Supporting Information for Publication

Diastereoselective Synthesis of Substituted Dihydropyrans via Oxonium-Ene Cyclization Reaction

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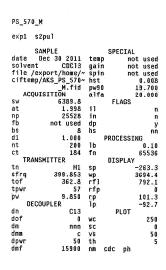
Table of content:

1. General Information S1

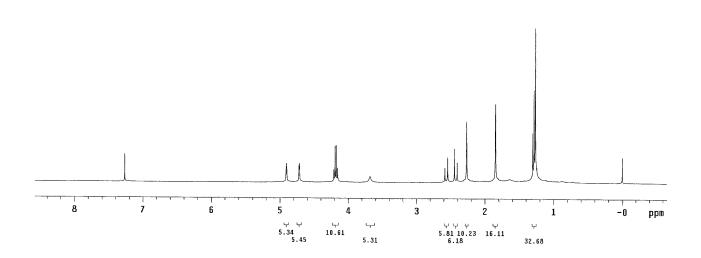
2. ¹H and ¹³C NMR spectra of all compounds, ¹⁹F NMR spectrum of **3e** and NOE spectrum of **3a** and **3k S2-S53**

General Information: All reagents are commercially obtained. ¹H NMR spectra were recorded in CDCl₃ on 400 MHz NMR spectrometer using TMS as internal standard. The ¹³C and ¹⁹F NMR spectra were recorded at 100 MHz and 376 MHz, respectively. For ¹³C and ¹⁹F NMR CDCl₃ and C₆F₆ were used as internal standard. IR spectra were recorded on FT-IR spectrometer. Mass spectra were recorded using Waters LC-MS/MS system (Q-TOF–Premier). HRMS (ESCi-TOF) were calibrated with sodium formate solution and leucine enkephalin (SIGMA) was used as an external standard.

¹H NMR spectra of **1a**



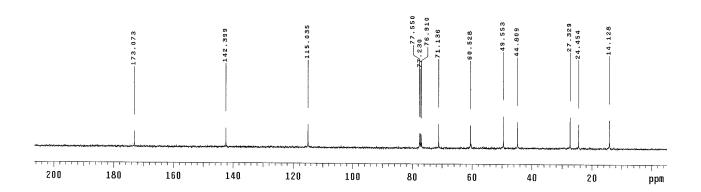




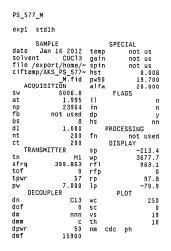
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	M_C13.fid	pw90 18.600
AC	QUISITION	alfa 20.000
SW	25125.6	FLAGS
at	1.199	tî n
np	60270	in n
fb	13800	dp y
bs	16	hs nn
d1	1.000	PROCESSING
nt	2000	lb 2.00
ct	384	fn 65.536
TR	ANSMITTER	DISPLAY
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sfra	100.554	wp 21295.5
tof	1536.3	rfl 9282.1
town	61	rfp 7764.9
pw	9.300	rp -62.5
	ECOUPLER	1p -334.9
dn	H1	PLOT
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dm.	ууу	sc 0
ďmm	3.3.3 W	vs 10
dpwr	42	th 2
dmf	8900	nm no ph
	0300	pii

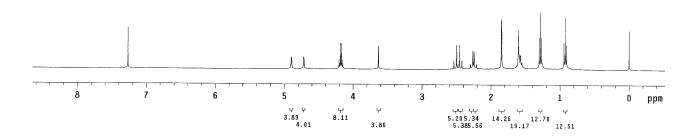




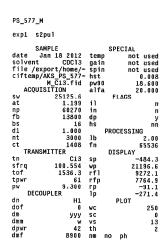
¹H NMR spectra of **1b**



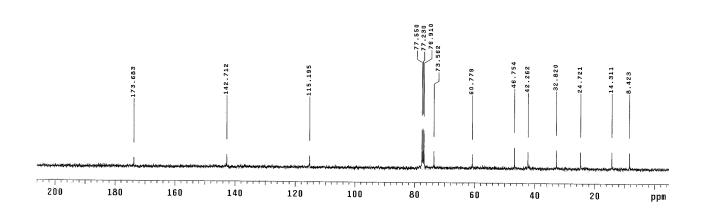




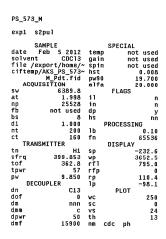
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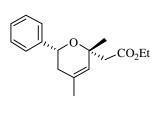


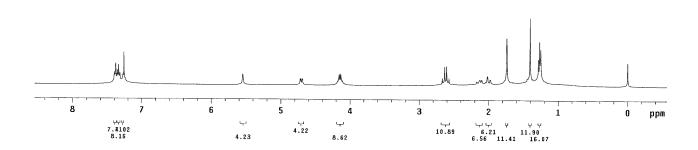




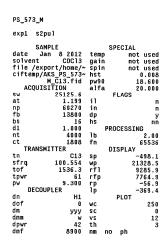
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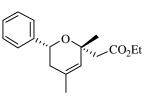


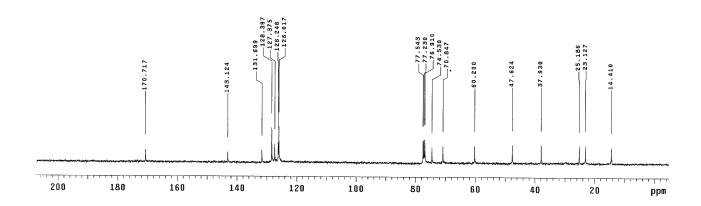




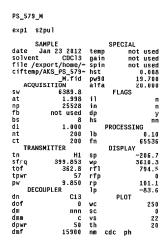
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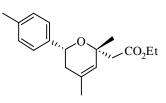


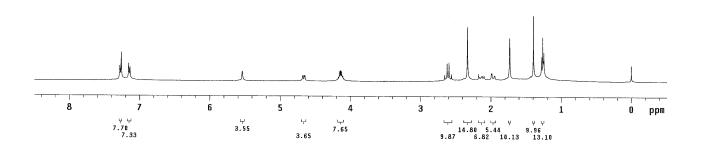




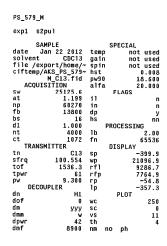
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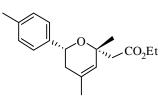


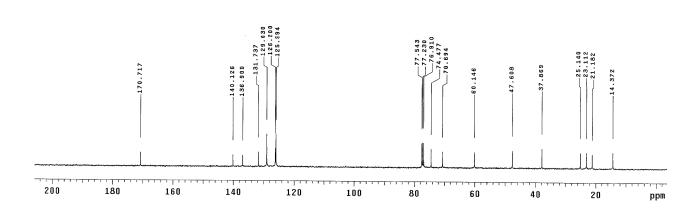




¹³C NMR spectra of **3b**

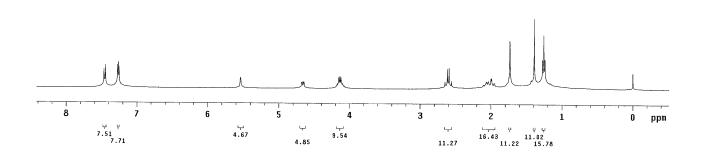




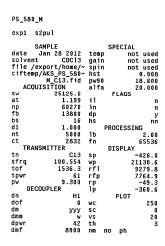


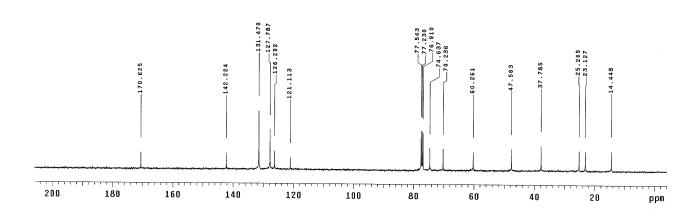
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file,	/export/home/~	spin		no	t	use	ed
cifter	np/AKS_PS_580~	hst			0	.00	18
	M_Pdt.fid	pw90			19	. 70	0 0
ACC	QUISITION	alfa			20	. 00	0 0
SW	6389.8		FL	AGS			
at	1.998	il					n
np	25528	in					n
fb	not used	dp					У
bs	8	hs				r	ıň
d1	1.000		PROC	ESSI	NG		
nt	200	1b				0.1	£ O
ct	64	fn				553	
TRA	NSMITTER		DIS	PLAY			
tn	H1	Sp			-2	06.	. 9
sfrq	399.853	wp			35	76.	. 8
tof	362.8	rf1			7	94.	. 7
tpwr	57	rfp					0
pw	9.850	rp			1	oo.	. 7
DE	COUPLER	1p			-	87.	. 0
dn	C13	•	Р	LOT			•
dof	Ō	WC				25	ś٨
dm	nnn	sc					Õ
dmm	С.	vs				2	25
dpwr	50	th					20
dmf	15908		cdc	ph		-	. •



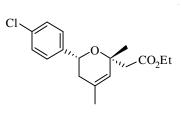
13 C NMR spectra of 3c

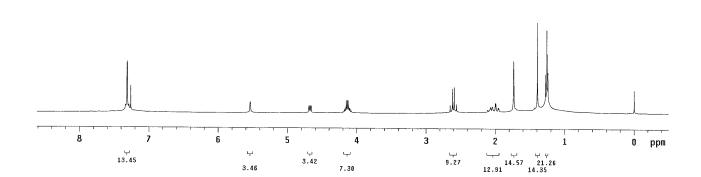




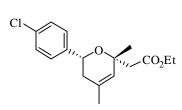
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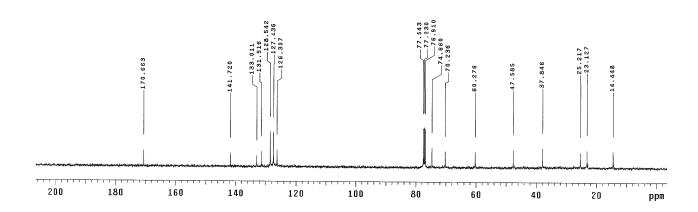




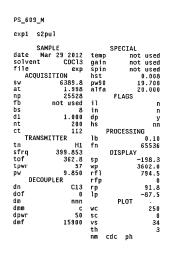


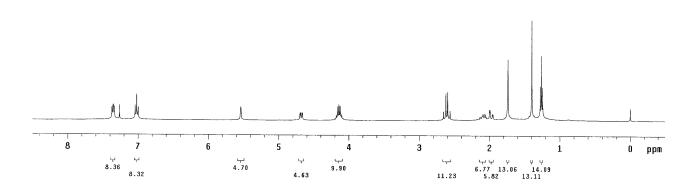
¹³C NMR spectra of **3d**



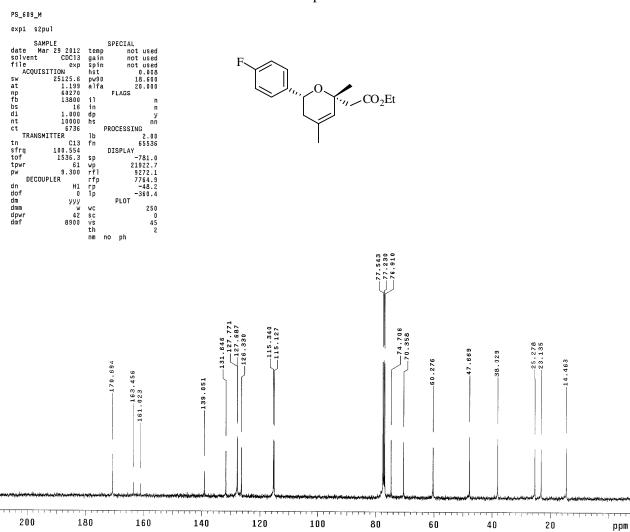


¹H NMR spectra of **3e**

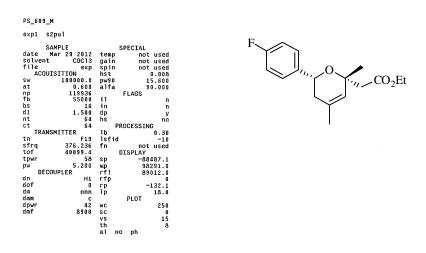


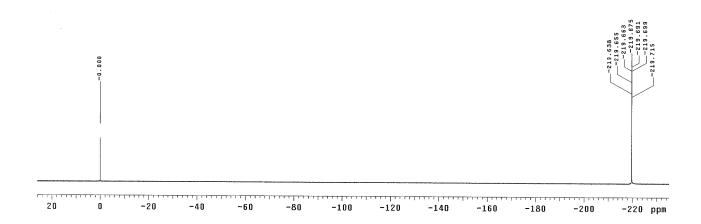


¹³C NMR spectra of **3e**

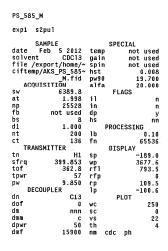


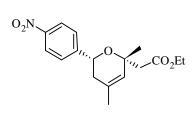
¹⁹F NMR spectra of **3e**

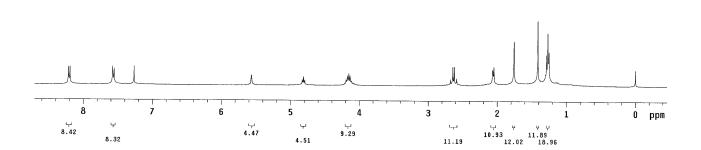




¹H NMR spectra of **3f**

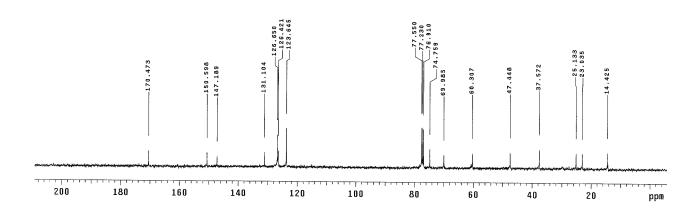






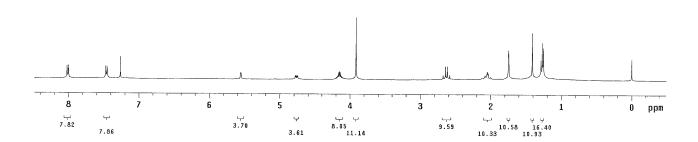
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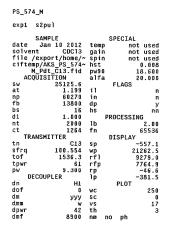


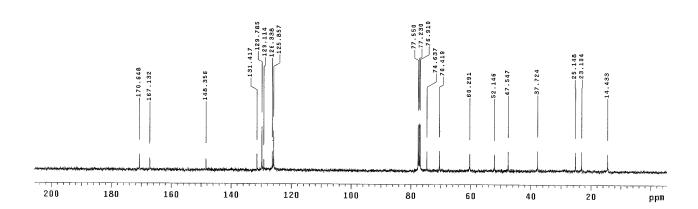
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solv	ent CDC13	gain not use	ď
file	/export/home/~	spin not use	
	emp/AKS PS 574~	hst 0.00	
	M Pdt.fid	pw90 19.70	
Δ	COUISITION	alfa 20.00	
sw	6389.8	FLAGS	•
at	1.998	11	n
np	25528	in	n
fb	not used		y
bs	8	hs n	
d1	1.000	PROCESSING	••
nt	200	1b 0.1	n
ct	200	fn 6553	
	RANSMITTER	DISPLAY	u
tn '	H1	SD -196.	o
sfrq		wp 3593.	
tof	362.8	rfl 792.	
tpwr			0
DW.	9.850		
ρw	DECOUPLER		
dn	C13	lp -89.	4
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dm	nnn		0
cí m m	C	vs 2	
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dmf	15900	nm cdc ph	

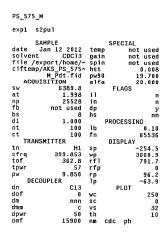


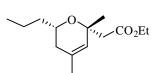
¹³C NMR spectra of **3g**

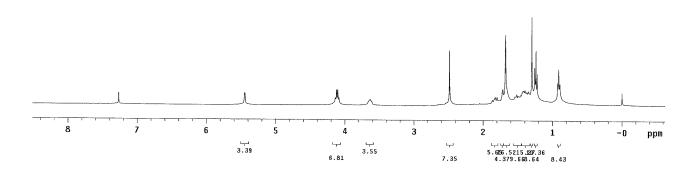




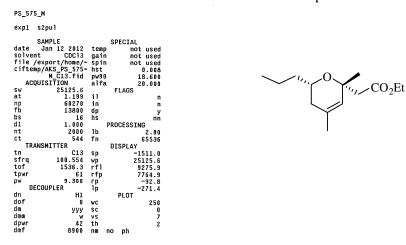
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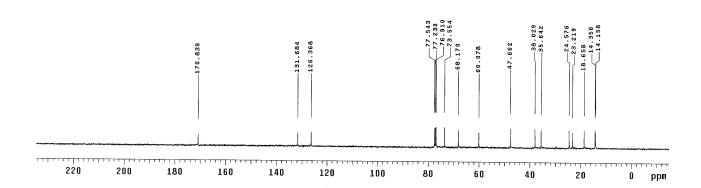




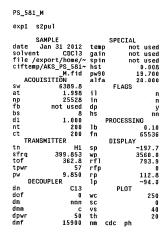


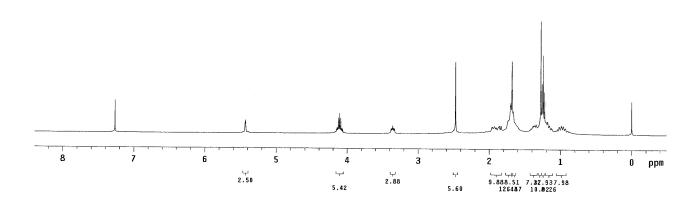
¹³C NMR spectra of **3h**





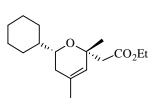
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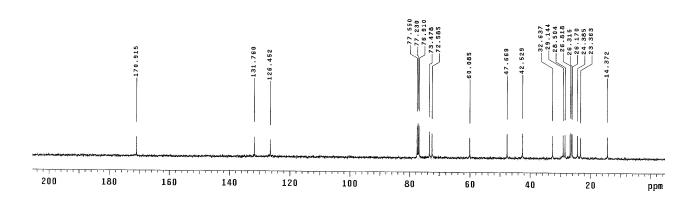




¹³C NMR spectra of **3i**

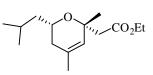
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cifter	np/AKS_PS_581~	hst			0.008
	M C13.fid	pw90			18.600
ACC	QUISITION	alfa			20.000
SW	25125.6		F	FLAGS	
at	1.199	i 1			n
np .	60270	in			n
fb	13800	dp			У
bs	16	hs			nn
d1	1.000		PRO	CESSI	NG
nt	4000	1b			2.00
ct	992	fn			65536
TR/	ANSMITTER		D)	ESPLAY	
tn	C13	Sp			-520.3
sfrq	100.554	wp		2	1196.6
tof	1536.3	rf1			9275.2
tpwr	61	rfp			7764.9
pw	9.300	rp.			-71.0
	COUPLER	1p			-322.6
d n	H1			PLOT	
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dm	ууу	SC			0
dmm	w	vs			12
dpwr	42	th			3
dmf	8900	nm	no	ph	

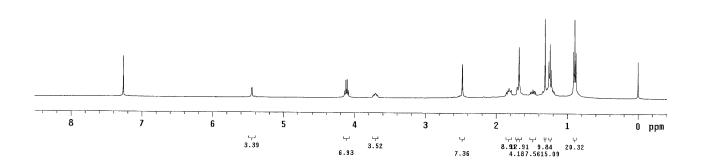




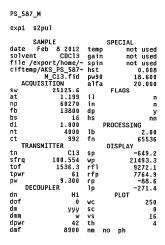
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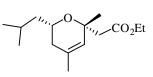
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of 362.8
wr 57
9.850 r TRANSMITTER DISPLAY sp wp rfl rfp rp lp 7164.0 3568.4 793.7 C13 0 nnn c 50 15900 PLOT wc sc vs th nm 250 0 27 9 cdc ph

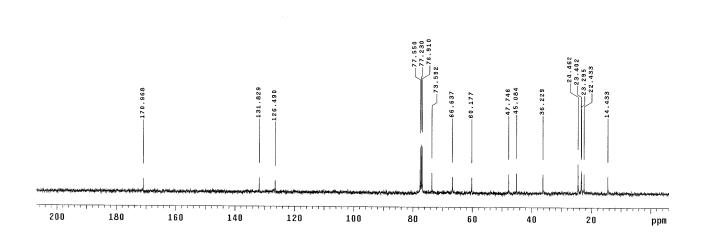




¹³C NMR spectra of **3j**

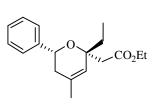


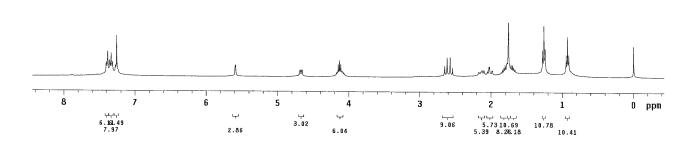




¹H NMR spectra of **3k**

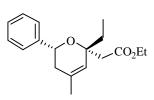
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	/export/		spir	1	not	
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	_	M.fid	pw90			9.700
	UISITIO		alfe			0.000
SW	6	389.8		FL.	AGS	
at		1.998	11			n
np		25528	in			n
fb	not	tused	dр			У
bs		8	hs			nn
d1		1.000		PROC	ESSIN	IG .
nt		200	1b			0.10
ct		200	fn			65536
	ANSMITTE			DIS	PLAY	
tn		H1	sp			173.6
sfrq	39	9.853	wp		3	551.7
tof		362.8	rfl			794.8
tpwr		57	rfp			0
pw		9.850	rp			107.6
	COUPLER		1p			-91.2
dn		C13		P	LOT	
dof		0	wc			250
dm		nnn	SC			0
dmm		С	٧s			19
dpwr		50	th			7
dmf		15900	nm	cdc	ph	

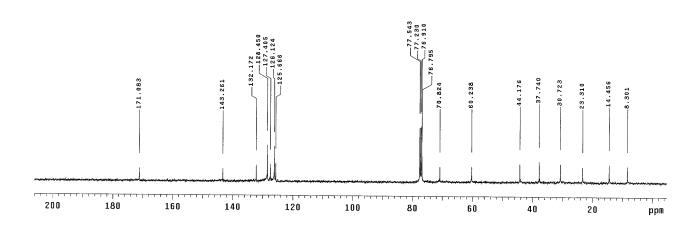




¹³C NMR spectra of **3k**

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cifte	mp/AKS_PS_5		hst		- (800.0
	M_C13.1	id	pw90		18	3.600
AC	QUISITION		alfa	ι	21	0.000
SW	25125			FL	AGS	
at	1.1		-11			n
np	602	270	in			n
fb	138		dp			У
bs		16	hs			nn
d1	1.0	100		PROC	ESSIN	3
nt	80	0.0	1b			2.00
ct	32	232	fn		•	55536
TR	ANSMITTER			DIS	PLAY	
tn	.0	:13	Sp			189.7
sfrq	100.5	54	wp		212	229.5
tof	1536	. 3	rfl		92	277.5
tpwr		61	rfp		7.7	64.9
pw	9.3	300	rp			78.5
DI	ECOUPLER		1p		-2	293.2
dn		H1	•	Р	LOT	
dof		0	wc			250
dm	7	уy	SC			0
dmm	•	w	VS			19
dpwr		42	th			3
dmf	89	0.0	nm	no	ph	•



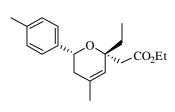


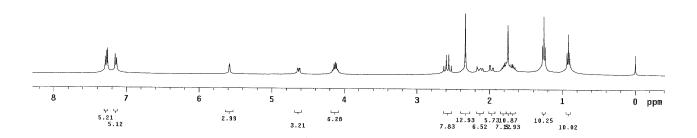
¹H NMR spectra of **3l**

PS_592_M

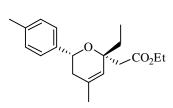
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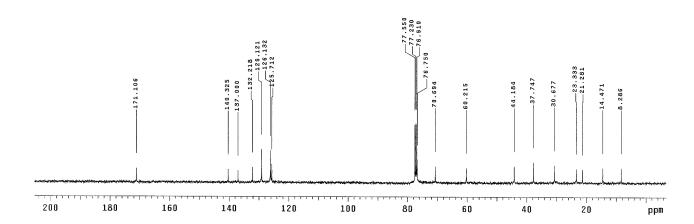
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sw 6389.8 at 1.998 din 19.700 also not used bs 8 din 1.998 din 19.700 also not used bs 8 din 1.998 din 19.700 also not used bs 8 din 1.998 din 19.700 also not used bs 8 din 19.700 also not used bs 19.700 also not used bs 19.700 also not used by 9.855 din 19.700 also not used bs 19.700 also not used by 9.955 din 19.700 also not used by 9.955 din 19.700 also not used also no



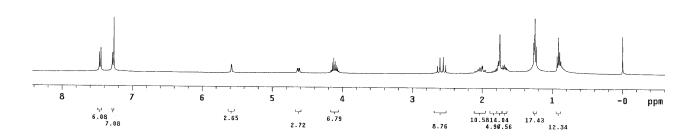


¹³C NMR spectra of **31**

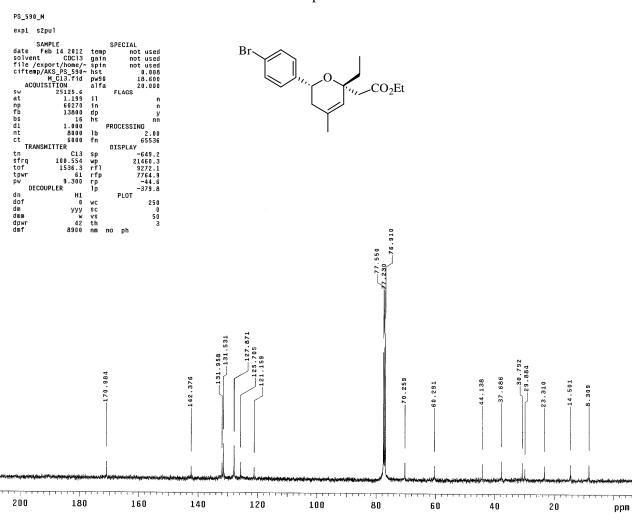




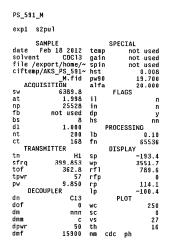
¹H NMR spectra of **3m**

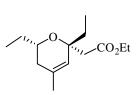


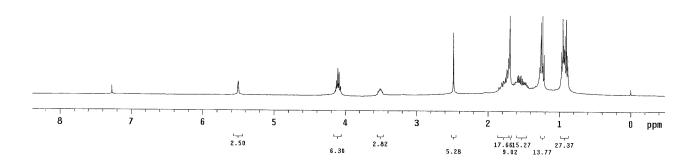
¹³C NMR spectra of **3m**



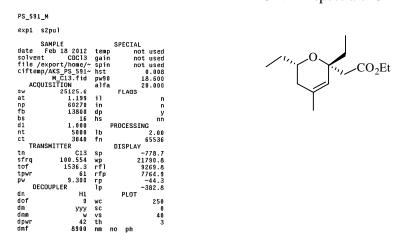
¹H NMR spectra of **3n**

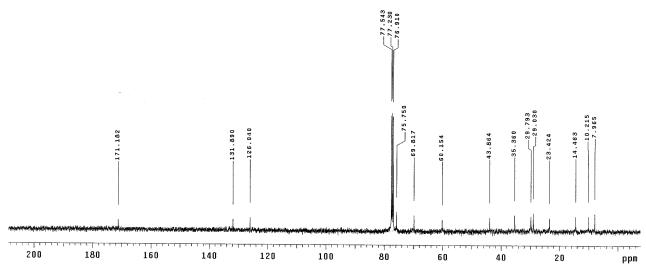




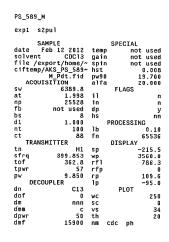


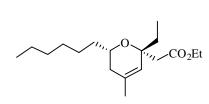
¹³C NMR spectra of **3n**

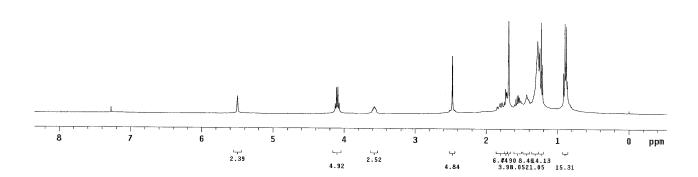




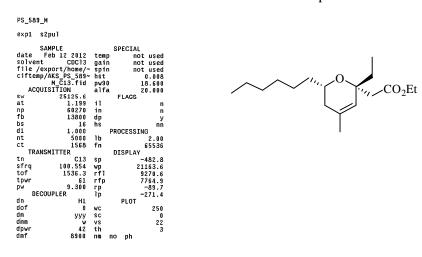
¹H NMR spectra of **30**

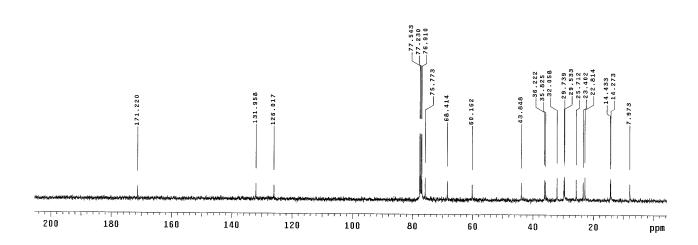




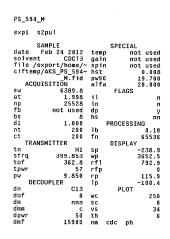


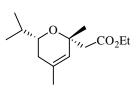
¹³C NMR spectra of **30**

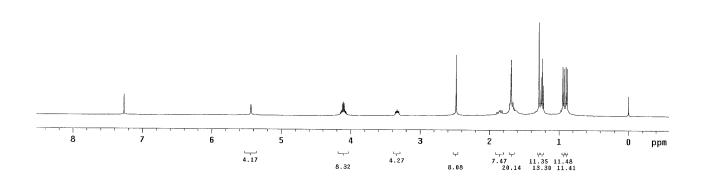




¹H NMR spectra of **7b**

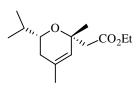


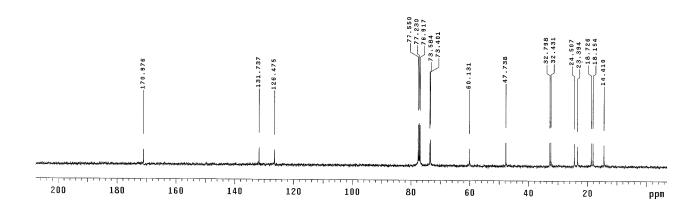




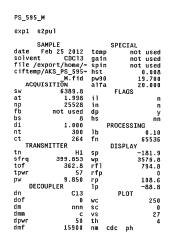
¹³C NMR spectra of **7b**

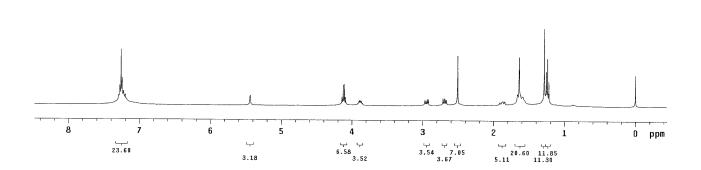
PS_59	4_M				
exp1	s2pu1				
	SAMPLE		SP	ECIAL	
date	Feb 25 2012	temp		no	t used
solve		gain		no	t used
file	/export/home/~	spin		no	t used
	mp/AKS_PS_594~	hst			0.008
	M_Pdt_C13.fid	pw90			18.600
	QUISITION	alfa			20.000
sw	25125.6		F	LAGS	
at	1.199	il			n
np	60270	in			n
fb	13800	dp			У
bs	16	hs			nn
d1	1.000		PRO	CESSI	NG
nt	4000	1b			2.00
ct	2000	fn			65536
TRA	ANSMITTER		DI	SPLAY	
tn	C13	sp			-714.3
sfrq	100.554	wp			1592.2
tof	1536.3	rf1			9271.3
tpwr	61	rfp			7764.9
wia	9.300	rp			-88.9
. DI	ECOUPLER	1p			-271.4
dn	H1			PLOT	
dof		wc			250
dm	ууу	SC			0
chum	3.33 W	vs			14
dpwr	42	th			3
dmf	8900		no	ph	ŭ



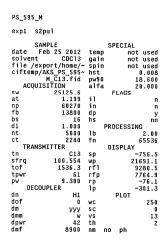


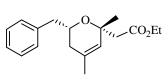
¹H NMR spectra of **7c**

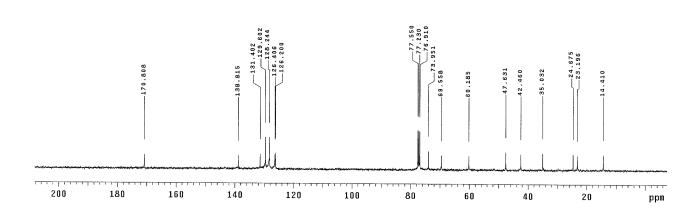




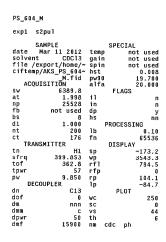
¹³C NMR spectra of **7c**

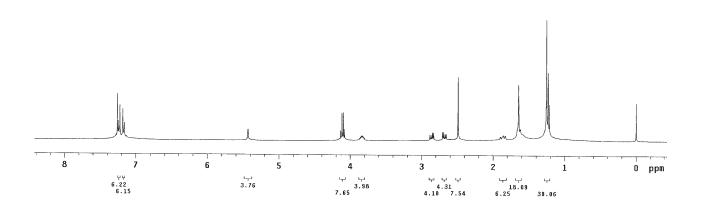






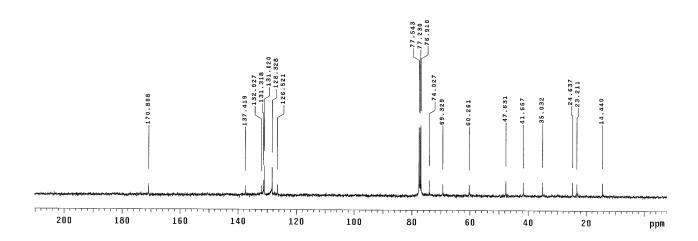
¹H NMR spectra of **7d**





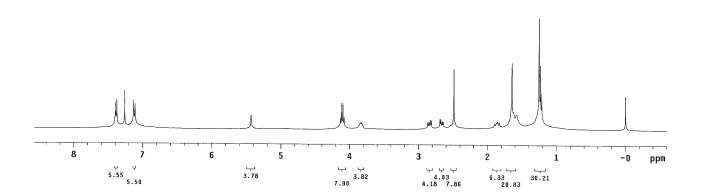
¹³C NMR spectra of **7d**

PS_604	1_M		
exp1	s2pu1		
	SAMPLE		SPECIAL
date	Mar 12 2012	temp	not used
solver		gain	not used
	/export/home/~	spin	not used
cifter	np/AKS_PS_604~	hst	0.008
	M1_C13.fid	pw90	18.600
AC	QUISITION	alfa	20.000
SW	25125.6		FLAGS
at	1.199	i)	n
np	60270	in	n
fb	13800	dp	У
bs	16	hs	nn
d1	1.000		ROCESSING
nt	5000	1b	2.00
ct	3424	fn	65536
	ANSMITTER	• • •	DISPLAY
		sp	DISPLAY -815.6
TRA	ANSMITTER		
TRA tn	ANSMITTER C13	sp	-815.6
TRA tn sfrq	ANSMITTER C13 100.554	sp wp rfl	-815.6 21955.7 9272.1
tn sfrq tof	C13 100.554 1536.3	sp wp	-815.6 21955.7
tn sfrq tof tpwr pw	ANSMITTER C13 100.554 1536.3 61	sp wp rfl rfp	-815.6 21955.7 9272.1 7764.9
tn sfrq tof tpwr pw	100.554 100.554 1536.3 61 9.300	sp wp rfl rfp rp	-815.6 21955.7 9272.1 7764.9 -90.0
tn sfrq tof tpwr pw	C13 100.554 1536.3 61 9.300 ECOUPLER	sp wp rfl rfp rp	-815.6 21955.7 9272.1 7764.9 -90.0 -271.4
tn sfrq tof tpwr pw Of	C13 100.554 1536.3 61 9.300 ECOUPLER H1	sp wp rfl rfp rp lp	-815.6 21955.7 9272.1 7764.9 -90.0 -271.4 PLOT
tn sfrq tof tpwr pw Of dn dof	C13 100.554 1536.3 61 9.300 COUPLER	sp wp rfl rfp rp lp	-815.6 21955.7 9272.1 7764.9 -90.0 -271.4 PLOT
TRA tn sfrq tof tpwr pw DE dn dof	C13 100.554 1536.3 61 9.300 COUPLER H1 0 yyy	sp wp rfl rfp rp lp wc sc	-815.6 21955.7 9272.1 7764.9 -90.0 -271.4 PLOT 250 0
TRA tn sfrq tof tpwr pw DE dn dof dm	C13 100.554 1536.3 61 9.300 ECOUPLER H1 0 yyy	sp wp rfl rfp rp lp wc sc vs th	-815.6 21955.7 9272.1 7764.9 -90.0 -271.4 PLOT 250 0

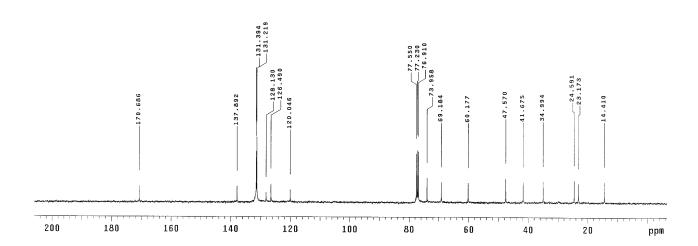


¹H NMR spectra of **7e**

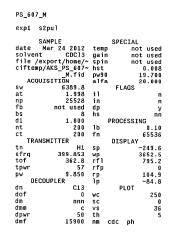
PS_5	96_M				
exp1	. s2pul				
exhi	. szpui				
	SAMPLE		SPE	CIAL	
date		temp		no	t used
solv		gain		no	t used
	/export/home/~	Spin		no	t used
cift	emp/AKS_PS_596~	hst			0.008
	M_Pdt.fid	pw90			19.700
	CQUISITION	alfa			20.000
SW	6389.8		FL	AGS	
at	1.998	il			n
np	25528	ín			n
fb	not used	dp			У
bs	8	hs			nn
d1	1.000	F	ROC	ESSI	NG
nt	200	1b			0.10
ct	200	fn			65536
1	RANSMITTER		DIS	PLAY	
tn	H1	sp			-248.8
sfrq	399.853	wp			3677.6
tof	362.8	rf1			794.5
tpwr	57	rfp			0
pw	9.850	rp.			98.8
	DECOUPLER	1p			-81.9
dn	C13		P	LOT	
dof	0	wc			250
dm	nnn	SC			O
đmm	С	v.s			39
down	50	th			10
dmf	15900		dc	ph	10
				F.,,	

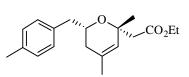


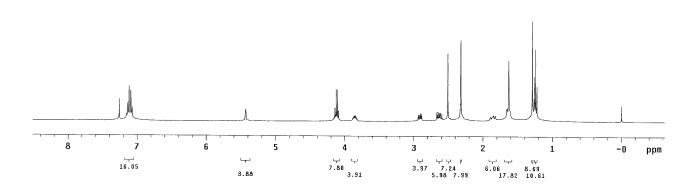
¹³C NMR spectra of **7e**



¹H NMR spectra of **7f**

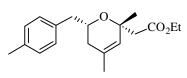


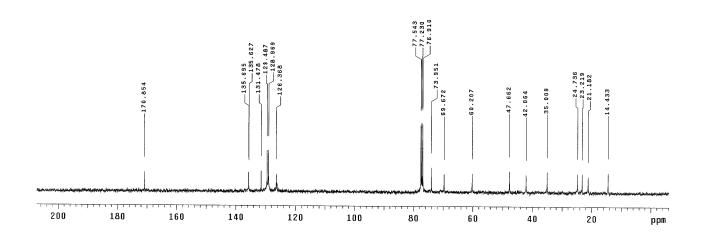




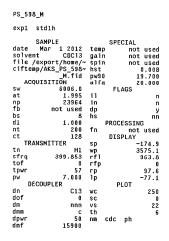
¹³C NMR spectra of **7f**

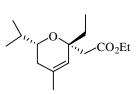
PS_60	7_M		
exp1	s2pul		
	SAMPLE		SPECIAL
date	Mar 24 2012	temp	not used
solve		gain	not used
	/export/home/~	spin	not used
cifte	mp/AKS_PS_607~	hst	0.008
	M_C13.fid	pw90	18.600
	QUISITION	alfa	20.000
sw	25125.6		FLAGS
at	1.199	il	n
np	60270	in	n
fb	13800	dp	У
bs	16	hs	nn
d1	1.000		PROCESSING
nt	4000	1b	2.00
ct	2464	fn	65536
	ANSMITTER		DISPLAY
tn	C13	Sp	-620.8
sfrq	100.554	wp	21460.3
tof	1536.3	rfl	9276.7
tpwr	61	rfp	7764.9
pw	9.300	rp'	-53.9
DI	ECOUPLER	1p	~355.9
dn	H1		PLOT
dof	0	wc	250
dm	yyy	sc	0
dmm	3,3 w	vs	24
dpwr	42	th	4
dmf	8900		no ph

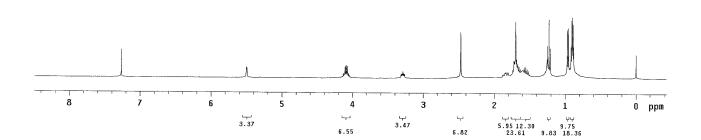




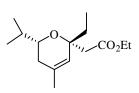
¹H NMR spectra of **7g**

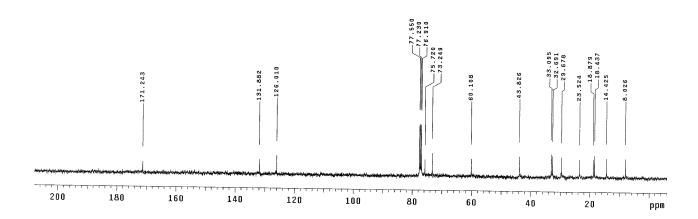




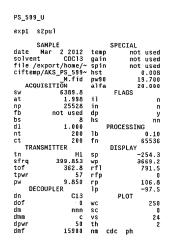


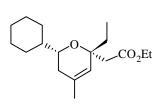
¹³C NMR spectra of **7g**

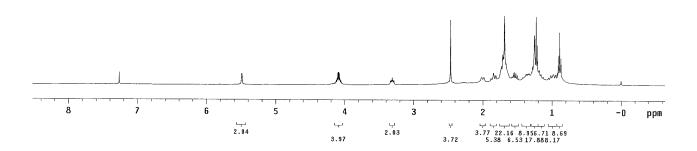




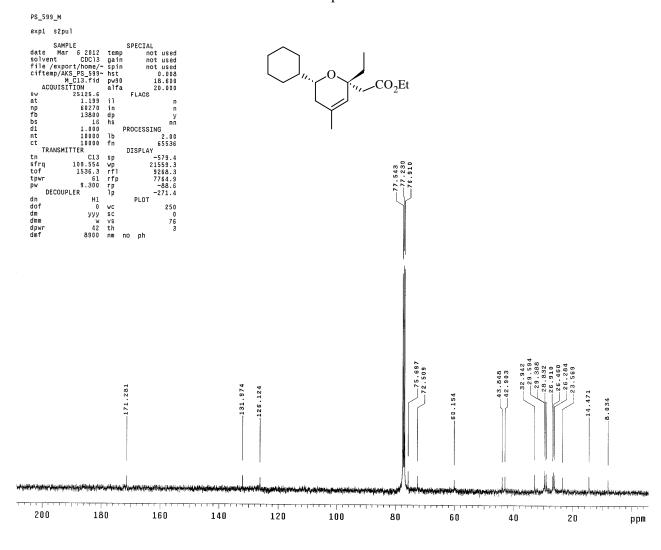
¹H NMR spectra of **7h**



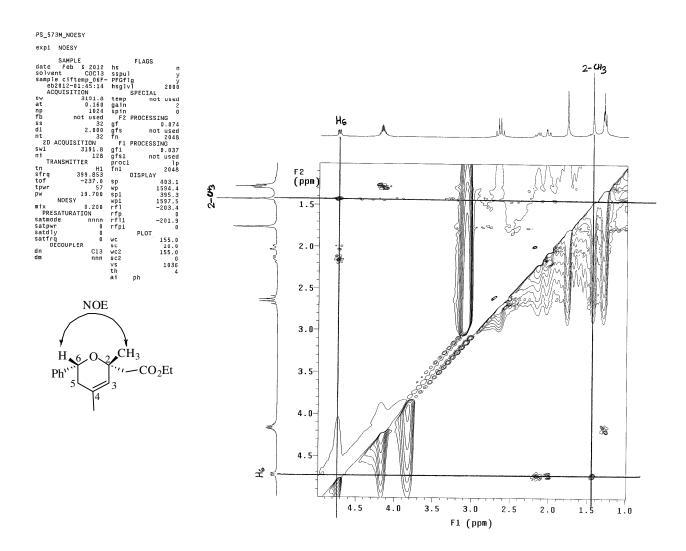




¹³C NMR spectra of **7h**

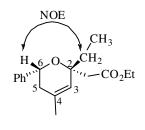


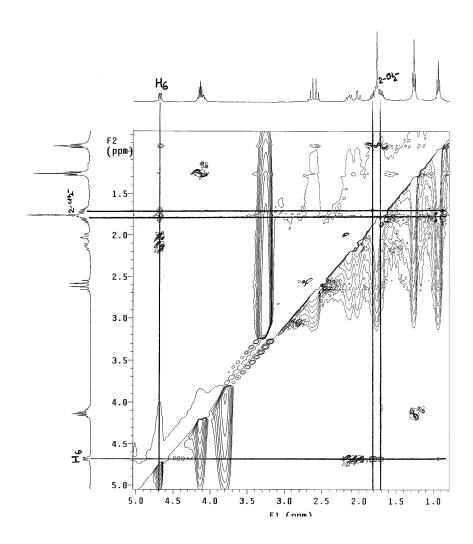
NOESY spectrum of 3a



NOESY spectrum of 3k







Crude ¹H NMR spectra of **3c**

