#### **Supplementary Information**

Synthesis, gene silencing activity, thermal stability, and serum stability of siRNA containing four (*S*)-5'-*C*-aminopropyl-2'-*O*-methylnucleosides (A, adenosine; U, uridine; G, guanosine; and C, cytidine)

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- 1. Figure S1–4. UV melting profiles of the unmodified and modified siRNAs.
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Figure S1. UV melting profiles of the unmodified and modified siRNAs in a buffer

containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



**Figure S2**. UV melting profiles of the unmodified and modified siRNAs in a buffer containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



Figure S3. UV melting profiles of the unmodified and modified siRNAs in a buffer

containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



**Figure S4**. UV melting profiles of the unmodified and modified siRNAs in a buffer containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.

Abbreviation	Abbreviation		upper: 1 nM
of siRNA	of ssRNA	sequence "	lower: 0.1 nM
Control	Buffer	-	$100 \pm 6.1$
		Sense (Passenger) strand	
-: DNA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$21.1\pm2.5$
SIKINA I	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$59.0 \pm 1.4$
		Antiense (Guide) strand	
	RNA 2	5'-GGCCUUUCACUACUCCUACUU-3'	$19.4 \pm 2.0$
siRNA 2	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$56.1\pm1.5$
siRNA 3	RNA 3	5'-GGCCUUUCACUACUCCUA <mark>CUU</mark> -3'	$16.9 \pm 1.7$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$58.7\pm3.1$
siRNA 4	RNA 4	5'-GGCCUUUCACUACUCCUACUU-3'	$20.0\pm0.79$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$58.1\pm5.3$
	RNA 5	5'-GGCCUUUCACUACUC <mark>CUA</mark> CUU-3'	$60.4\pm4.0$
siRNA 5	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$28.5\pm1.7$
	RNA 6	5'-GGCCUUUCACUACUCCUACUU-3'	$20.8 \pm 2.5$
SIKNA 6	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$56.4\pm2.8$
	RNA 7	5'-GGCCUUUCACUACUCCUACUU-3'	21.6 ± 2.5
sikna /	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$57.9\pm4.0$

Table S1. Sequences of siRNAs 1–7 and their ability to suppress gene expression.

Abbreviation	Abbreviation		upper: 1 nM
of siRNA	of ssRNA	sequence "	lower: 0.1 nM
Control	Buffer	-	$100 \pm 12.7$
		Sense (Passenger) strand	
CDNA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$21.8\pm5.6$
SIKINA I	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$62.5\pm1.6$
		Antiense (Guide) strand	
	RNA 9	5'-GGCCUUUCACUACUCCUACUU-3'	$27.5\pm3.7$
SIRNA 8	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$65.8 \pm 3.6$
siRNA 9	RNA 10	5'-GGCCUUUCACUACUCCUACUU-3'	$63.1 \pm 6.4$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$90.3\pm5.0$
siRNA 10	RNA 11	5'-GGCCUUUCACUACUCCUACUU-3'	$32.6\pm2.3$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$78.8\pm 6.8$
-:DNIA 11	RNA 12	5'-GGCCUUUCACUACUCCUACUU-3'	$91.4\pm6.5$
siRNA 11	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$46.9 \pm 1.5$
siRNA 12	RNA 13	5'-GGCCUUUCACUACUCCUACUU-3'	$22.2\pm2.5$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$65.0\pm1.5$
a:DNIA 12	RNA 14	5'-GGCCUUUCACUACUCCUACUU-3'	18.5 ±1.1
sikna 13	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$73.8\pm3.8$

Table S2. Sequences of siRNAs 1, 8–13 and their ability to suppress gene expression.

Abbreviation	Abbreviation		upper: 1 nM
of siRNA	of ssRNA	sequence "	lower: 0.1 nM
Control	Buffer	-	$100\pm2.8$
		Sense (Passenger) strand	
siRNA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$21.1\pm1.6$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$59.9\pm3.7$
		Antiense (Guide) strand	
siRNA 14	RNA 15	5'-GGCCUUUCACUACUCCUACUU-3'	$15.5 \pm 1.4$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$47.0\pm2.3$
siRNA 15	RNA 16	5'-GGCCUUUCACUACUCCUACUU-3'	$17.2 \pm 1.3$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$48.5\pm5.0$

Table S3. Sequences of siRNAs 1, 14, 15 and their ability to suppress gene expression.

Abbreviation	Abbreviation		upper: 10 nM
of siRNA	of ssRNA	sequence "	lower: 1 nM
Control	Buffer	-	$100\pm9.5$
		Sense (Passenger) strand	
"DNIA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$11.8\pm0.86$
SIKINA I	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$24.7\pm2.3$
		Antiense (Guide) strand	
-:DNA 16	RNA 17	5'-GGCCUUUCACUACUCCUACUU-3'	$9.7\pm0.53$
SIKINA 10	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$24.9 \pm 1.2$
siRNA 17	RNA 18	5'-GGCCUUUCACUACUCCUACUU-3'	$11.1 \pm 0.34$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$31.0\pm0.90$
siRNA 18	RNA 19	5'-GGCCUUUCACUACUCCUACUU-3'	$14.0\pm1.5$
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$26.1\pm0.62$
-:DNIA 10	RNA 20	5'-GGCCUUUCACUACUCCUACUU-3'	$34.3 \pm 3.1$
sirna 19	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$17.6\pm2.5$
-:DNIA 20	RNA 21	5'-GGCCUUUCACUACUCCUACUU-3'	$9.7\pm0.59$
sikna 20	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$22.7\pm0.68$
CINIA 21	RNA 22	5'-GGCCUUUCACUACUCCUACUU-3'	$23.9 \pm 1.2$
sikna 21	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$54.3\pm2.4$

Table S4. Sequences of siRNAs 1, 16–21 and their ability to suppress gene expression.

Abbreviation	Abbreviation	a	upper: 10 nM
of siRNA	of ssRNA	sequence "	lower: 1 nM
Control	Buffer	-	$100\pm 6.0$
		Sense (Passenger) strand	
DNA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$25.7\pm2.5$
SIKINA I	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$37.9\pm 1.3$
		Antiense (Guide) strand	
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$57.7\pm0.98$
SIKINA 22	RNA 23	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$93.6\pm7.3$
DNIA 22	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$99.1\pm3.9$
SIRINA 25	RNA 24	3'-UUCCGGAAAGUGAUGAGGAU <mark>G</mark> -5'	$95.3\pm5.4$
siRNA 24	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$54.1\pm1.9$
	RNA 25	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$83.3\pm4.7$
siRNA 25	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$86.7\pm4.6$
	RNA 26	3'-UUCCGGAAAGUGAUGAGGA <mark>U</mark> G-5'	$96.7\pm3.3$
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$23.7\pm2.0$
SIKNA 26	RNA 27	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$38.7\pm3.0$
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$64.3\pm 6.6$
s1RNA 27	RNA 28	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$82.0\pm0.90$
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$22.9 \pm 1.4$
siRNA 28	RNA 29	3'-UUCCGGAAAGUGAUGAG <mark>G</mark> AUG-5'	$43.9\pm3.2$
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$47.5\pm0.90$
sikna 29	RNA 30	3'-UUCCGGAAAGUGAUGAG <mark>G</mark> AUG-5'	$68.1\pm5.1$

Table S5. Sequences of siRNAs 1, 22–29 and their ability to suppress gene expression.

Abbreviation	Abbreviation		upper: 10 nM
of siRNA	of ssRNA	sequence "	lower: 1 nM
Control	Buffer	-	$100\pm7.9$
		Sense (Passenger) strand	
'D \ [ 4 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$17.3\pm1.0$
SIKNA I	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$41.3\pm3.8$
		Antiense (Guide) strand	
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$18.1 \pm 1.3$
SIKNA 30	RNA 31	3'-UUCCGGAAAGUGAUGA <mark>G</mark> GAUG-5'	$30.3\pm0.64$
-:DNIA 21	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$43.6\pm3.5$
SIKNA 31	RNA 32	3'-UUCCGGAAAGUGAUGA <mark>G</mark> GAUG-5'	$60.2\pm 6.3$
-:DNIA 22	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$20.6\pm1.2$
SIKNA 32	RNA 33	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$33.4 \pm 2.8$
siRNA 33	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$34.5\pm3.4$
	RNA 34	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$64.1\pm1.2$
-:DNIA 24	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$23.9\pm1.5$
SIKINA 54	RNA 35	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$43.7\pm2.4$
-:DNIA 25	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$23.9\pm1.0$
SIKINA 55	RNA 36	3'-UUCCGGAAAGUGAU <mark>G</mark> AGGAUG-5'	$39.8\pm 1.4$
siRNA 36	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$23.8 \pm 1.9$
	RNA 37	3'-UUCCGGAAAGUGAUGAGGAUG-5'	$44.4\pm2.6$
CDNA 27	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	$38.1\pm2.4$
s1KNA 37	RNA 38	3'-UUCCGGAAAGUGA <mark>U</mark> GAGGAUG-5'	$60.8\pm3.8$

Table S6. Sequences of siRNAs 1, 30–37 and their ability to suppress gene expression.

Abbreviation of	Abbreviation of	Passenger strand (5'-3') <sup><i>a</i></sup>	T (°C) b	AT (°C) c
siRNA	ssRNA	Guide strand (3'-5')	$I_{\rm m}$ (C) °	$\Delta I_{\rm m}$ (°C) °
siRNA 1	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	78.0	-
	RNA 8	3'-UUCCGGAAAGUGAUGAGGAUG-5'	/8.0	
~:DNIA 22	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	78.0	-
SIKINA 22	RNA 23	3'-UUCCGGAAAGUGAUGAGGAUG-5'	/8.0	
	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	0 רר	-0.2
SIKINA 23	RNA 24	3'-UUCCGGAAAGUGAUGAGGAU <mark>G</mark> -5'	//.8	
siRNA 24	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'		-
	RNA 25	3'-UUCCGGAAAGUGAUGAGGAUG-5'	//./	
siRNA 25	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	78.0	0.3
	RNA 26	3'-UUCCGGAAAGUGAUGAGGA <mark>U</mark> G-5'	/8.0	
siRNA 26	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	70.1	
	RNA 27	3'-UUCCGGAAAGUGAUGAGGAUG-5'	/8.1	-
siRNA 27	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	78.0	0.1
	RNA 28	3'-UUCCGGAAAGUGAUGAGG <mark>A</mark> UG-5'	/8.0	-0.1

**Table S7**. Sequences of ssRNAs, siRNAs, and  $T_{\rm m}$  values of siRNAs.

<sup>*a*</sup>Blue and red letters denote 2'-O-methylnucleosides and (S)-5'-C-aminopropyl-2'-O-methylnucleosides, respectively.

<sup>b</sup>The T<sub>m</sub> values were determined using 3 µM dsRNA in a buffer containing 10 mM sodium phosphate (pH of 7.0) and 100 mM NaCl.

<sup>*c*</sup> $\Delta T_{\rm m}$  represents  $[T_{\rm m} ({\rm siRNA}_{(S)-5'-C-{\rm aminopropyl-2'-O-methyl}}) - T_{\rm m} ({\rm siRNA}_{2'-O-{\rm methyl}})].$ 

Abbreviation of	Abbreviation of	Passenger strand (5'-3') <sup><i>a</i></sup>	T (°C) b	AT (°C) c
siRNA	ssRNA	Guide strand (3'-5')	$I_{\rm m}$ (C) °	$\Delta I_{\rm m}$ ( C) °
CINIA 29	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	70.2	-
SININA 20	RNA 29	3'-UUCCGGAAAGUGAUGAGGAUG-5'	/0.3	
TINA 20	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	ר רר	-0.6
SIKINA 29	RNA 30	3'-UUCCGGAAAGUGAUGAG <mark>G</mark> AUG-5'	//./	
'DNL 20	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'		-
SIKINA 30	RNA 31	3'-UUCCGGAAAGUGAUGAGGAUG-5'	//./	
CDNA 21	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	77 5	-0.2
SIKINA 31	RNA 32	3'-UUCCGGAAAGUGAUGA <mark>G</mark> GAUG-5'	11.5	
~:DNIA 22	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	77 4	
\$1KNA 32	RNA 33	3'-UUCCGGAAAGUGAUGAGGAUG-5'	//.4	-
siRNA 33	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	77 (	0.2
	RNA 34	3'-UUCCGGAAAGUGAUGAGGAUG-5'	//.0	0.2

**Table S8**. Sequences of ssRNAs, siRNAs, and  $T_{\rm m}$  values of siRNAs.

<sup>*a*</sup>Blue and red letters denote 2'-O-methylnucleosides and (S)-5'-C-aminopropyl-2'-O-methylnucleosides, respectively.

<sup>*b*</sup>The  $T_{\rm m}$  values were determined using 3  $\mu$ M dsRNA in a buffer containing 10 mM sodium phosphate (pH of 7.0) and 100 mM NaCl. <sup>*c*</sup> $\Delta T_{\rm m}$  represents [ $T_{\rm m}$  (siRNA<sub>(S)-5'-C-aminopropyl-2'-O-methyl</sub>) –  $T_{\rm m}$  (siRNA<sub>2'-O-methyl</sub>)].

Abbreviation of	Abbreviation of	Passenger strand (5'-3') <sup><i>a</i></sup>	$T_{\rm m}$ (°C) <sup>b</sup>	$\Delta T_{\rm m}$ (°C) <sup>c</sup>
siRNA	ssRNA	Guide strand (3'-5')		
GDNA 24	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	77.0	-
SININA 54	RNA 35	3'-UUCCGGAAAGUGAUGAGGAUG-5'	11.9	
GDNA 25	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	79 /	0.5
SIKINA 33	RNA 36	3'-UUCCGGAAAGUGAU <mark>G</mark> AGGAUG-5'	/ 8.4	
siRNA 36	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	9 רד	-
	RNA 37	3'-UUCCGGAAAGUGAUGAGGAUG-5'	//.8	
siRNA 37	RNA 1	5'-GGCCUUUCACUACUCCUACUU-3'	27.2	0.5
	RNA 38	3'-UUCCGGAAAGUGA <mark>U</mark> GAGGAUG-5'	//.3	-0.5

**Table S9**. Sequences of ssRNAs, siRNAs, and  $T_m$  values of siRNAs.

<sup>*a*</sup>Blue and red letters denote 2'-O-methylnucleosides and (S)-5'-C-aminopropyl-2'-O-methylnucleosides, respectively.

<sup>b</sup>The T<sub>m</sub> values were determined using 3 µM dsRNA in a buffer containing 10 mM sodium phosphate (pH of 7.0) and 100 mM NaCl.

<sup>*c*</sup> $\Delta T_{\rm m}$  represents  $[T_{\rm m} ({\rm siRNA}_{(S)-5'-C-{\rm aminopropyl-2'-O-methyl}}) - T_{\rm m} ({\rm siRNA}_{2'-O-{\rm methyl}})].$ 



**Figure S5**. UV melting profiles of the unmodified and modified siRNAs in a buffer containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



**Figure S6**. UV melting profiles of the unmodified and modified siRNAs in a buffer containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



**Figure S7**. UV melting profiles of the unmodified and modified siRNAs in a buffer containing 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl.



**Figure S8**. Models of the complex of Argonaute-2 and guide strand positions 6–8 of siRNA based on the crystal structure with a guide and passenger strand duplex (PDB ID code: 4W5O)<sup>1</sup>. (A) unmodified siRNA, (B) modeling structure obtained on substitution with (*S*)-5'-*C*-aminopropyl-2'-*O*-methyl modification at guide strand position 7. As shown, the guide strand position 7 colored yellow (A) and green (B).

(B)

#### **Molecular Modeling Method**

The model of the complex between human Argonaute-2 and the seed region pairing of an siRNA were retrieved from the Protein Data Bank (ID code: 4W5O)<sup>1</sup>. The missing loops in the crystal structure of human Argonaute-2 and an siRNA were built with the MOE (Molecular Operating Environment) program using the "Loop modeler." Subsequently, the (*S*)-5-*C*-aminopropyl-2-*O*-methyl modification was built with the MOE program using the structure-editing tool "Builder." All modeling structures were energy-minimized by MOE using the Amber 14 force field.

#### Reference.

 N. T. Schirle, J. Sheu-Gruttadauria, I. J. MacRae. Structural basis for microRNA targeting. *Science*, 2014, **346**, 608–613.

# NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and NOESY)



<sup>1</sup>H NMR spectrum of compound 6

 $^{13}C{^{1}H}NMR$  spectrum of compound 6







 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound 7



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# $^{1}\text{H}$ NMR spectrum of compound **8**



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{8}$ 





 $^{13}C{^{1}H}NMR$  spectrum of compound 9



 $^{1}\text{H}$  NMR spectrum of compound 10



 $^{13}C\{^{1}H\}NMR$  spectrum of compound 10



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<sup>1</sup>H NMR spectrum of compound **11** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound 11





<sup>1</sup>H NMR spectrum of compound **12** ( $\beta$ -anomer)



 $^{13}C{^{1}H}NMR$  spectrum of compound **12** ( $\beta$ -anomer)



 $^{1}\text{H}$  NMR spectrum of compound **13** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound 13



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<sup>1</sup>HNMR spectrum of compound **14** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound 14







 $^{13}C{^{1}H}NMR$  spectrum of compound 15





 $^{13}C{^{1}H}NMR$  spectrum of compound 16



<sup>1</sup>H NMR spectrum of compound **17** 



 $^{13}C{^{1}H}NMR$  spectrum of compound 17





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\mathbf{18}$ 





 $^{113}C{^{1}H}NMR$  spectrum of compound **19** 





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\mathbf{20}$ 





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\boldsymbol{21}$ 



<sup>31</sup>P NMR spectrum of compound **22** 





 $^{13}C\{^{1}H\}NMR$  spectrum of compound  ${\bf 23}$ 



<sup>1</sup>H NMR spectrum of compound **24** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound  $\bf 24$ 





 $^{113}C\{^{1}H\}NMR$  spectrum of compound  $\mathbf{25}$ 





 $^{13}C\{^{1}H\}NMR$  spectrum of compound 26



<sup>1</sup>H NMR spectrum of compound **27** 



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound 27





 $^{13}C\{^{1}H\}NMR$  spectrum of compound  ${\bf 28}$ 





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\mathbf{29}$ 



<sup>1</sup>H NMR spectrum of compound **30** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound  ${\bf 30}$ 



<sup>1</sup>H NMR spectrum of compound **31** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound  $\boldsymbol{31}$ 



 $^{1}H$  NMR spectrum of compound **32** 



 $^{13}C\{^{1}H\}NMR$  spectrum of compound  $\boldsymbol{32}$ 



<sup>31</sup>P NMR spectrum of compound **33** 





 $^{13}C{^{1}H}NMR$  spectrum of compound 34



NOESY spectrum of compound 34





 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}\mathrm{NMR}$  spectrum of compound  $\mathbf{35}$ 



# NOESY spectrum of compound 35

