759 46 (3.293) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (46:48)

Q-tof UE521

1: TOF MS ES+

9.52e+002



Minimum: -1.5
Maximum: 5.0 10.0 150.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
775.2214	775.2205	0.9	1.2	14.5	7.5	C35 H32 N2 O3 F13
	775.2194	2.0	2.6	18.5	6.4	C38 H31 N2 O2 F12
	775.2165	4.9	6.3	10.5	12.9	C30 H32 N4 O5 F13
	775.2154	6.0	7.7	14.5	8.5	C33 H31 N4 O4 F12

Kadam, Asha, (2)F-QN

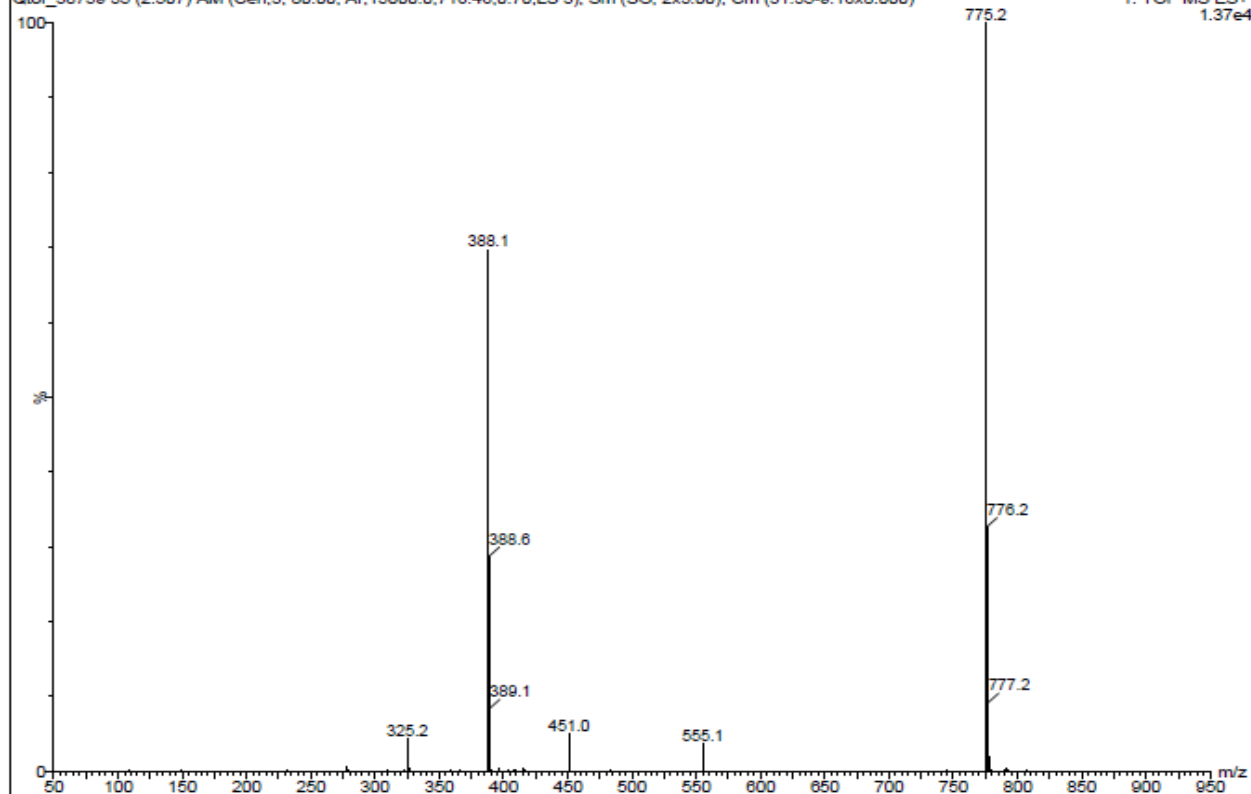
University of Illinois, SCS, Mass Spectrometry Lab

Q-tof UE521

Qtof_38759 35 (2.507) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (31:35-9:16x8.000)

1: TOF MS ES+

1.37e4



3. LC-MS spectra of product 2h

Print of all graphic windows

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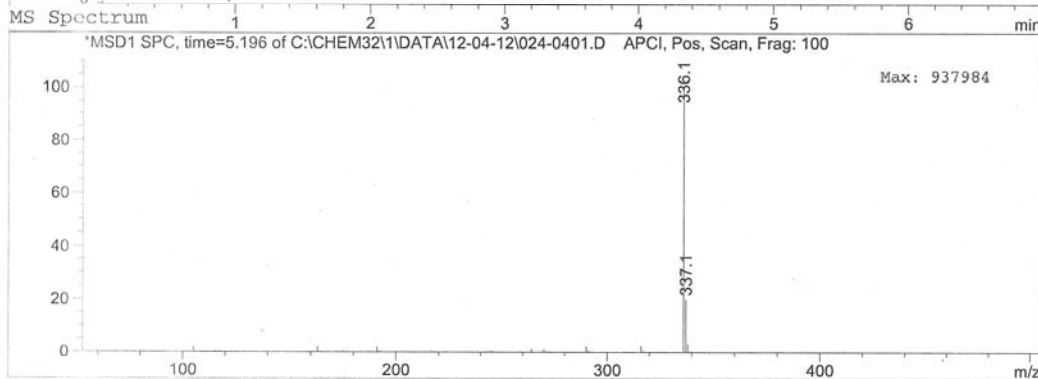
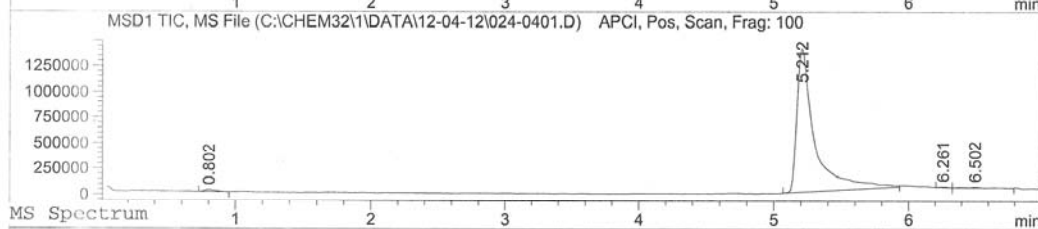
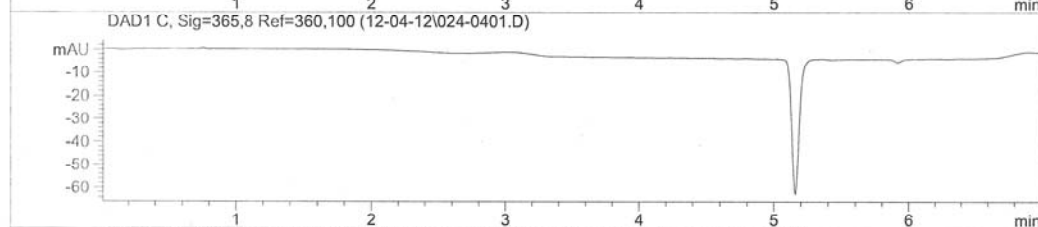
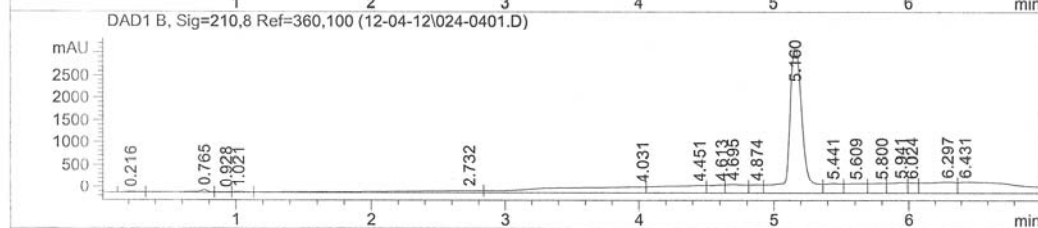
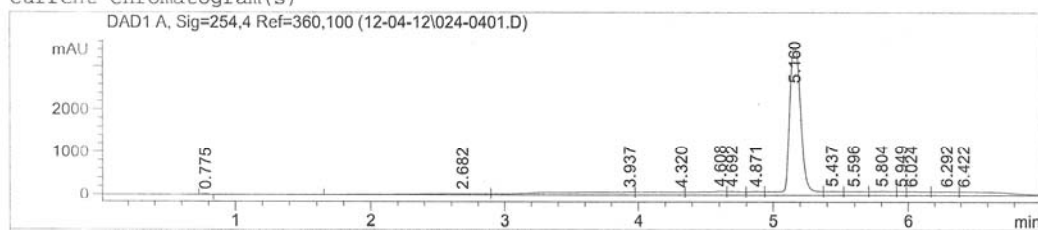
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	Inj Volume : 4 µl

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Last changed : 3/23/2012 1:40:38 PM by Asha

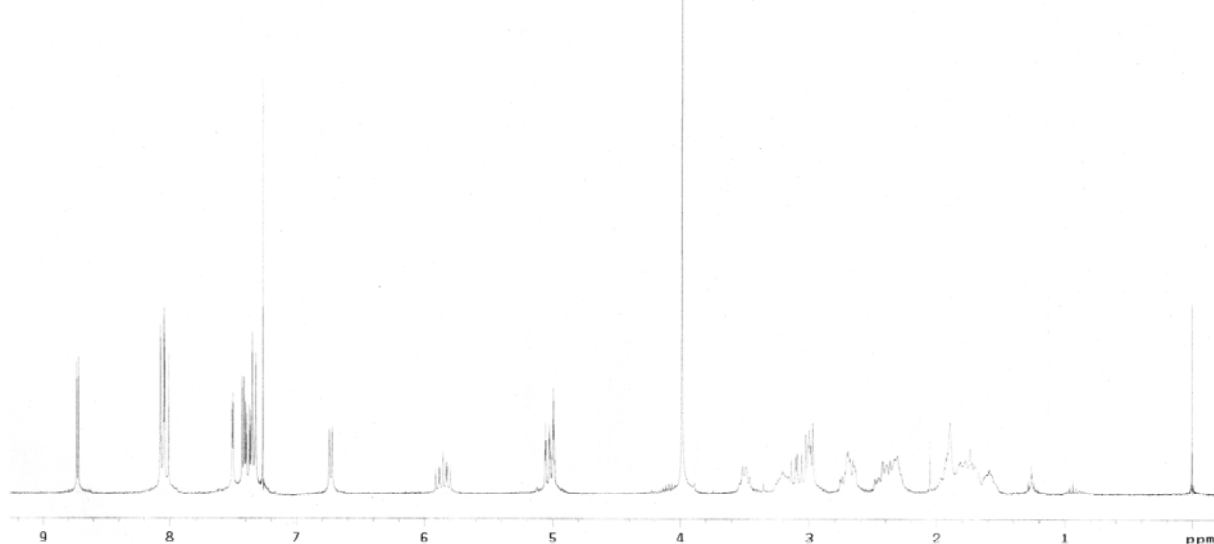
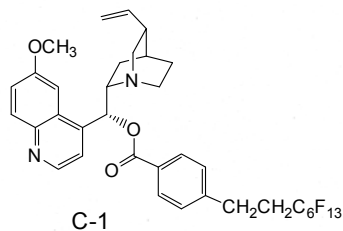
Current Chromatogram(s)



4. NMR spectra of catalysts and products

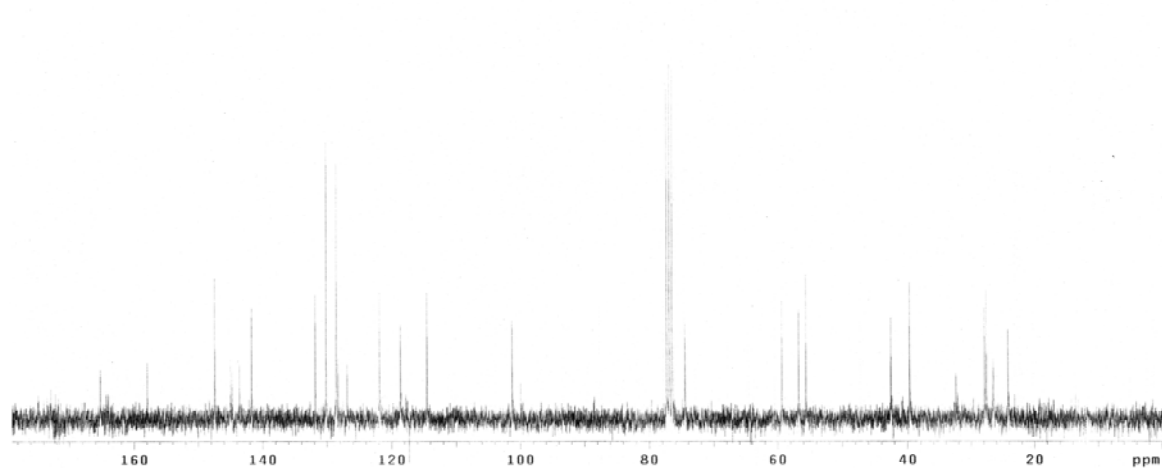
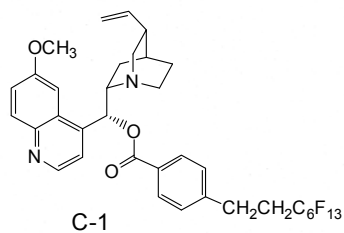
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 Acq. time 1.996 sec
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 Total time 0 min, 49 sec



13C OBSERVE

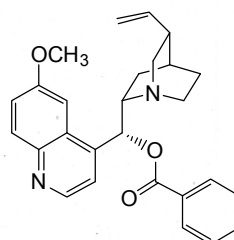
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 2000 repetitions
 OBSERVE C13, 75.4669004 MHz
 DECOUPLE H1, 300.1261260 MHz
 Power 36 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
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 FT size 131072
 Total time 1 hr, 10 min, 25 sec



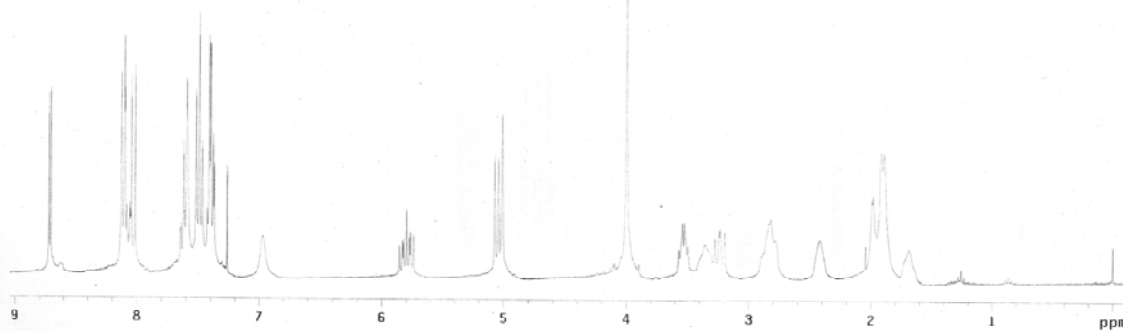
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 Total time 0 min, 49 sec



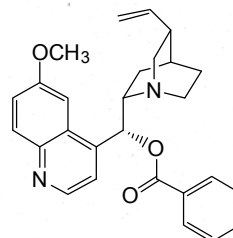
C-2



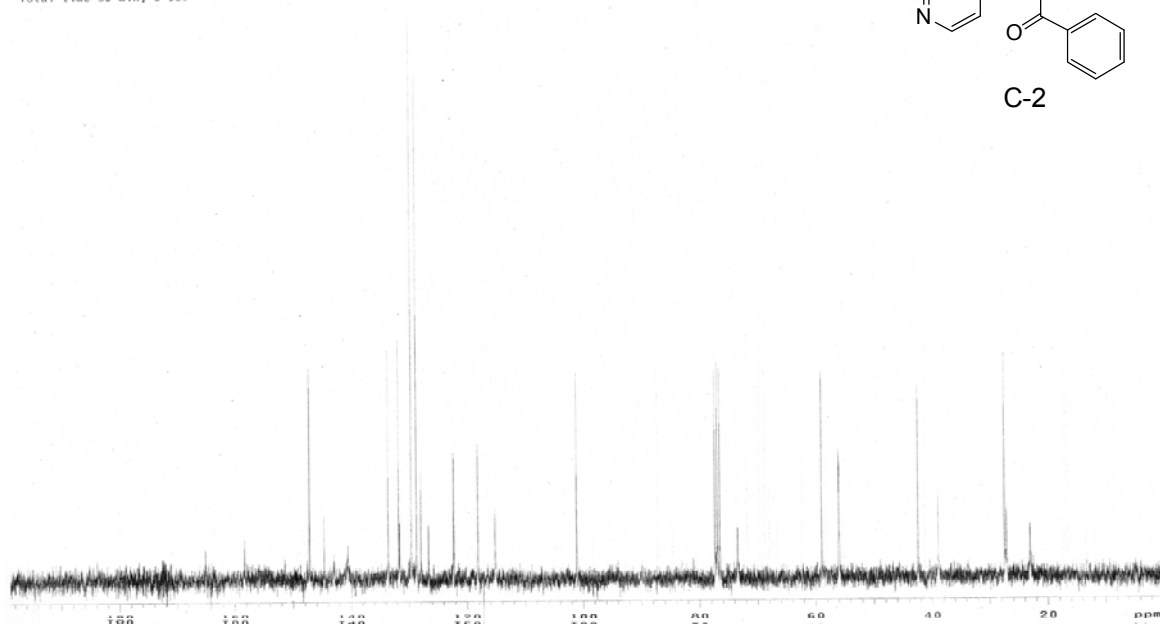
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 Total time 36 min, 3 sec



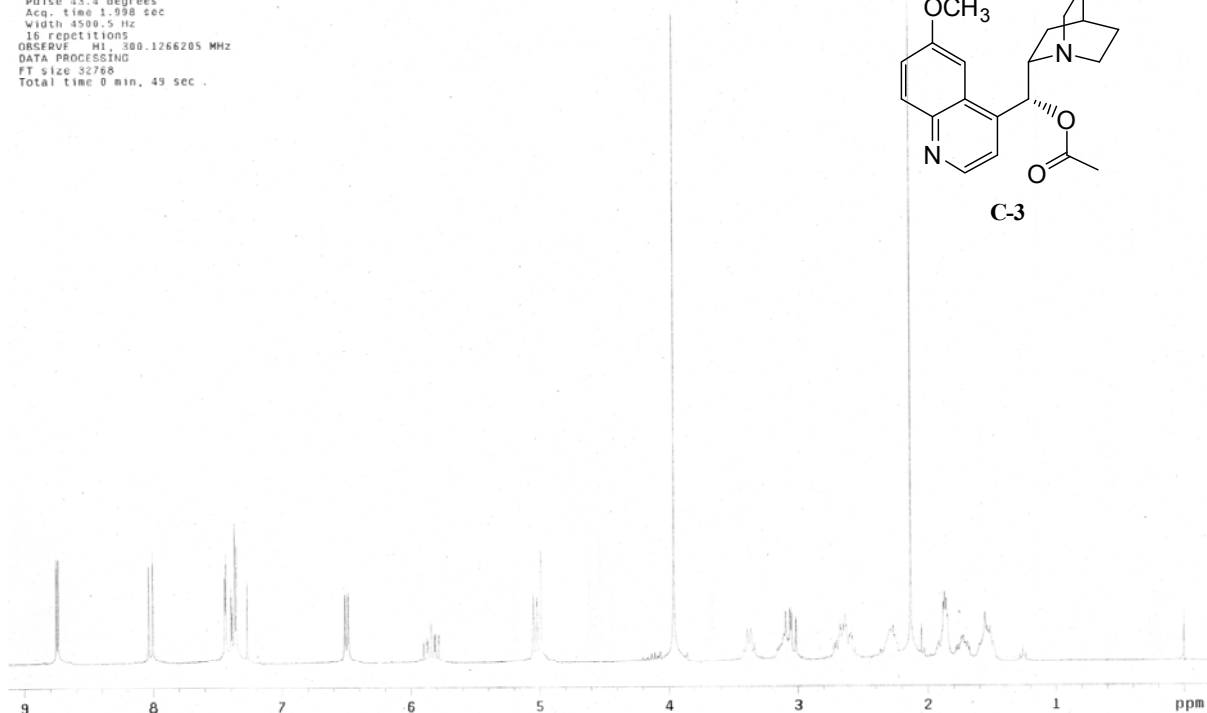
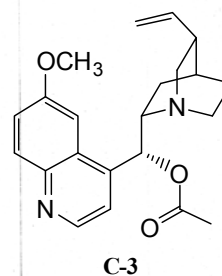
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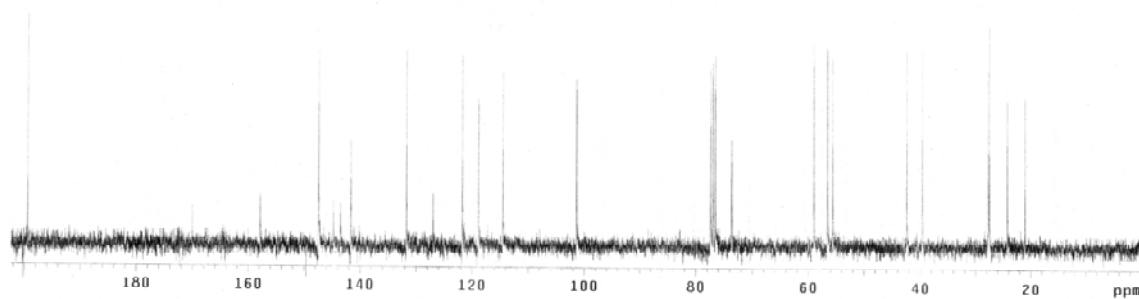
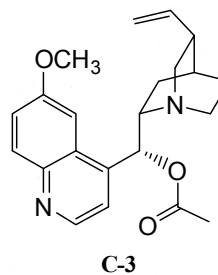
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Width 4500.5 Hz
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OBSERVE H1, 300.1266205 MHz
DATA PROCESSING
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13C OBSERVE

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Ambient temperature
GEMINI-300MS "Mighty300"

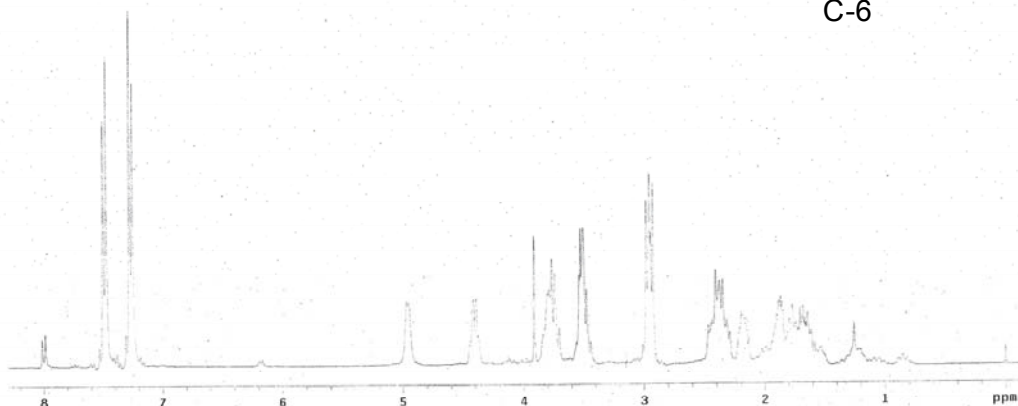
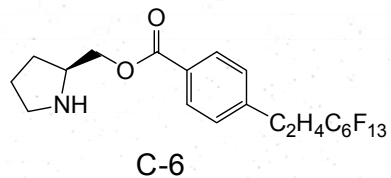
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Power 16 dB
continuously on
WALTZ-16 MODULATED
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec



STANDARD 1H OBSERVE

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Ambient temperature
GEMINI-3000S "Mighty300"

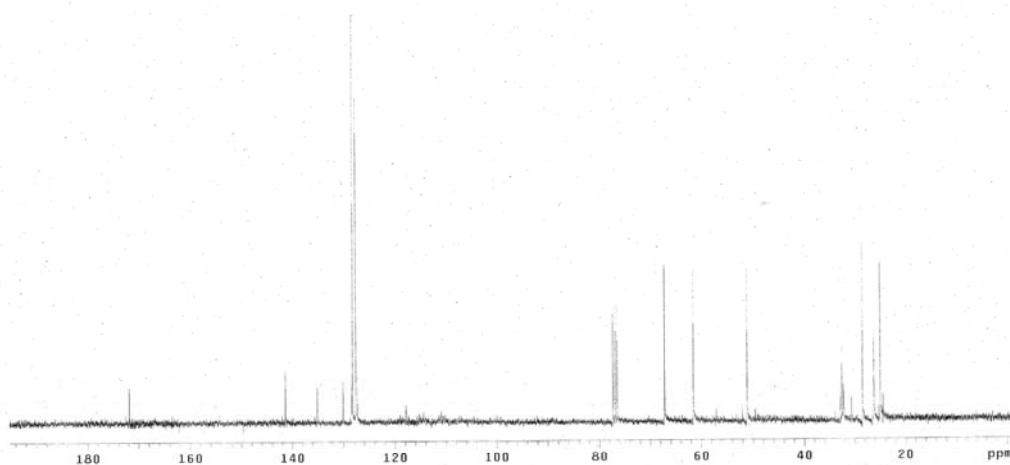
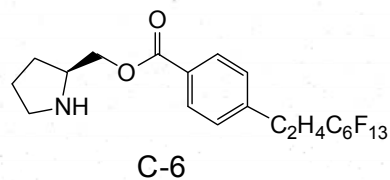
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13C OBSERVE

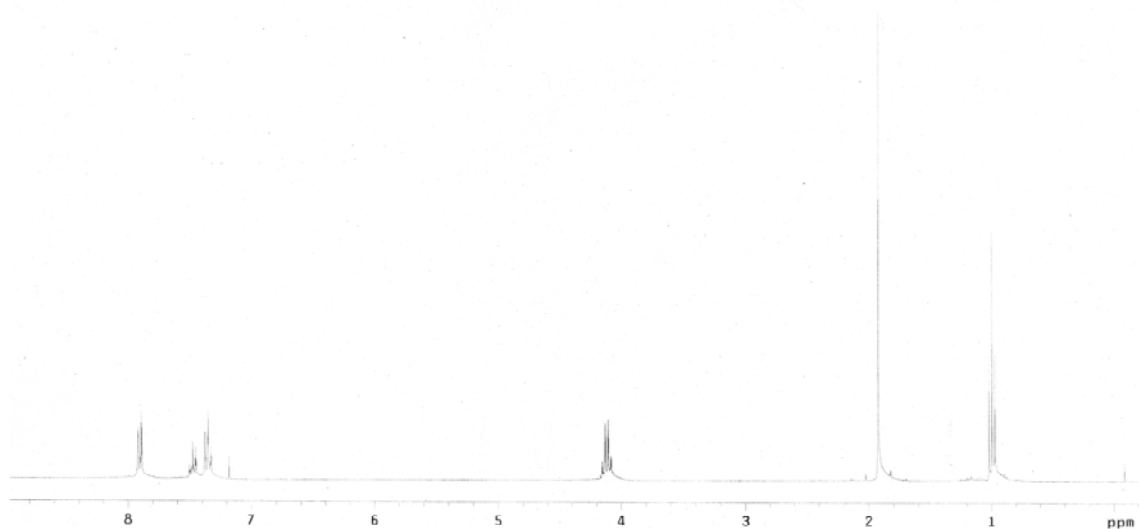
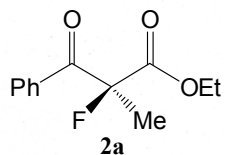
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Line broadening 1.0 Hz
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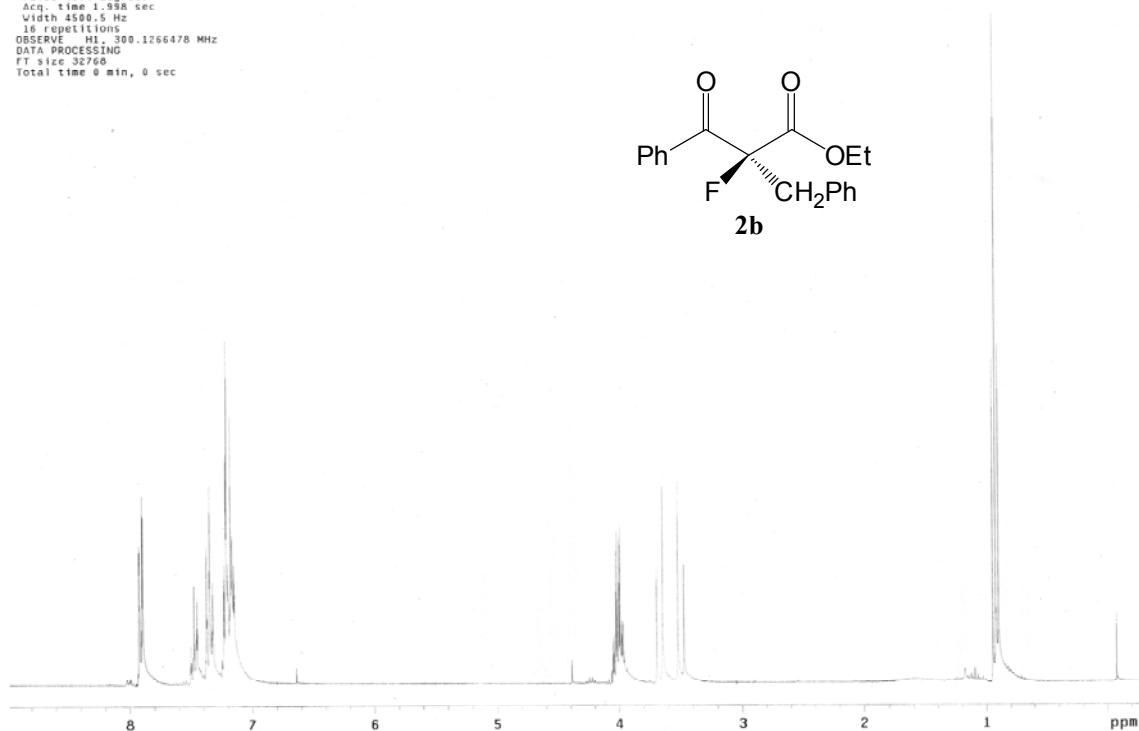
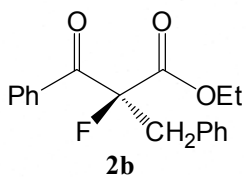
STANDARD 1H OBSERVE

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Width 4500.5 Hz
16 repetitions
OBSERVE M1, 300.1266478 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



STANDARD 1H OBSERVE

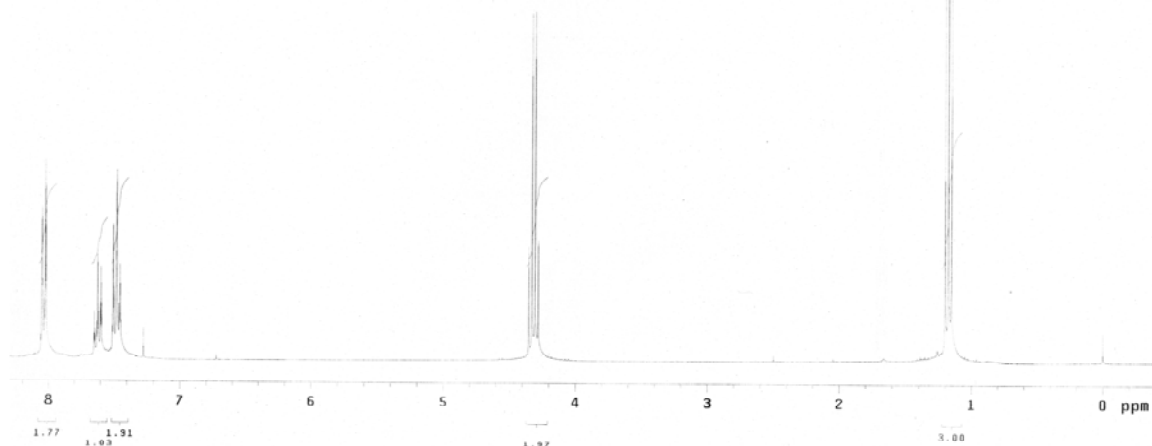
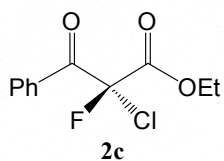
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
GEMINI-300BB "Mighty300"
Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE M1, 300.1266478 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-3000B "Mighty300"

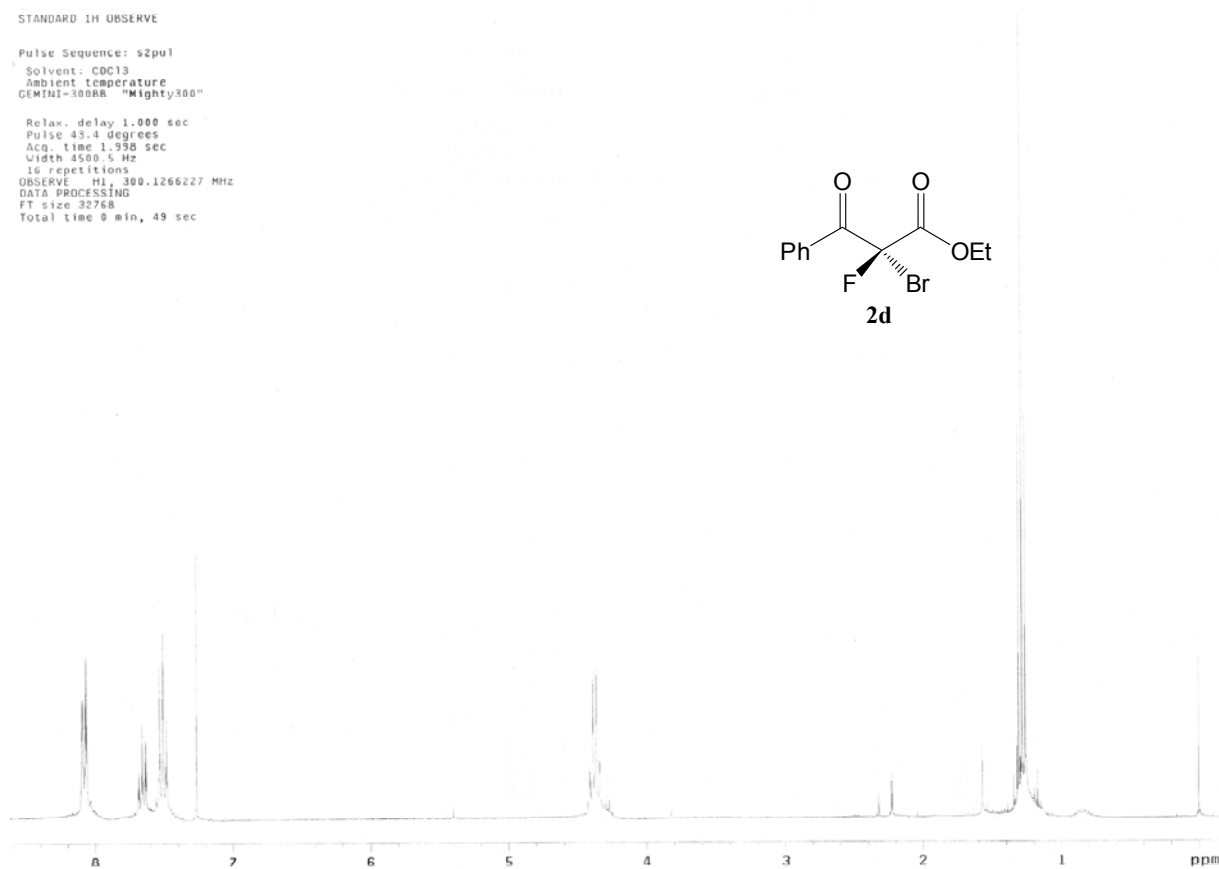
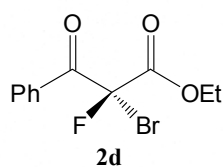
Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266199 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-3000B "Mighty300"

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266227 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "Mighty300"

Relax. delay 1.000 sec

Pulse 43.4 degrees

Acq. time 1.998 sec

Width 4500.5 Hz

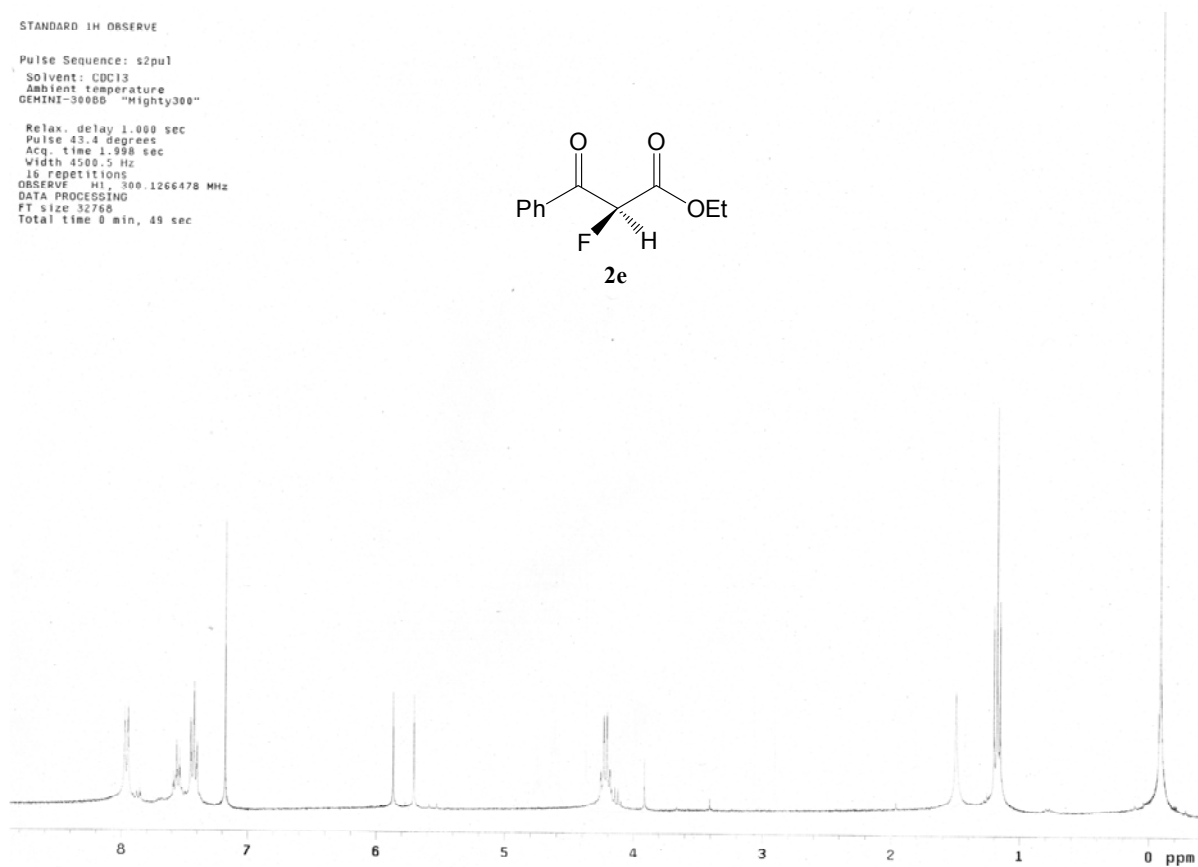
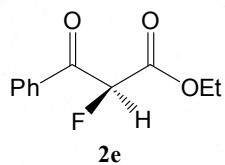
16 repetitions

OBSERVE H1, 300.1266478 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 49 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "Mighty300"

Relax. delay 1.000 sec

Pulse 43.4 degrees

Acq. time 1.998 sec

Width 4500.5 Hz

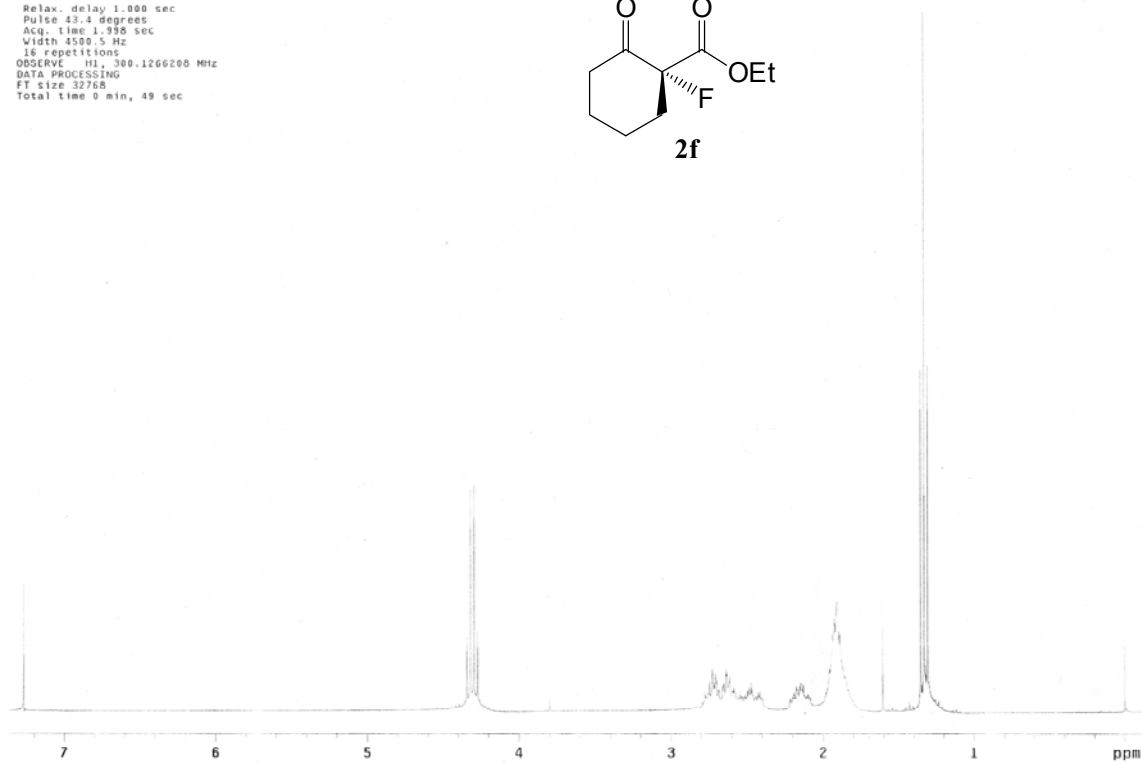
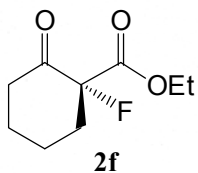
16 repetitions

OBSERVE H1, 300.1266260 MHz

DATA PROCESSING

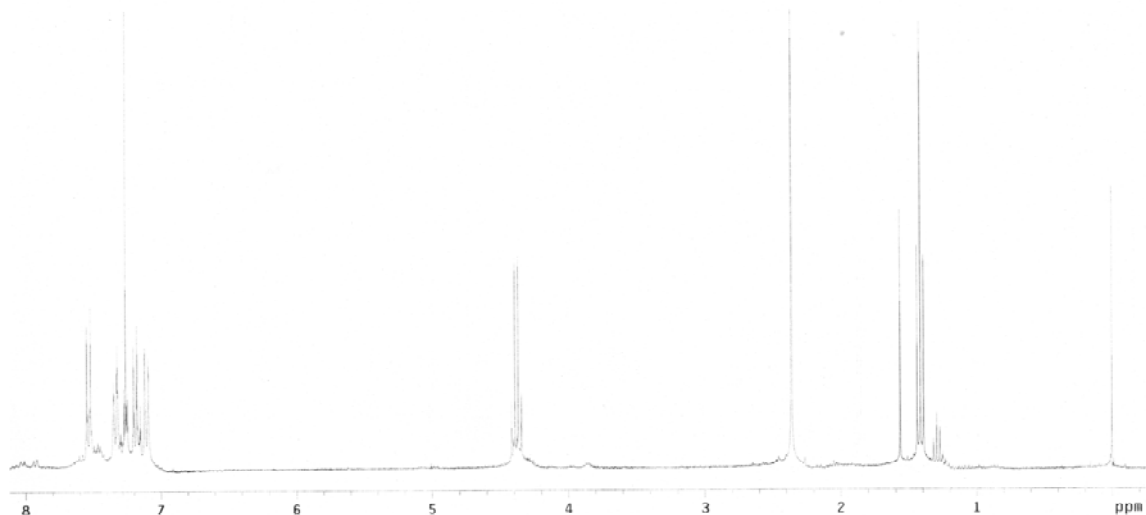
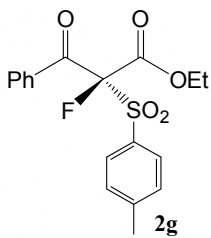
FT size 32768

Total time 0 min, 49 sec



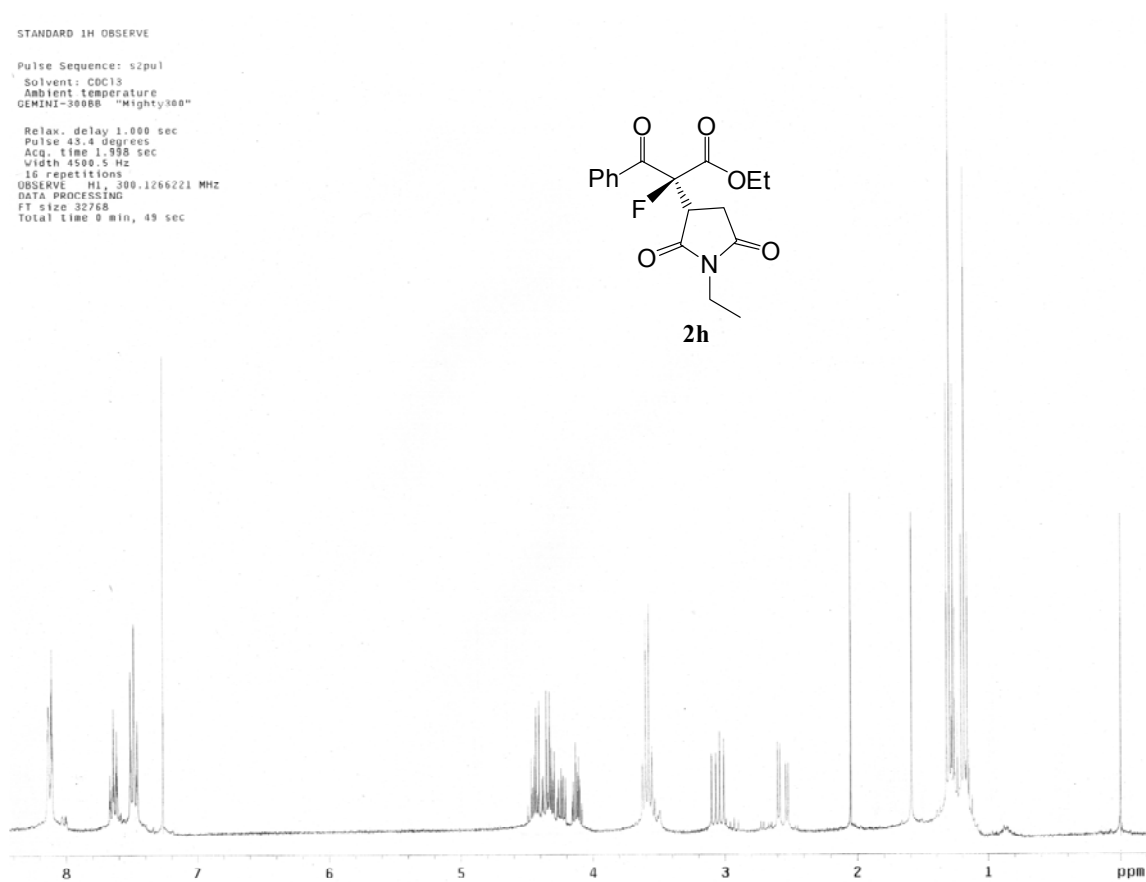
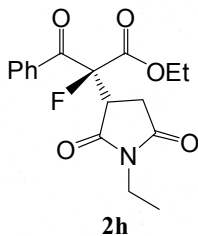
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 GEMINI-3000B "Mighty300"
 Relax. delay 1.000 sec
 Pulse 43.4 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 15 repetitions
 OBSERVE H1, 300.1266230 MHz
 DATA PROCESSING
 FT size 32768
 Total time 9 min, 49 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 GEMINI-3000B "Mighty300"
 Relax. delay 1.000 sec
 Pulse 43.4 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 16 repetitions
 OBSERVE H1, 300.1266221 MHz
 DATA PROCESSING
 FT size 32768
 Total time 9 min, 49 sec

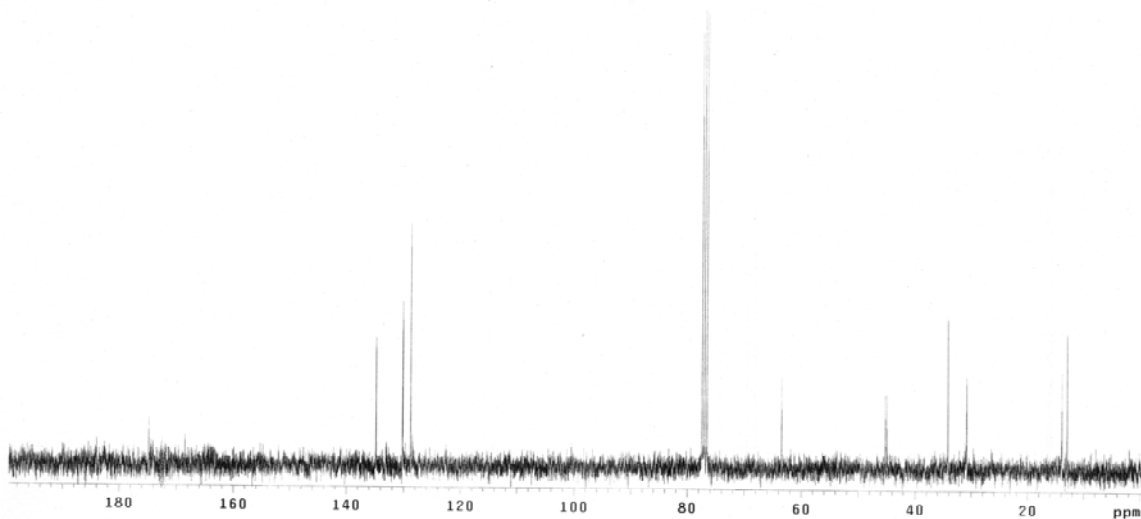
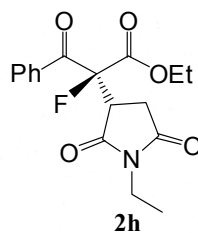


13C OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "Mighty300"

Pulse 67.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1824 repetitions
OBSERVE C13, 75.4669004 MHz
DECOUPLE H1, 300.1281260 MHz
Power 36 dB
continuously on
VALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min, 3 sec

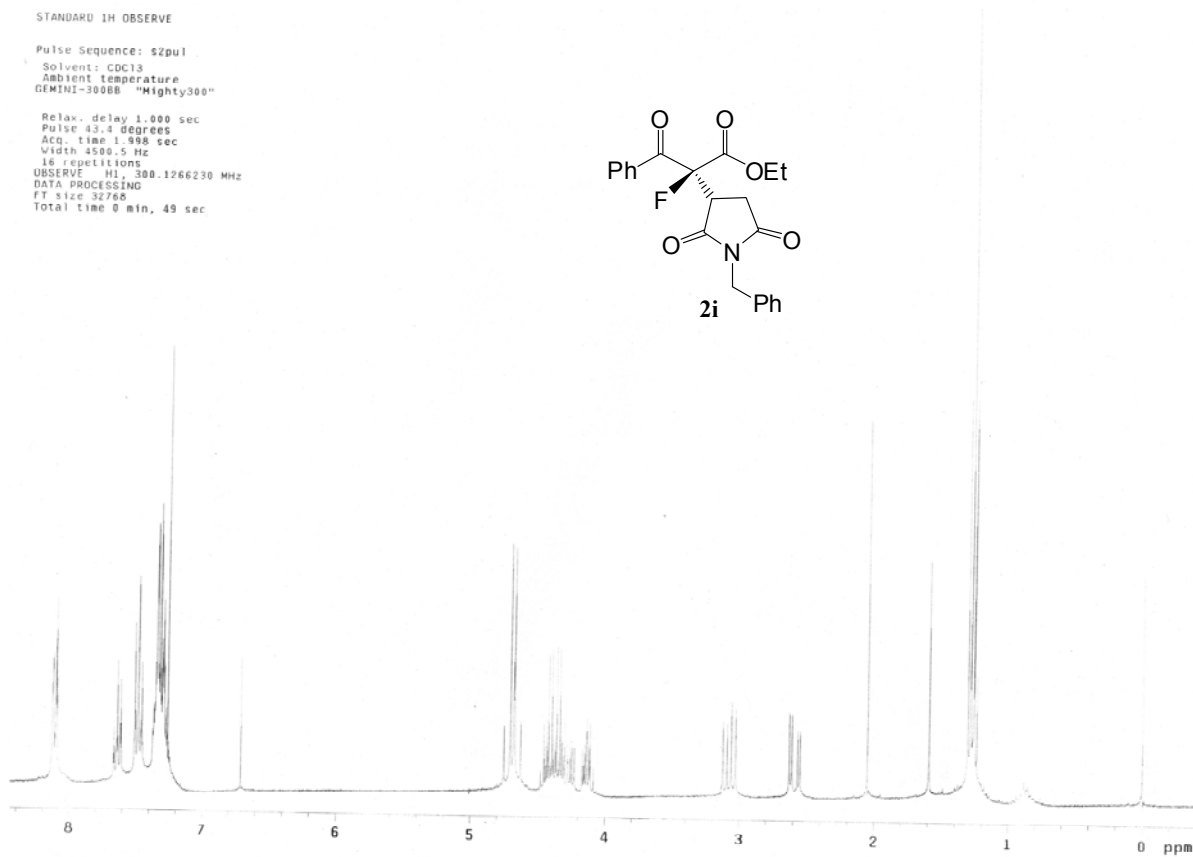
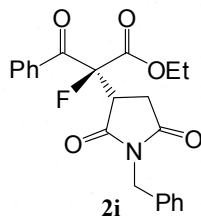


STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3
Ambient temperature
GEMINI-300BB "Mighty300"

Relax. delay 1.000 sec
Pulse 43.4 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.1266230 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



13C OBSERVE

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

GEMINI-30000 "Mighty300"

Pulse 67.0 degrees

Acq time 1.815 sec

Width 18761.7 Hz

1824 repetitions

OBSERVE C13, 75.8660001 MHz

DECOUPLE H1, 300.1281260 MHz

Power 35 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line Broadening 1.0 Hz

FT size 131072

Total time 36 min, 3 sec

