

Supporting Information

Unexpected Insertion of CO₂ into Pentacoordinate P-N bond: the Atherton-Todd-Type Reaction of Hydrospiroporphorane with Amines

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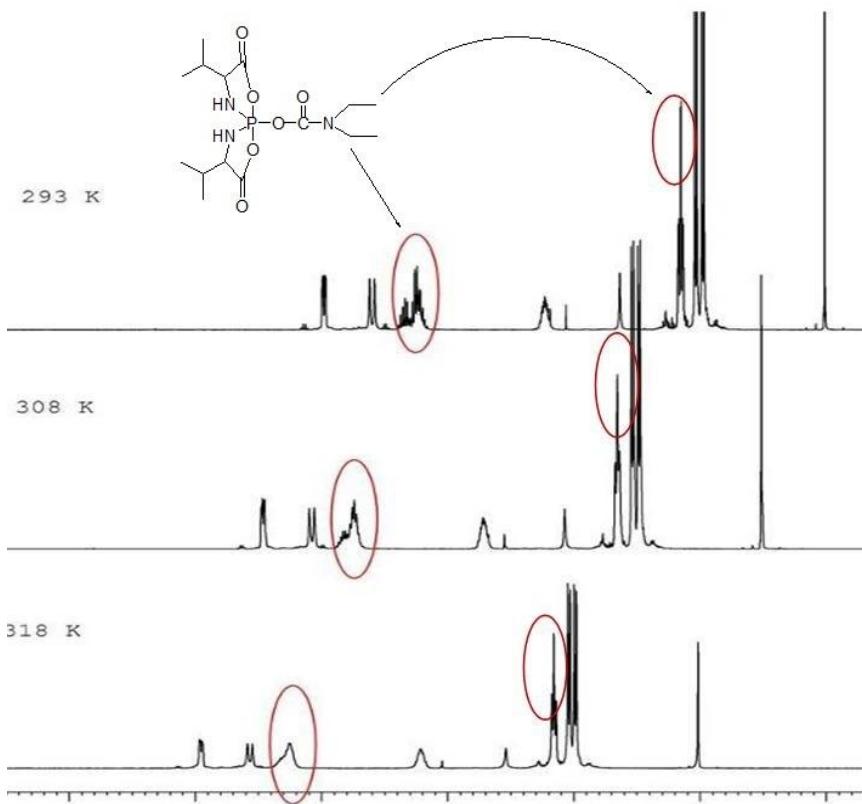
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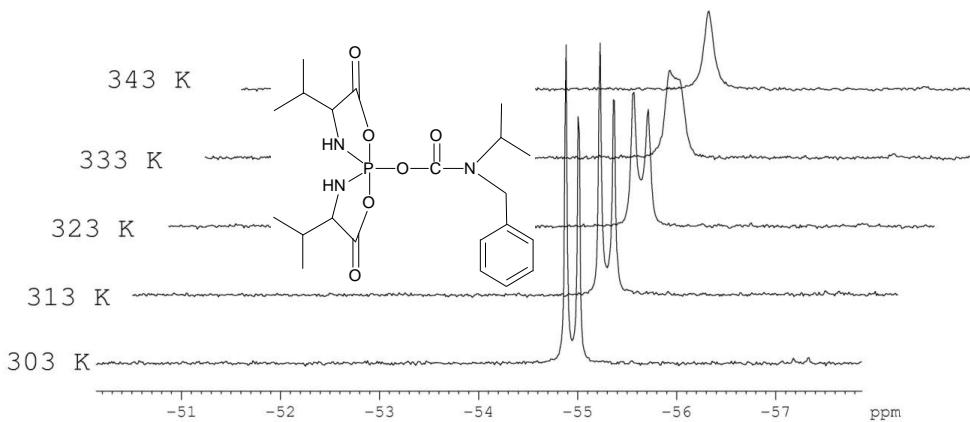
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1. The spectra of the temperature-dependent NMR dynamic experiment of 3a'1



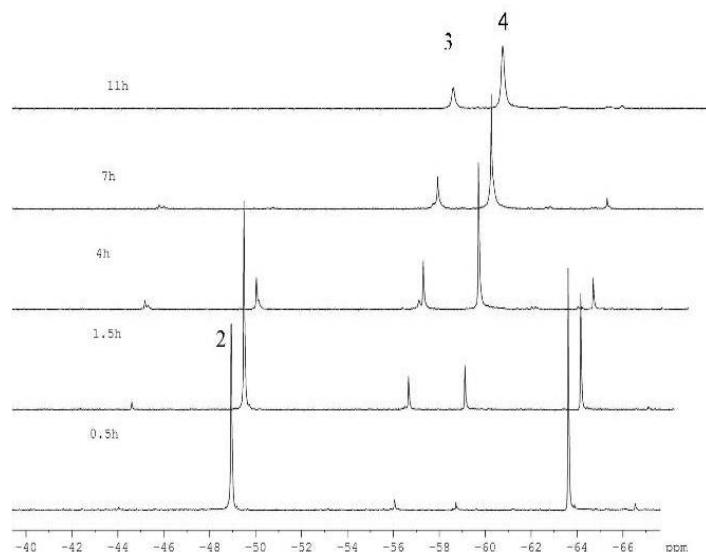
2. The spectra of the temperature-dependent NMR dynamic experiment of 3a'9



3. The ³¹P NMR tracing spectra of the CO₂ insertion reaction

To a stirred solution of compound **1a** (0.5 mmol) in CH₃CN (3 mL), CCl₄ (1.0 mmol), Et₃N (1.0 mmol) and K₂CO₃ (1.5 mmol) were successively added at room temperature in air atmosphere. The reaction mixture was stirred and the ³¹P NMR of reaction solution was determined at different reaction time. If the reaction proceeded in CO₂ atmosphere, no byproduct **4** was produced. However, the intermediate **2** transformed to the CO₂ insertion product so quickly that it could not be observed in the

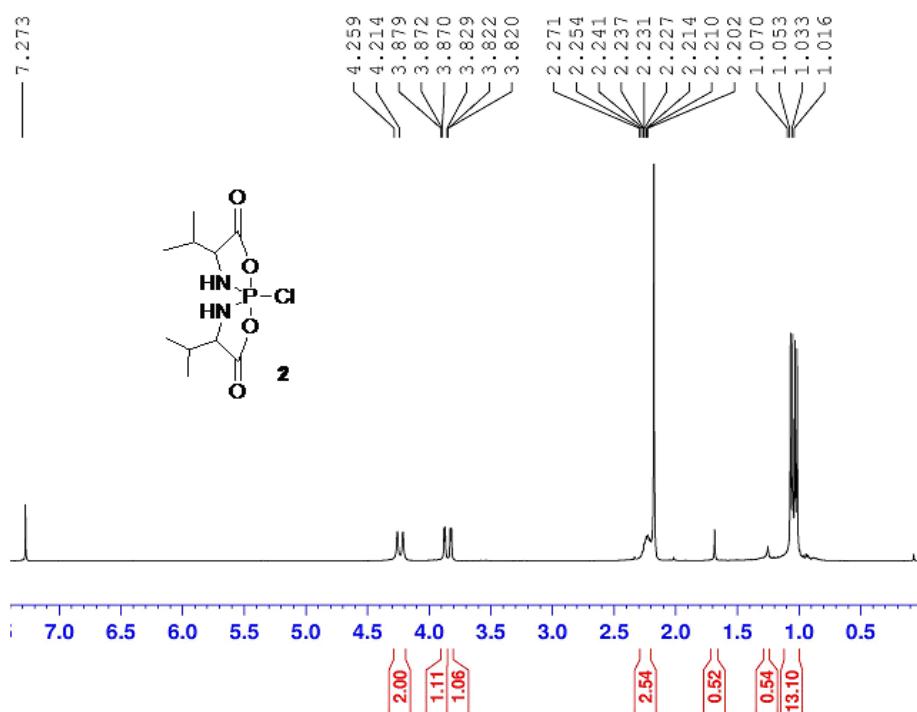
tracing spectra. Therefore, the ^{31}P NMR tracing spectra in air atmosphere is shown to prove the existence of intermediate **2**. After the intermediate **2a** was isolated, the reaction between the intermediate **2a** and diethyl amine in CO_2 atmosphere was also performed and the CO_2 insertion product **3a'1** could be obtained.



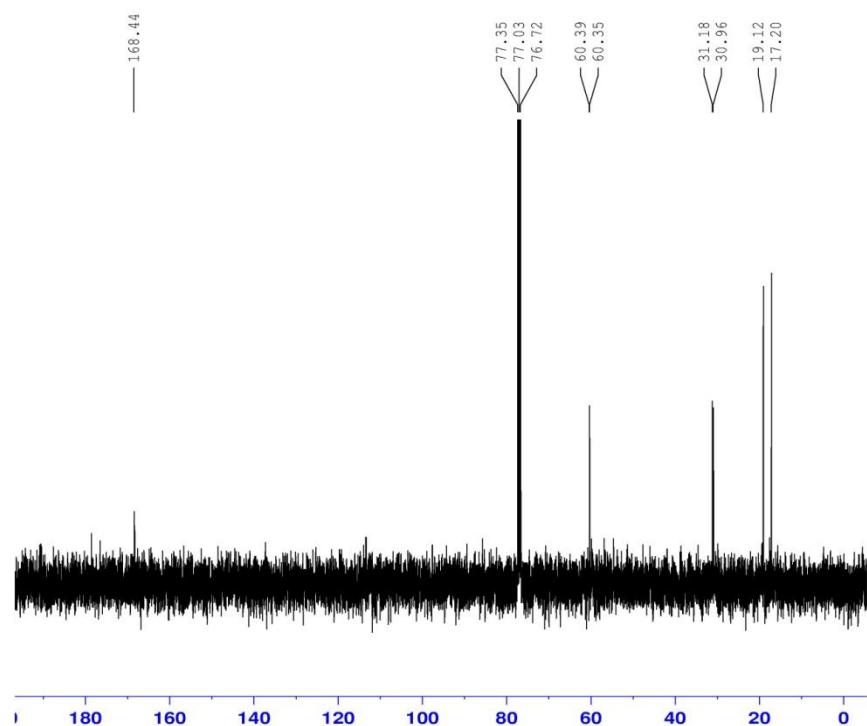
4. NMR Spectra for compound **2a**, **2b**, **2c'**

The NMR spectra were determined in CDCl_3 and IR spectra were measured by KBr pellets.

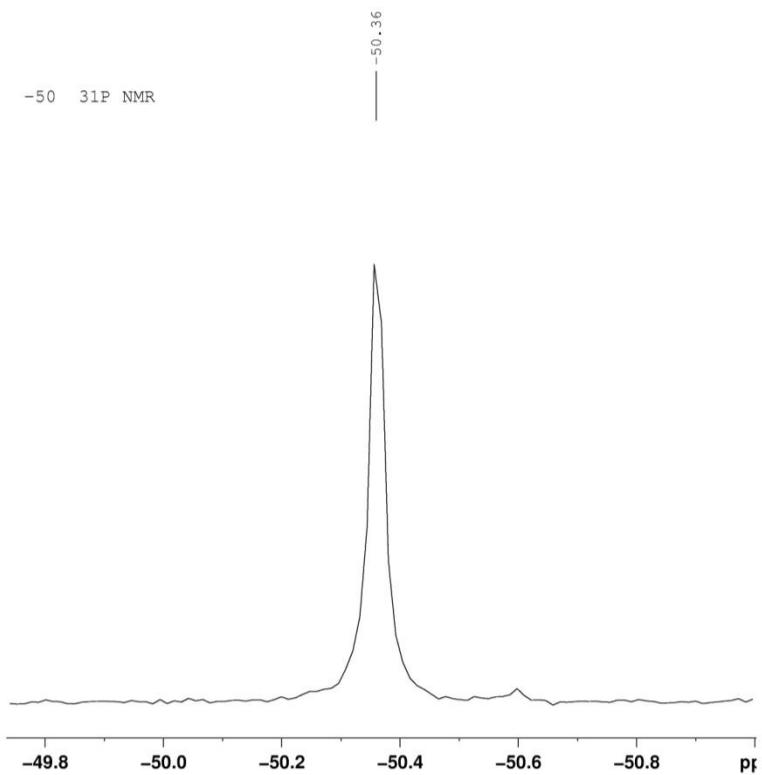
^1H NMR of **2a**



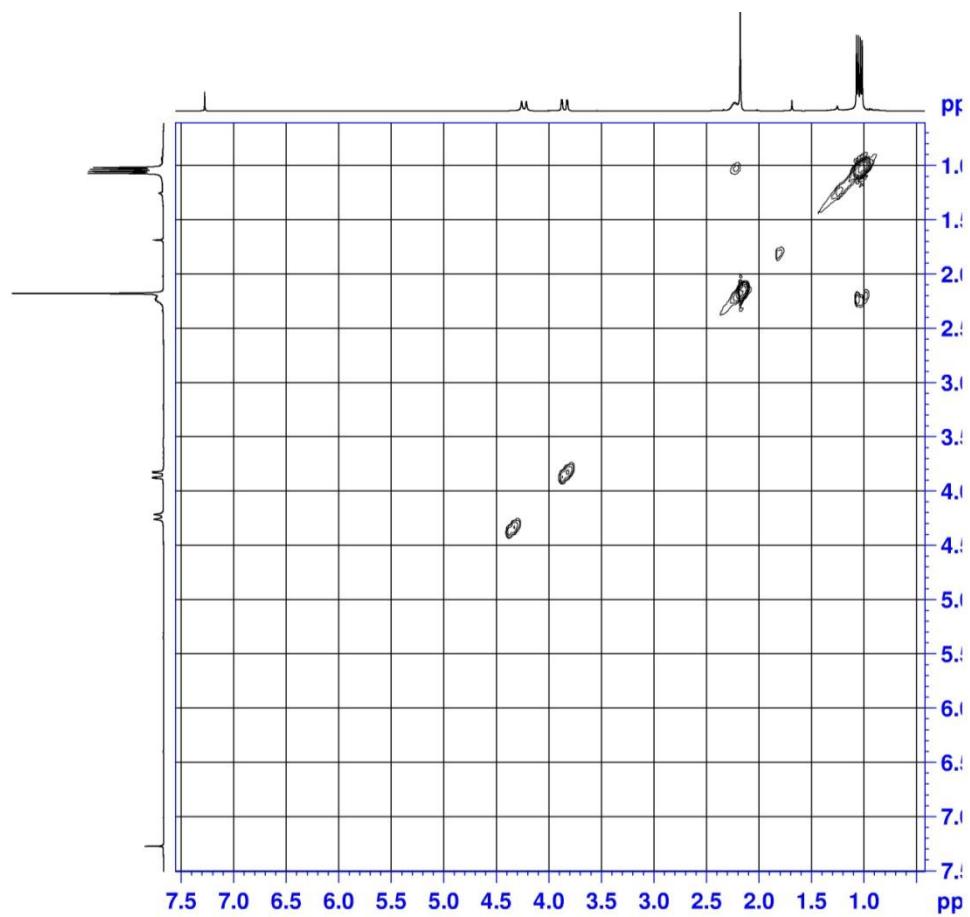
¹³C NMR of 2a



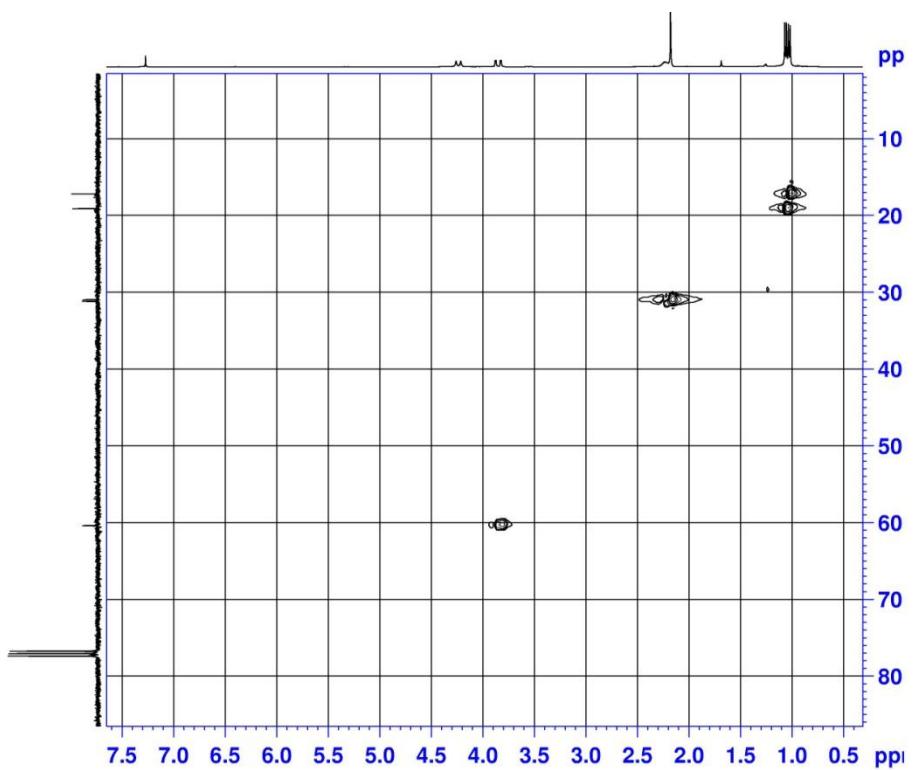
³¹P NMR of 2a



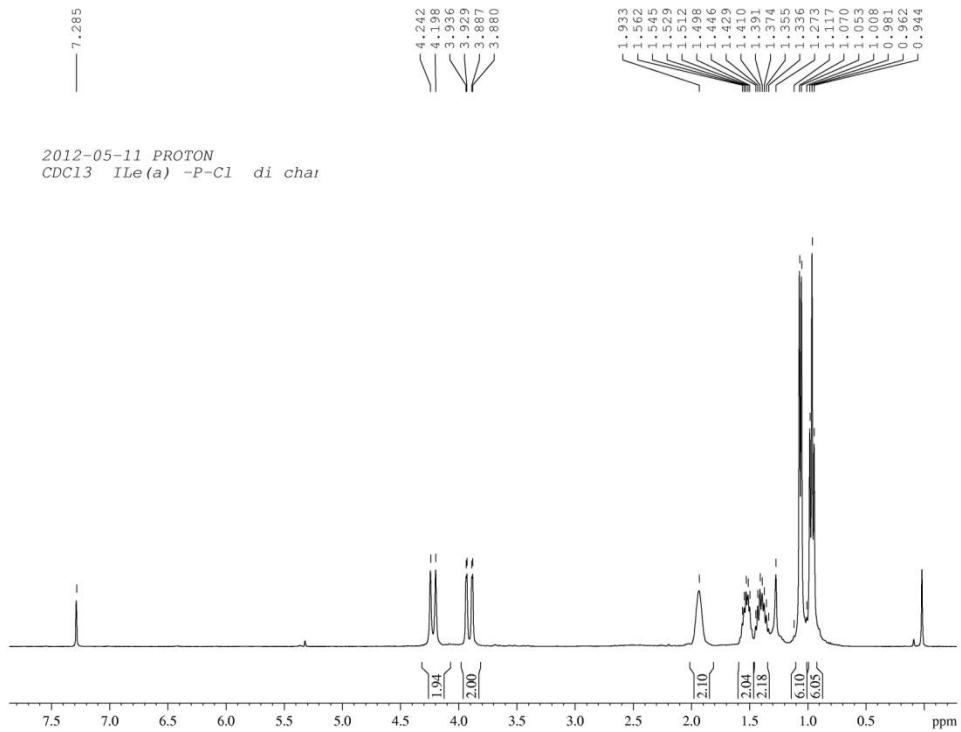
H-H COSY of 2a



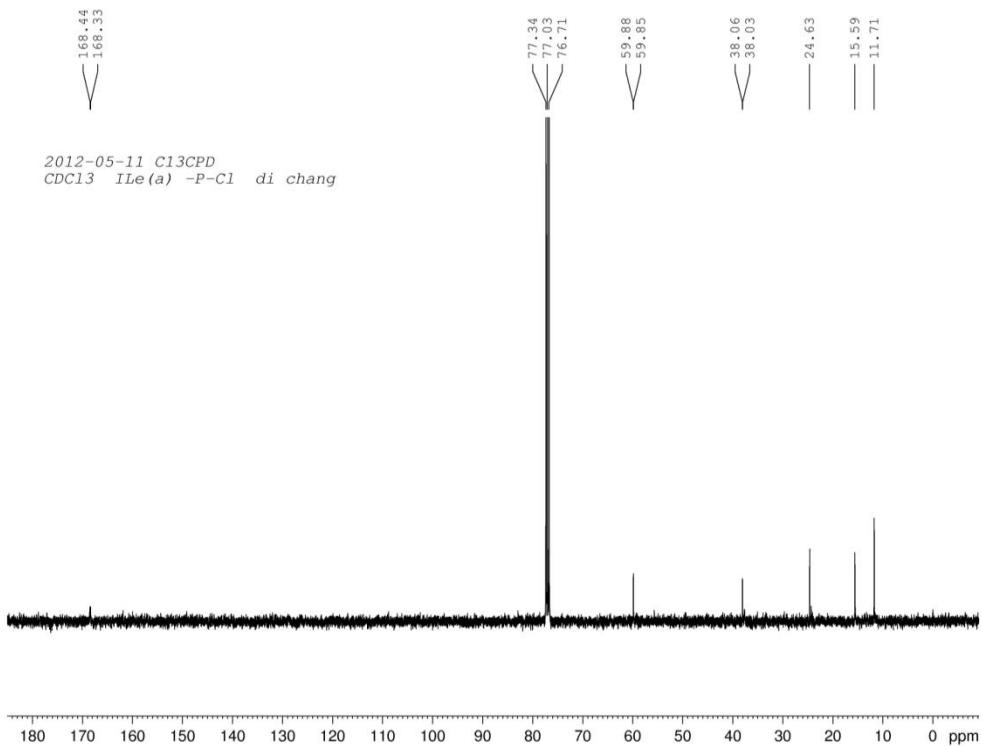
HSQC of 2a



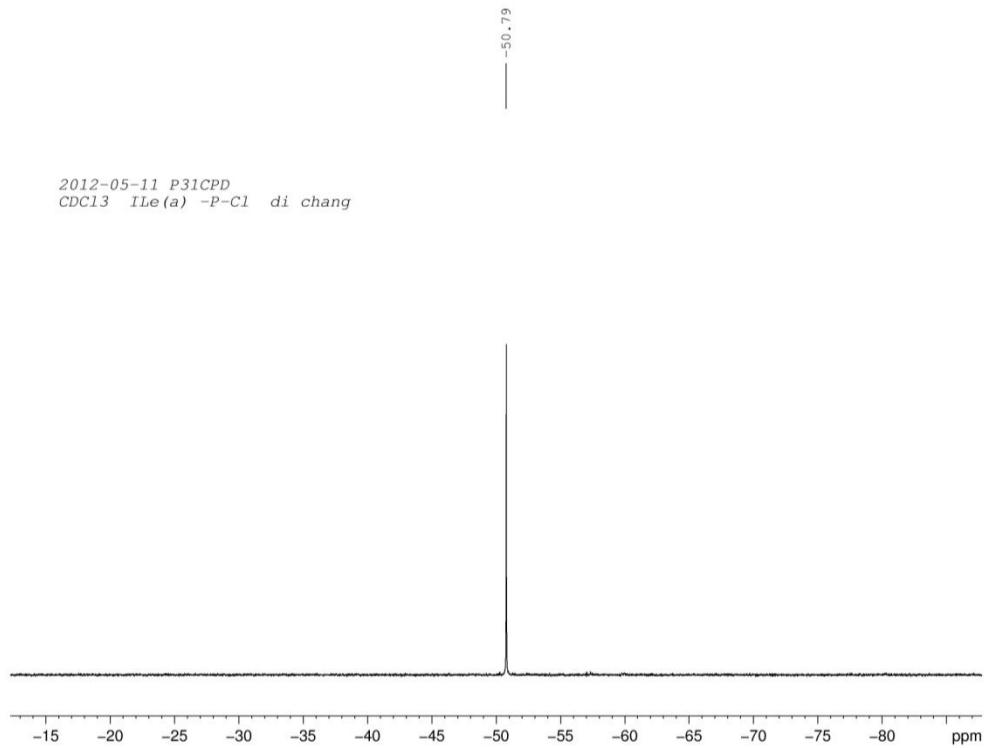
¹ H NMR of 2b



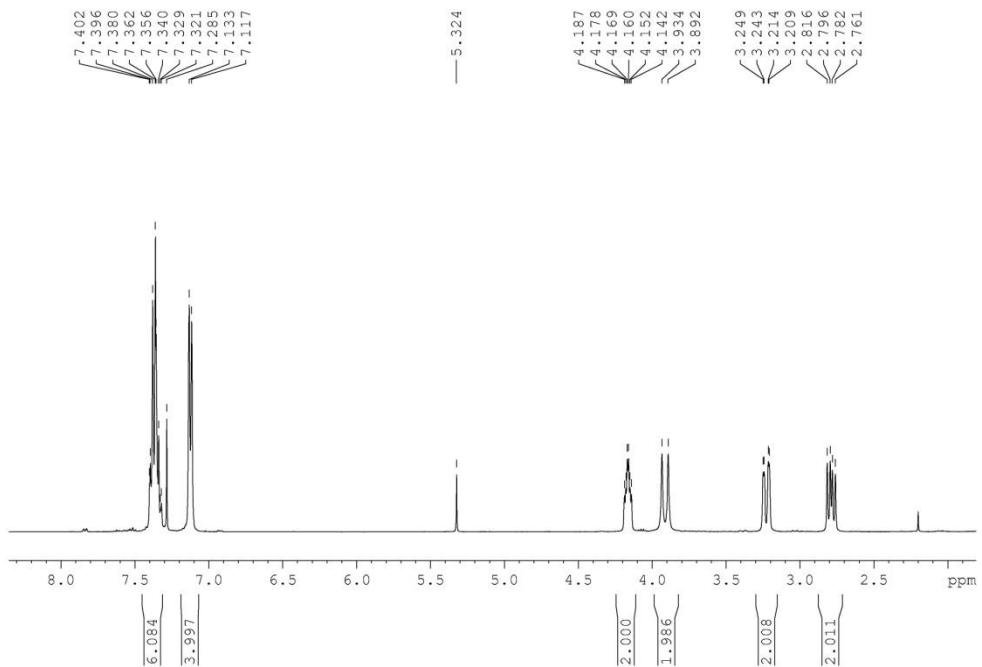
¹³ C NMR of 2b



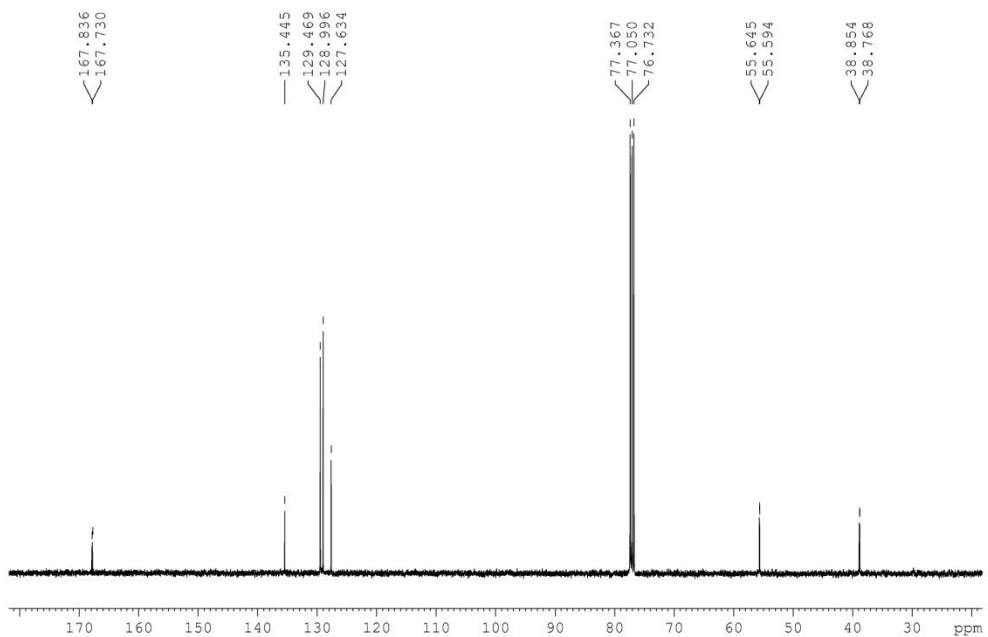
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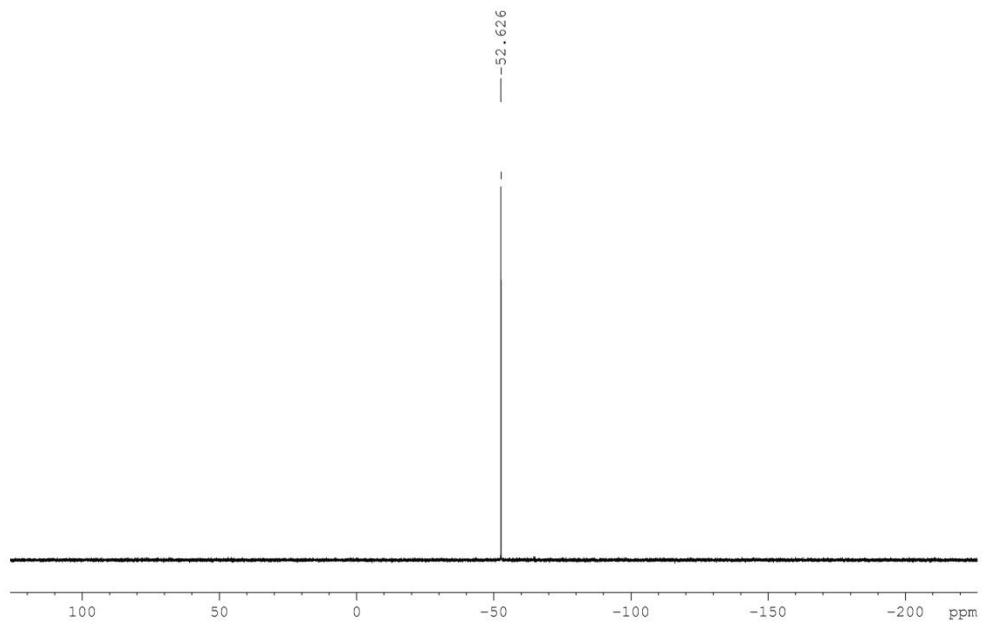
^1H NMR of 2c'



¹³C NMR of 2c'

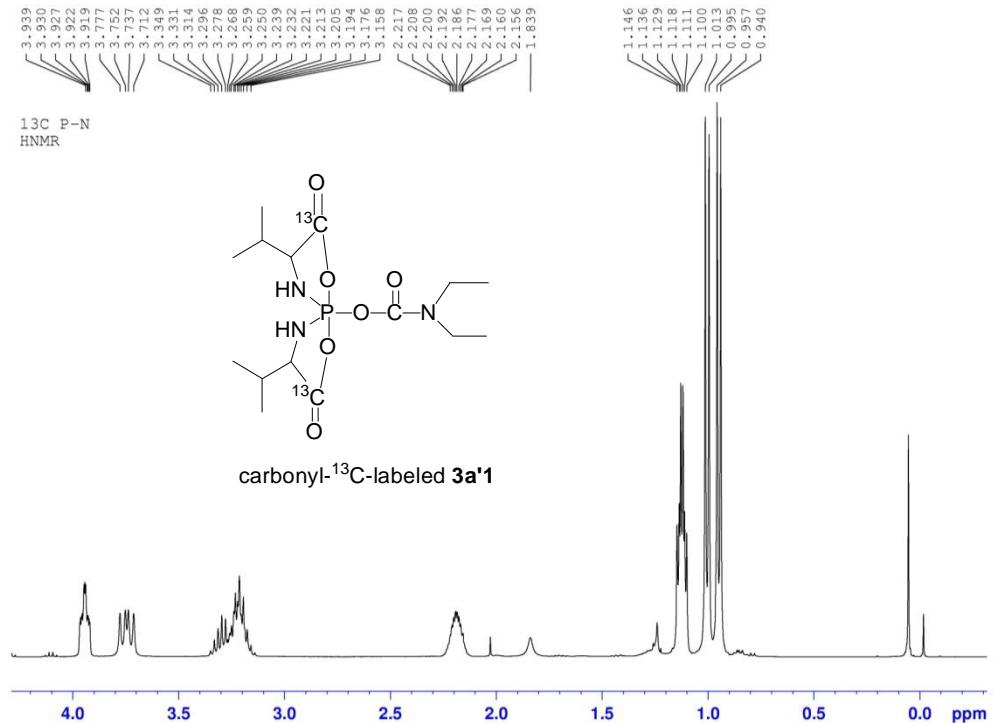


³¹P NMR of 2c'

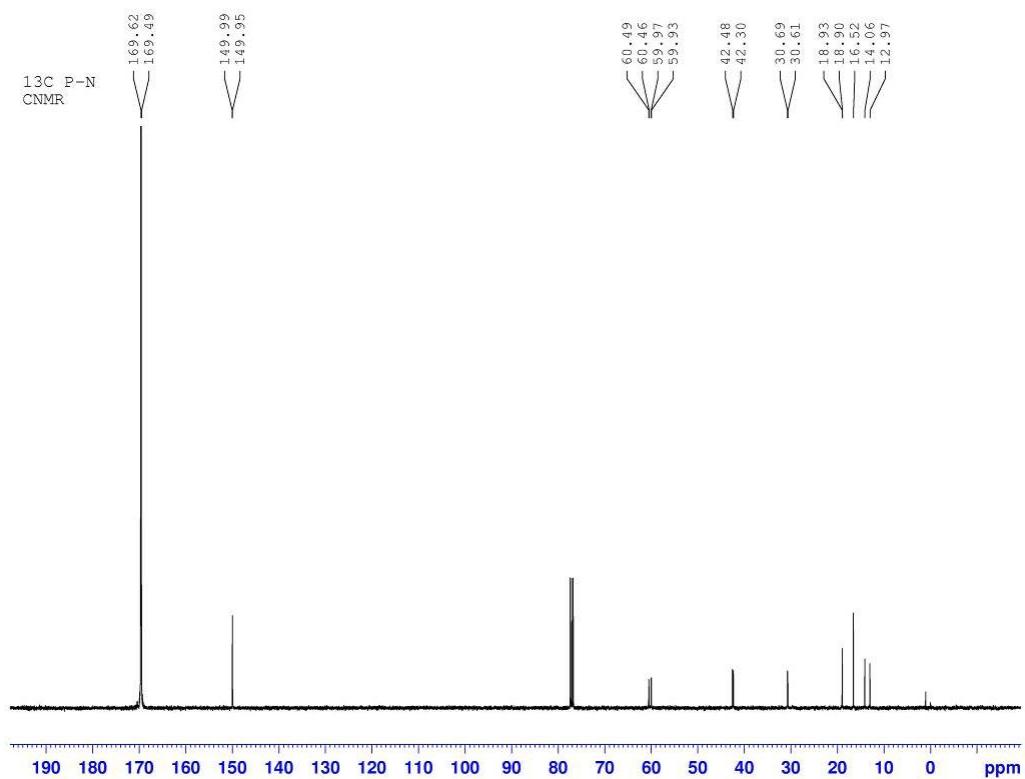


5. NMR and IR Spectra for compounds 3a'1-3a'11

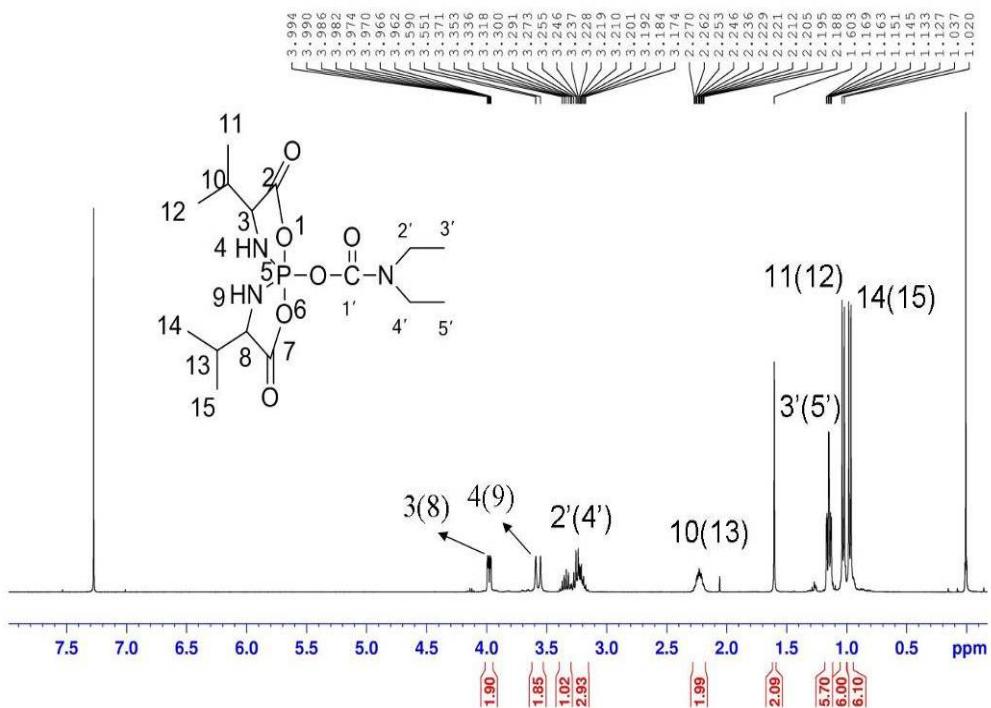
¹H NMR of carbonyl-¹³C-labeled 3a'1



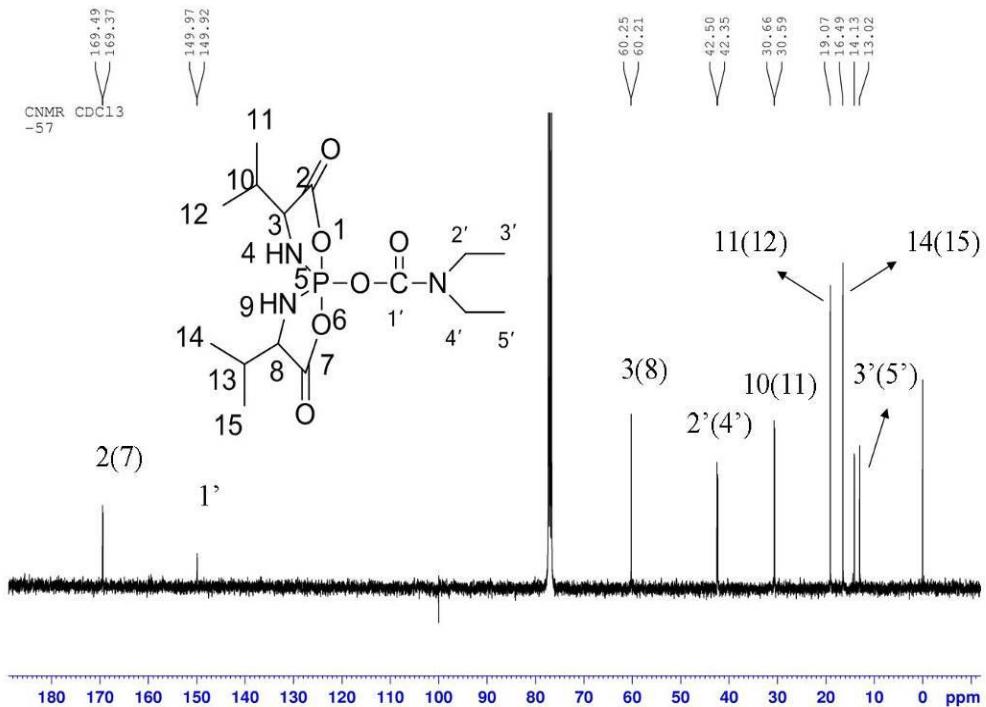
¹³C NMR of carbonyl-¹³C-labeled 3a'1



¹ H NMR of 3a'1

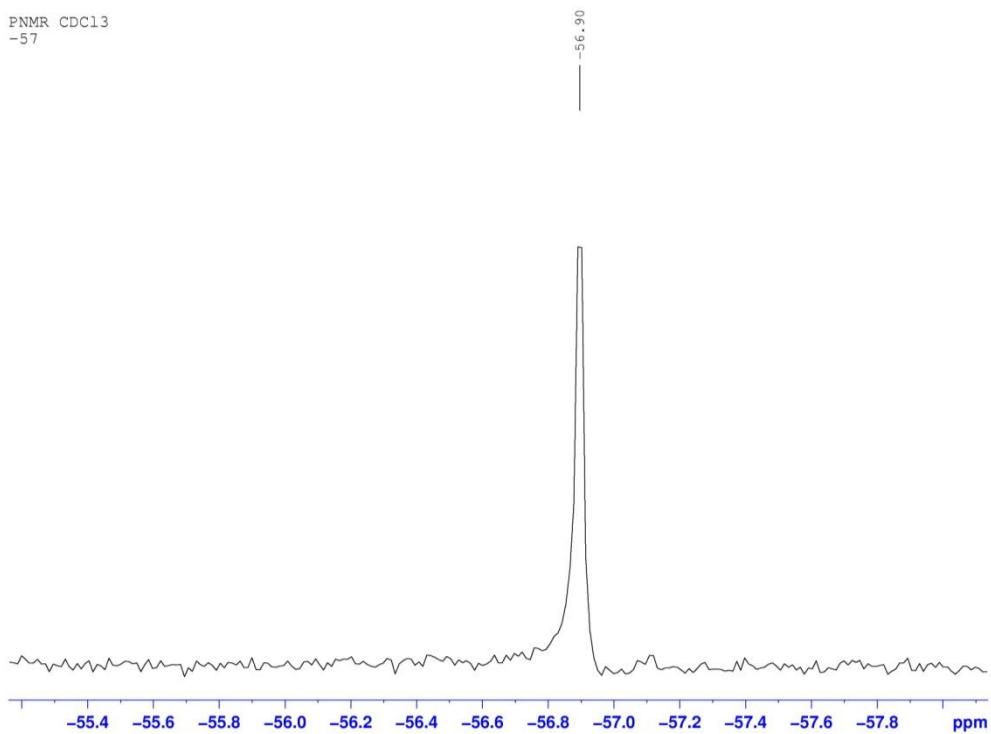


¹³C NMR of 3a'1



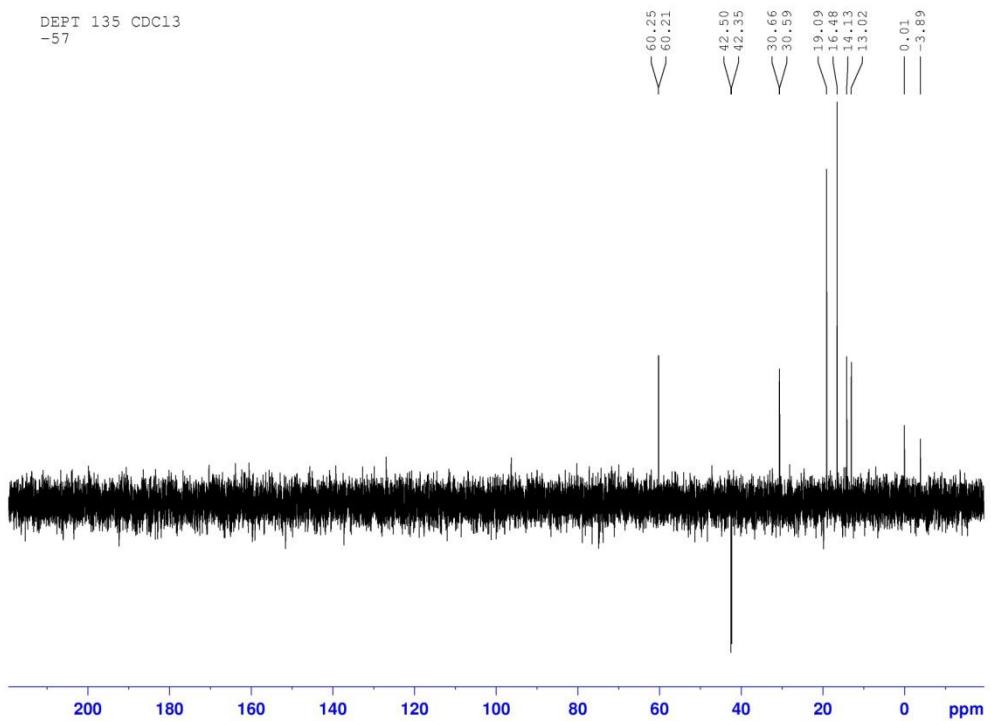
^{31}P NMR of 3a'1

PNMR CDC13
-57

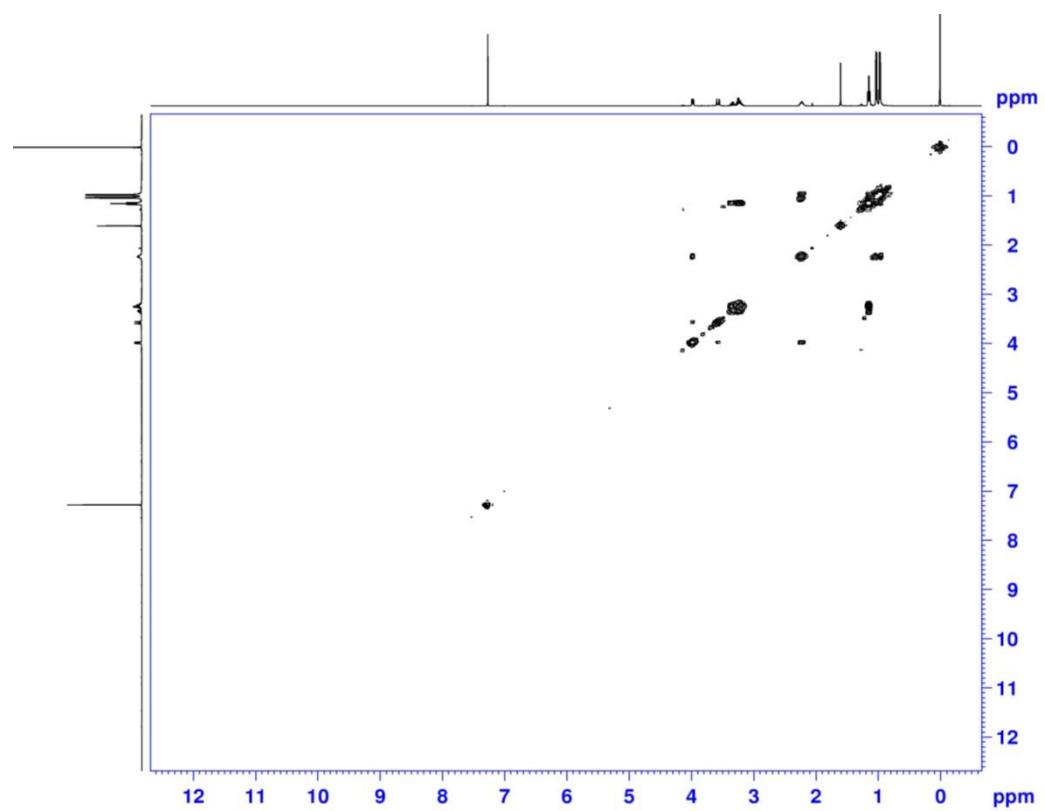


DEPT 135 NMR of 3a'1

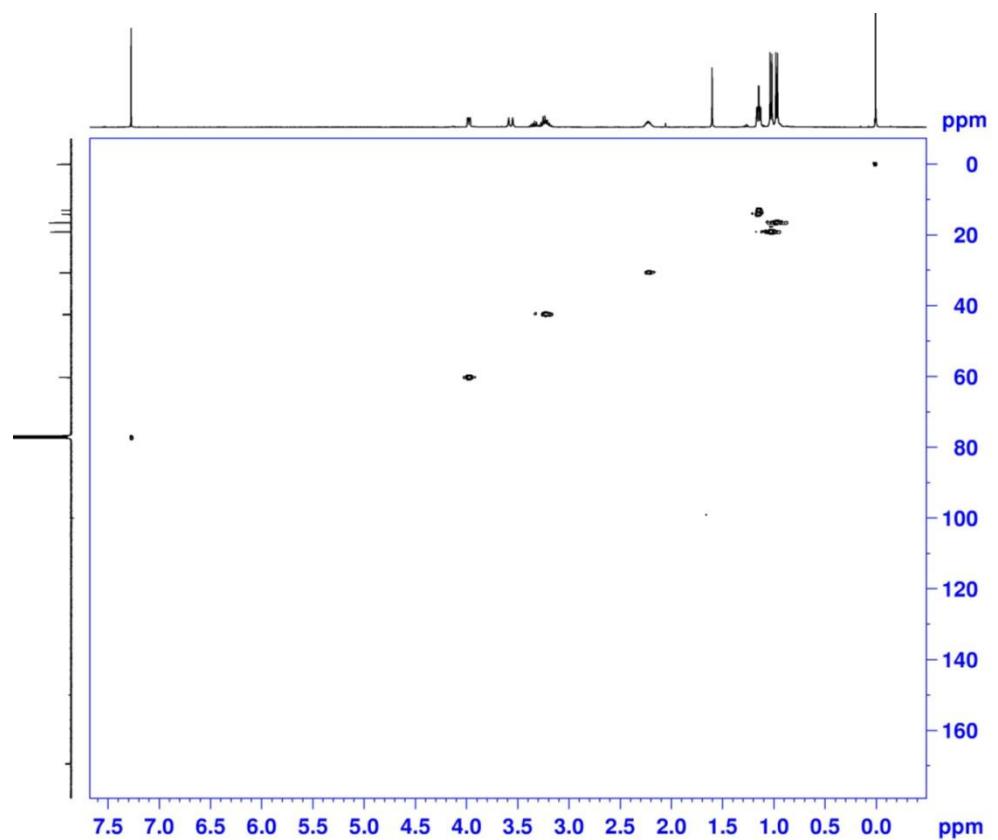
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-57



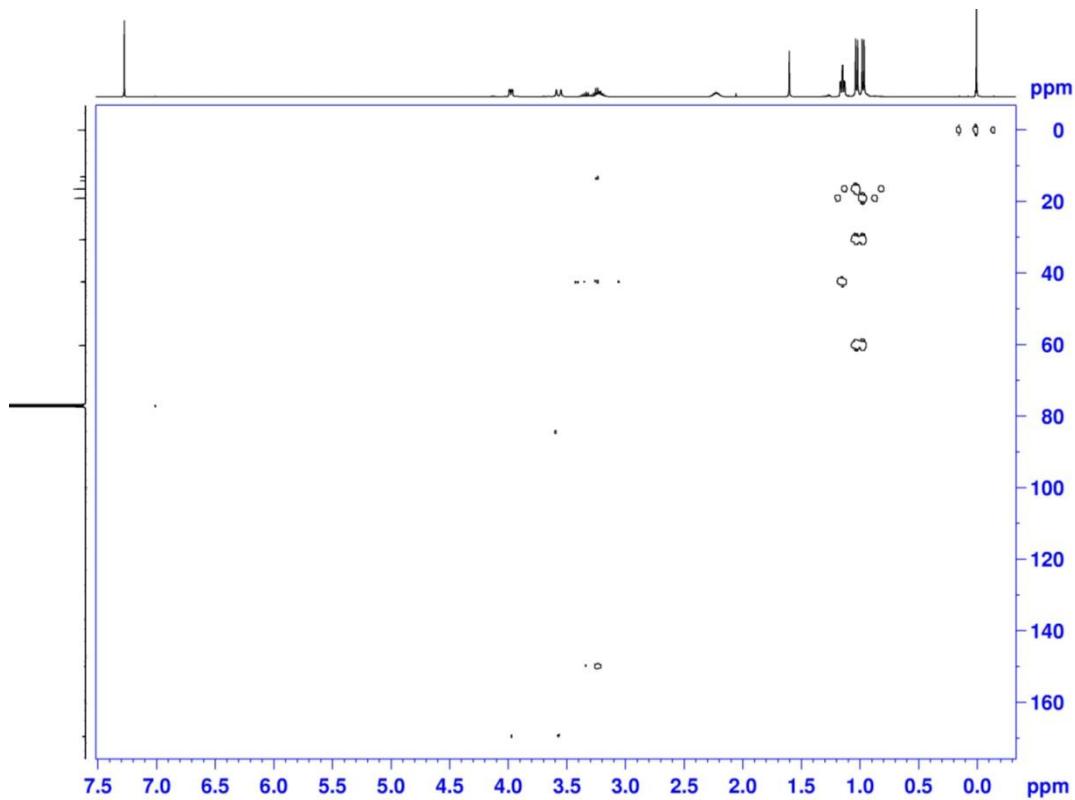
H-H COSY of 3a'1



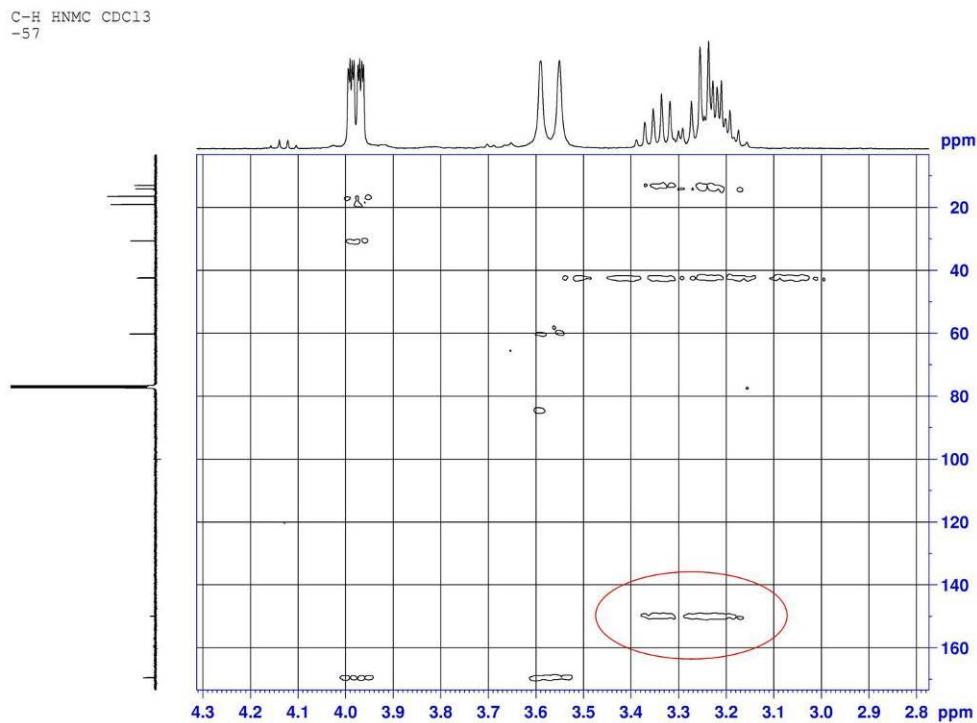
HSQC of 3a'1



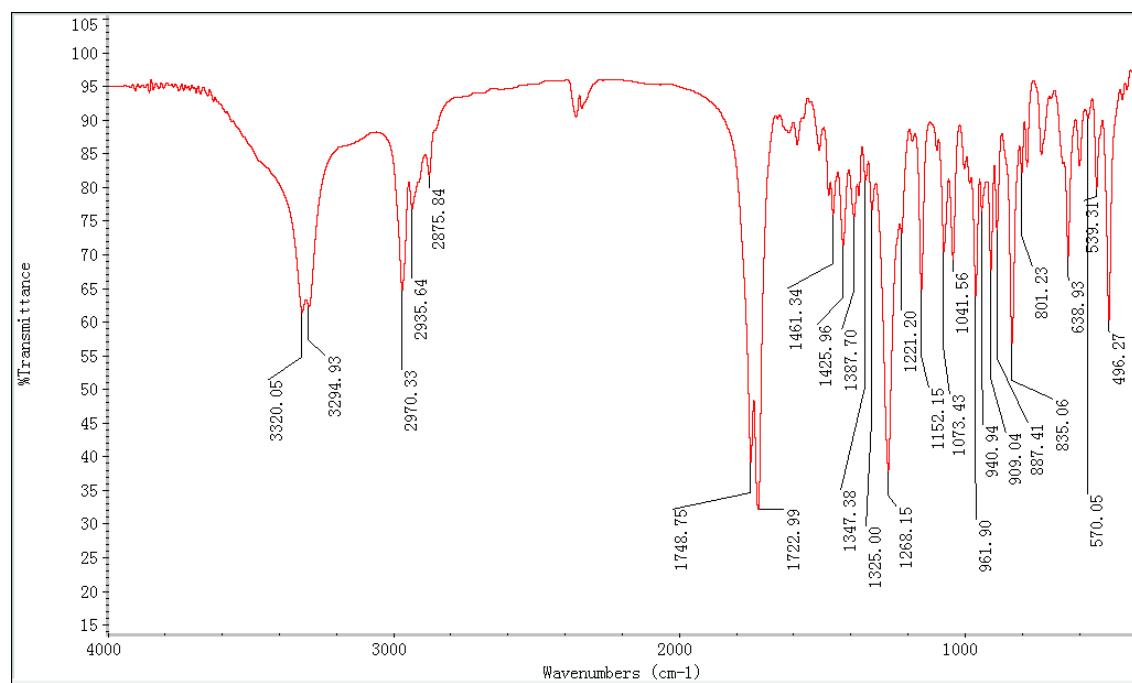
HMBC of 3a'1



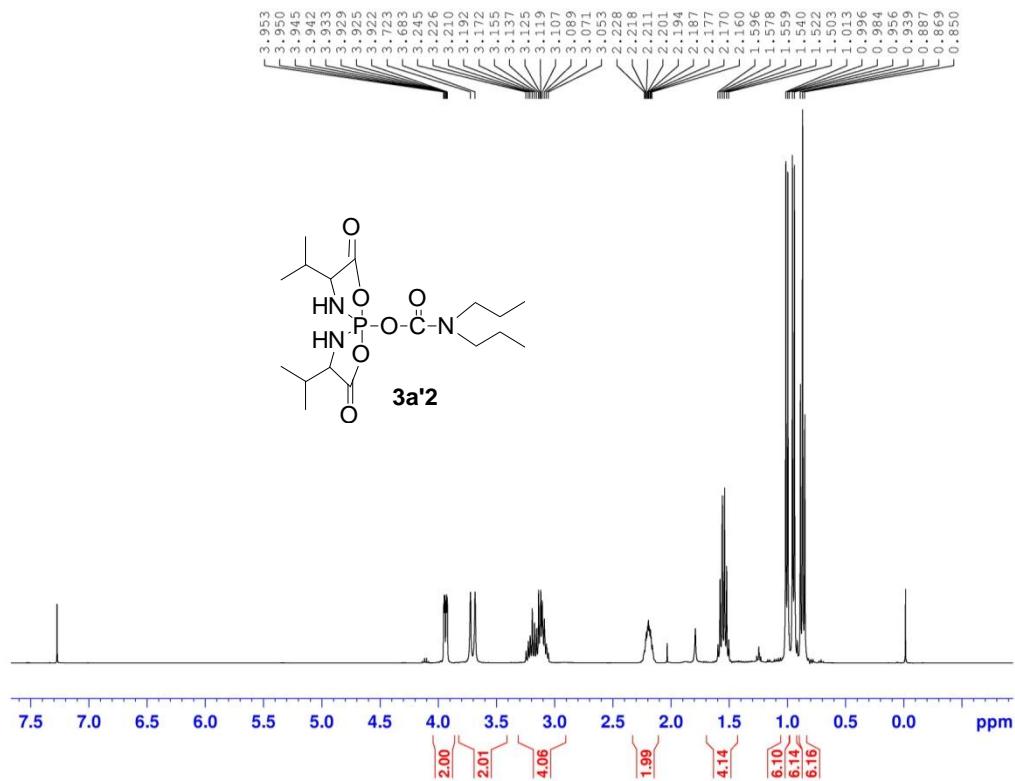
Enlarged HMBC of 3a'1



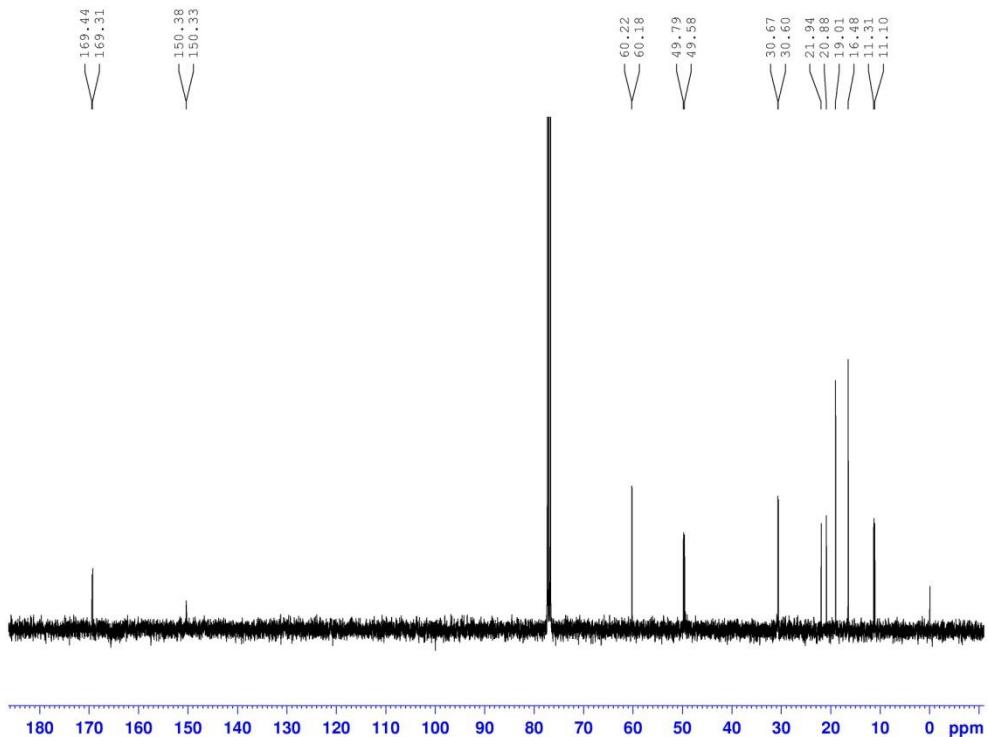
IR of 3a'1



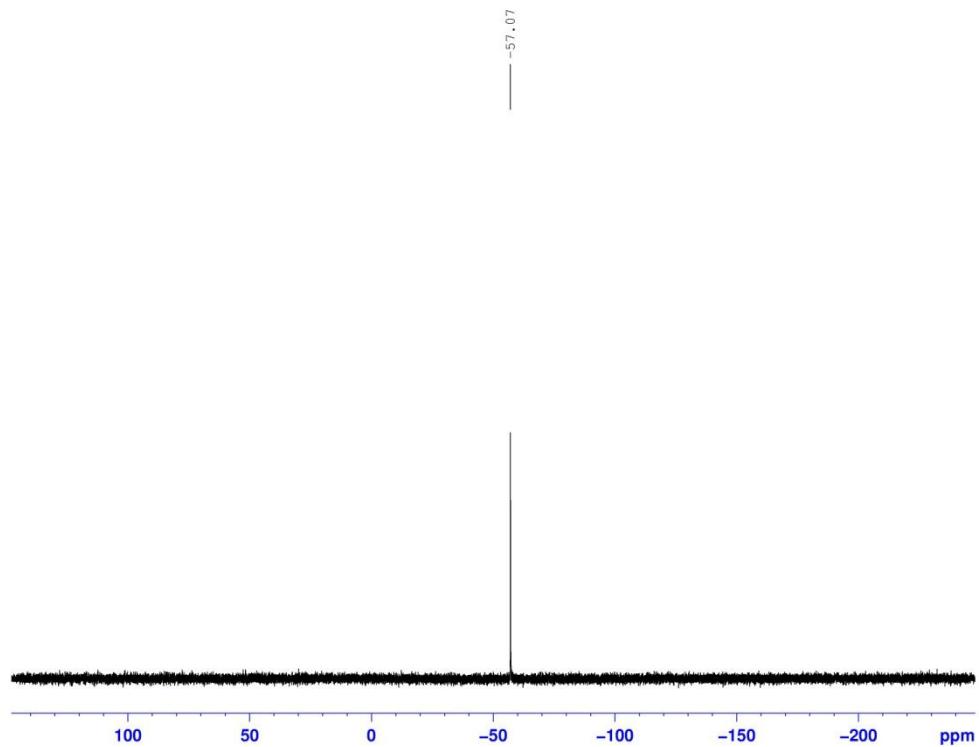
¹ H NMR of 3a'2



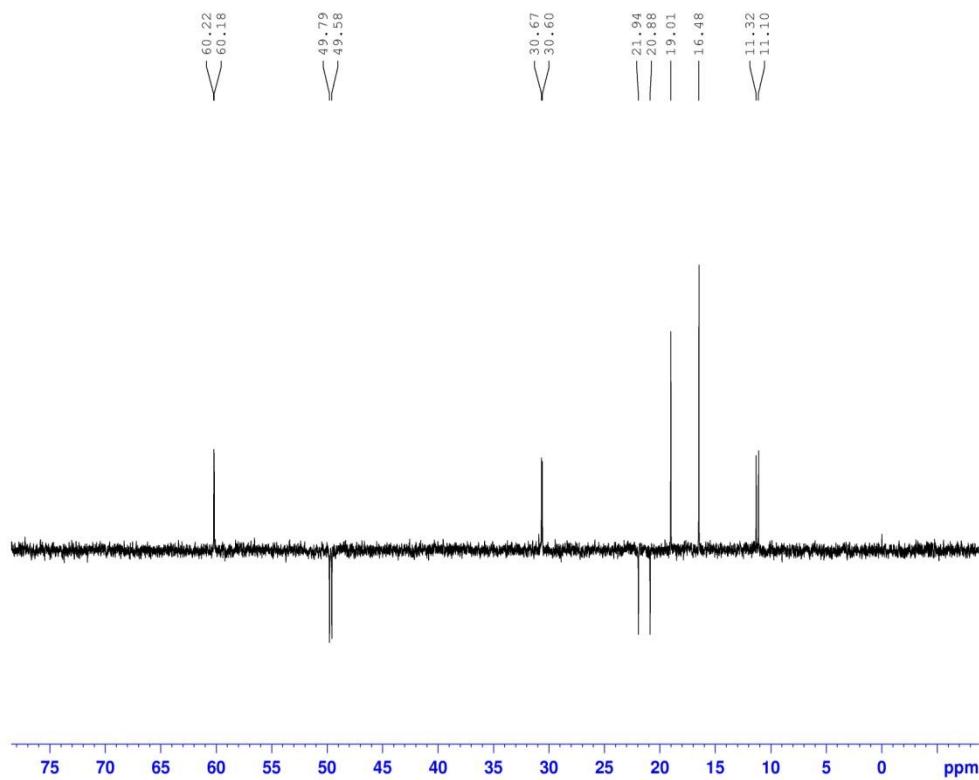
^{13}C NMR of 3a'2



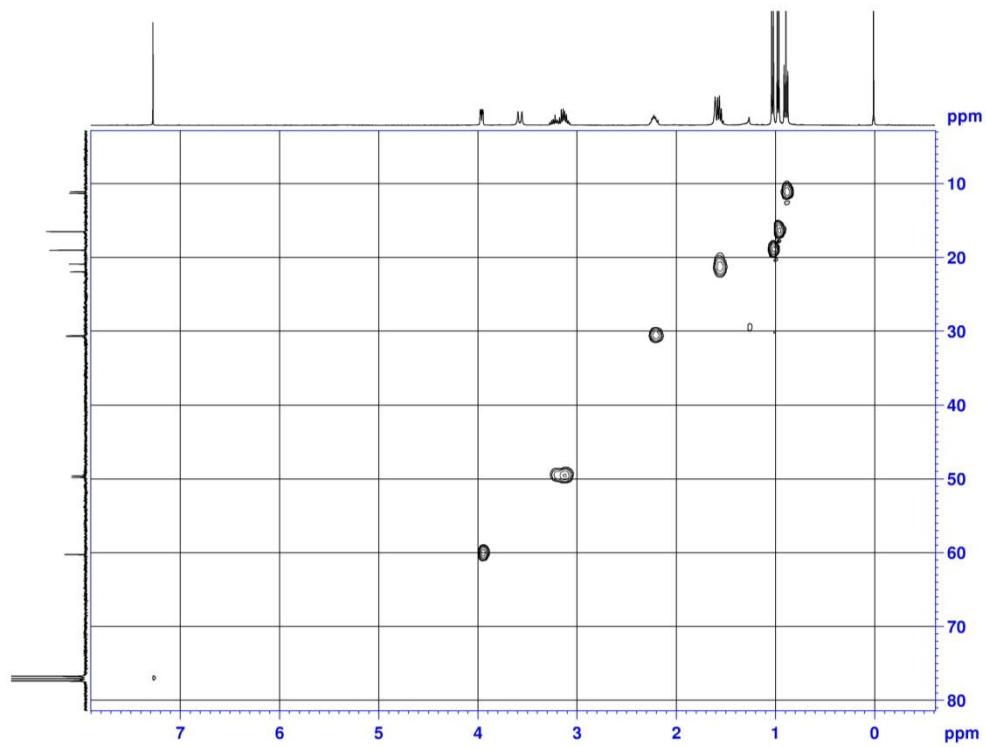
^{31}P NMR of 3a'2



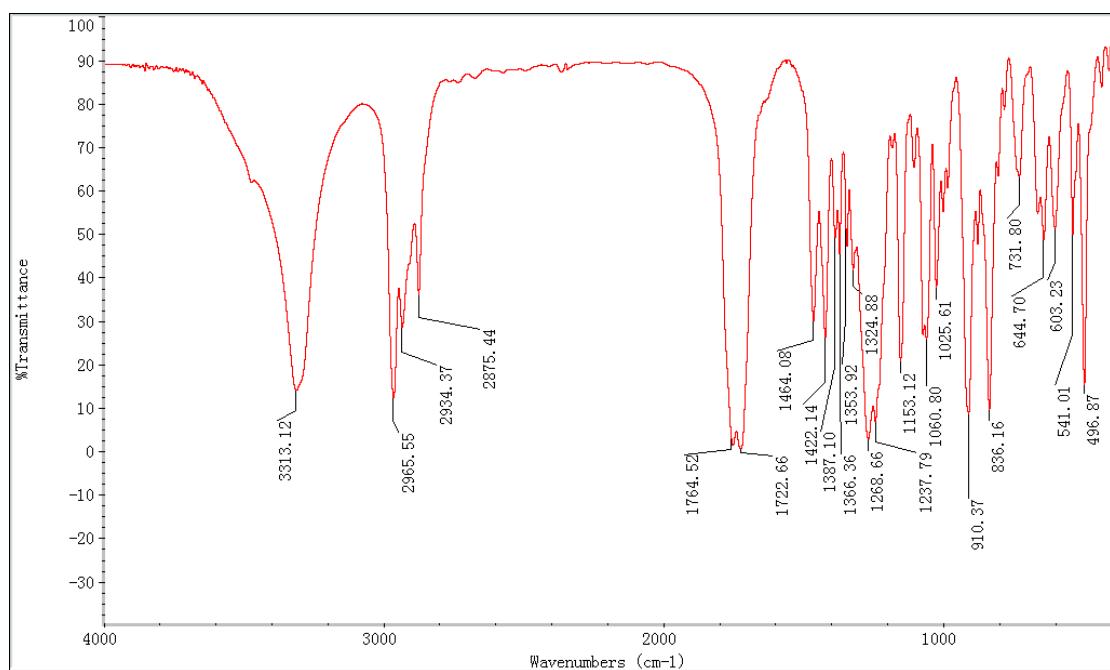
DEPT 135 of 3a'2



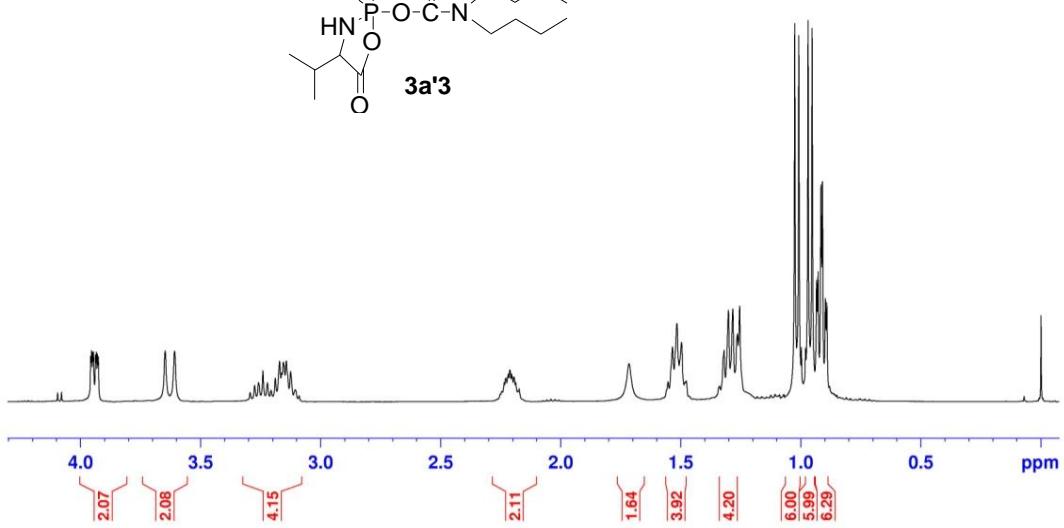
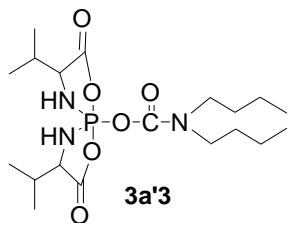
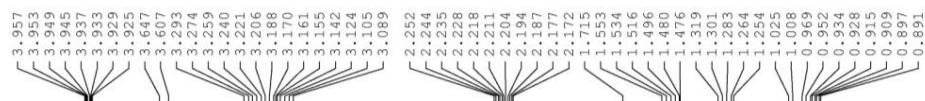
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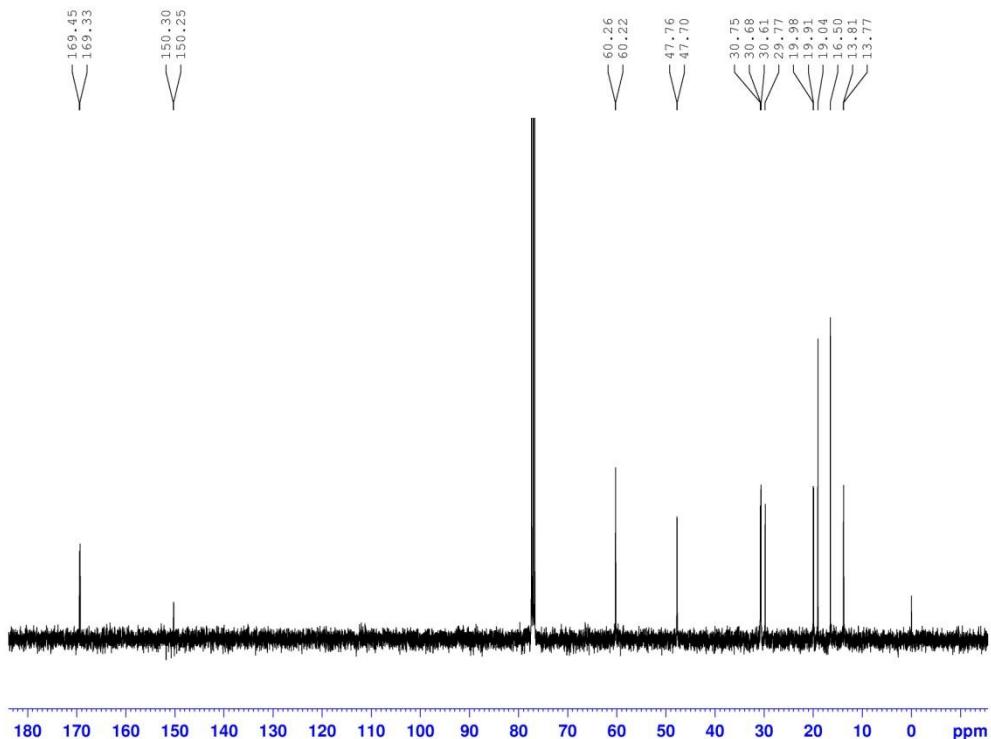
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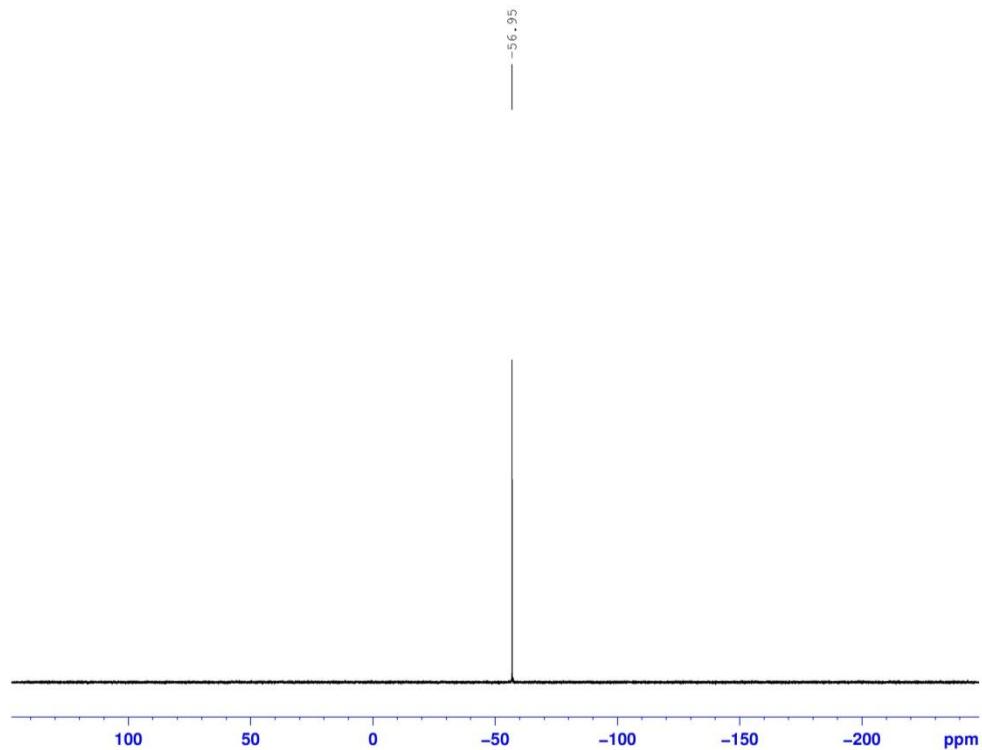
¹ H NMR of 3a'3



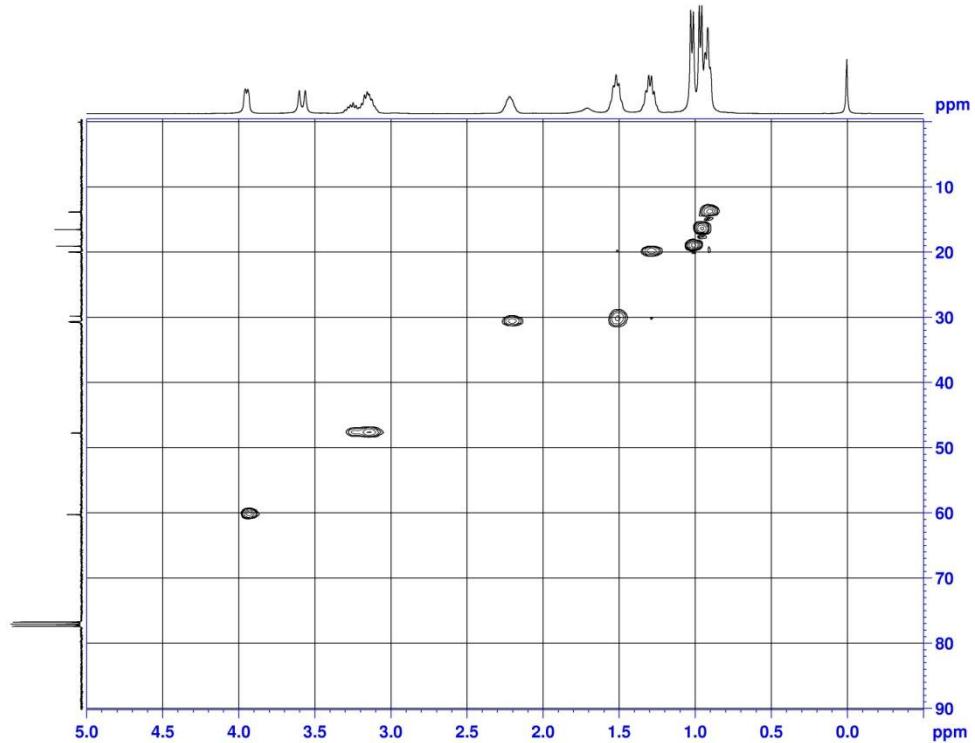
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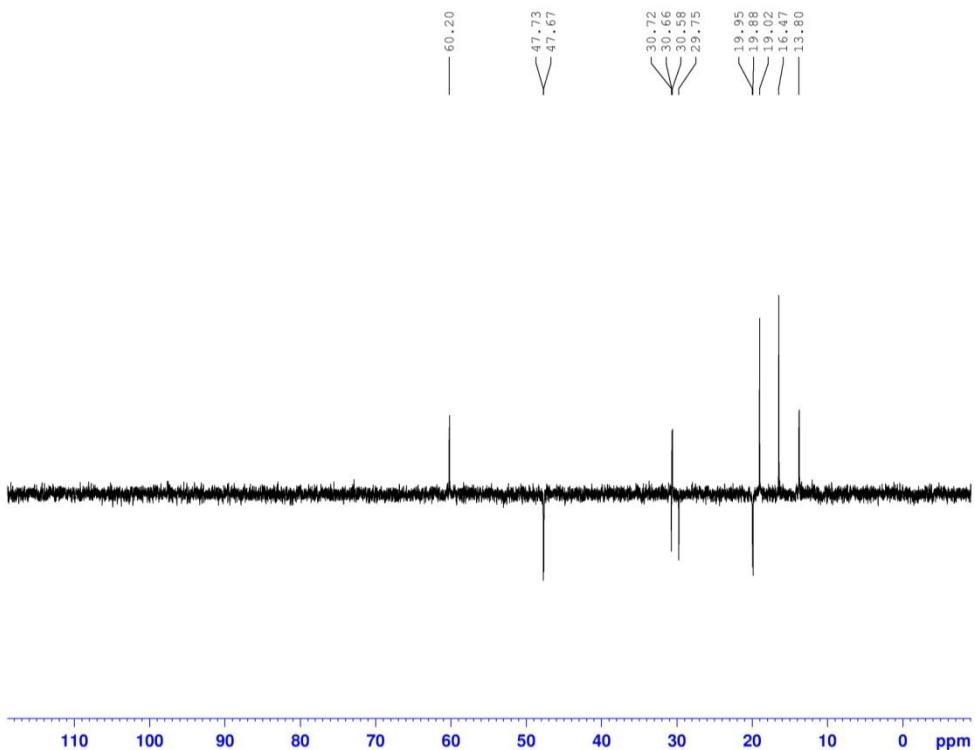
³¹P NMR of 3a'3



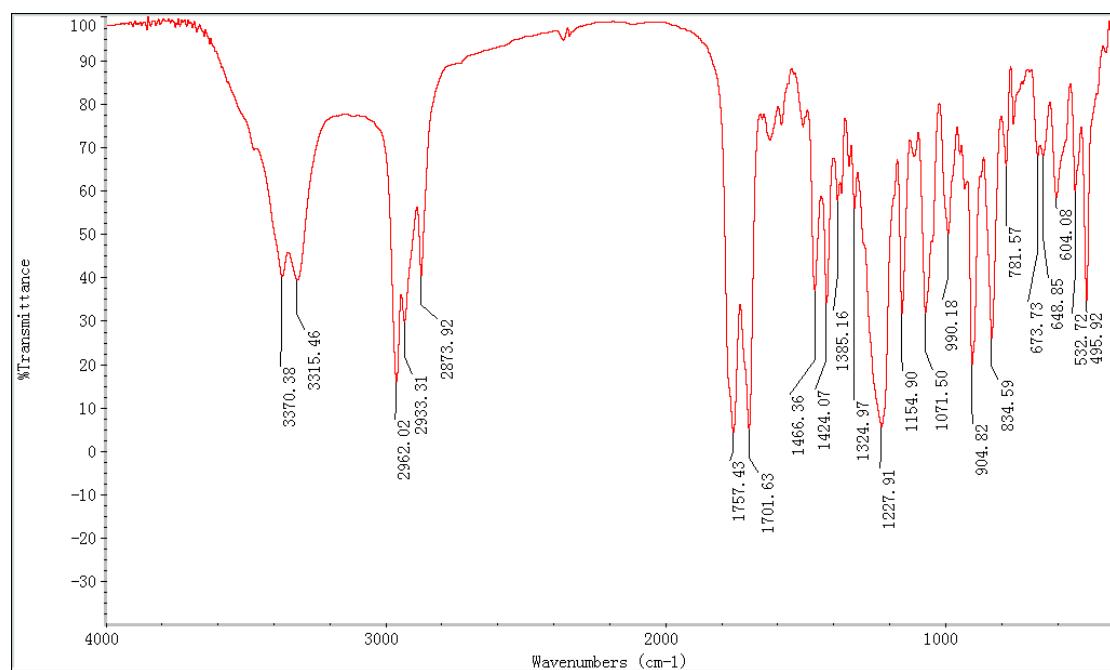
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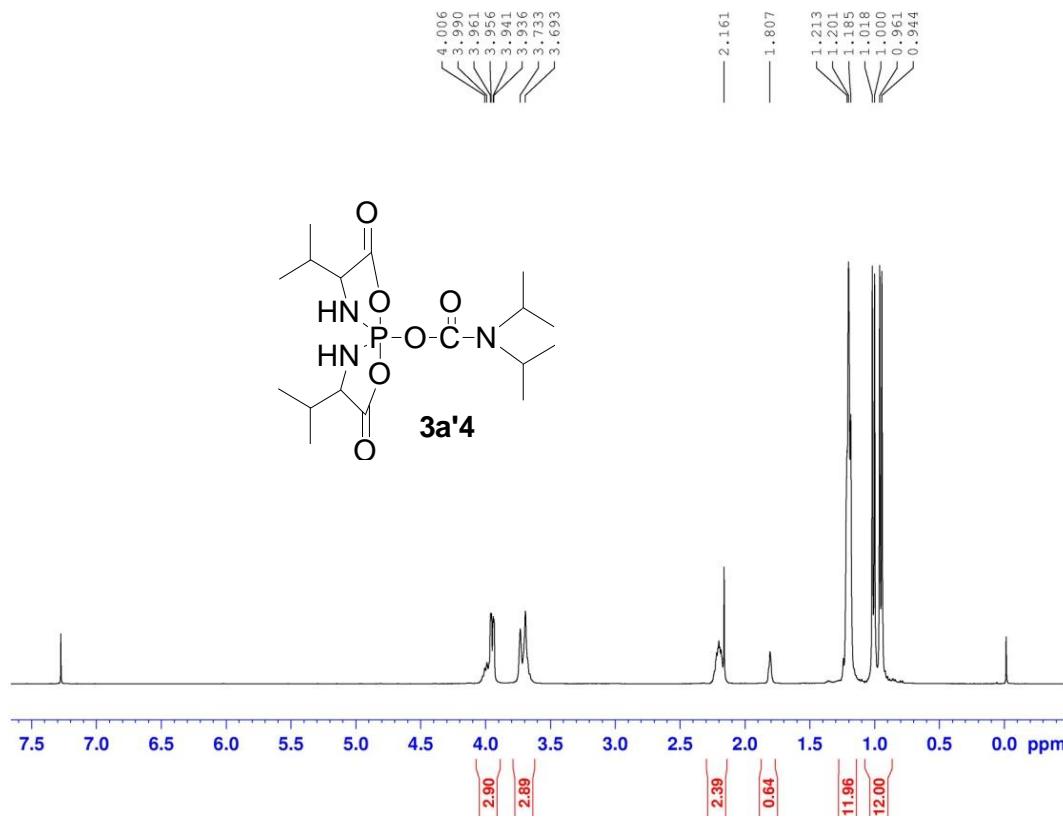
DEPT 135 of 3a'3



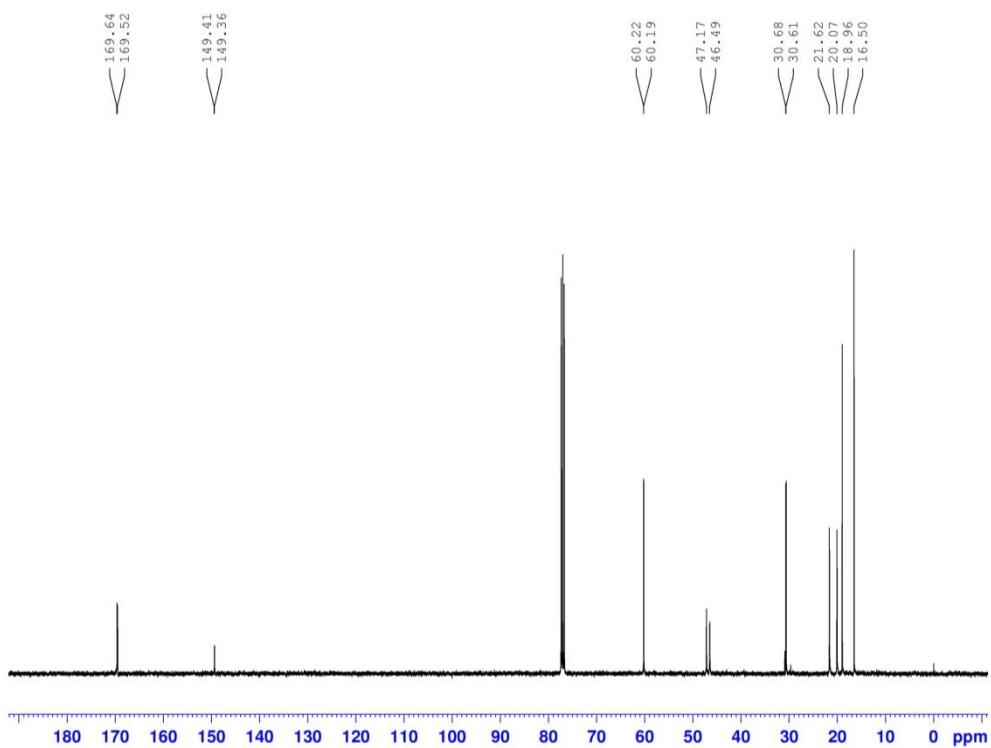
IR of 3a'3



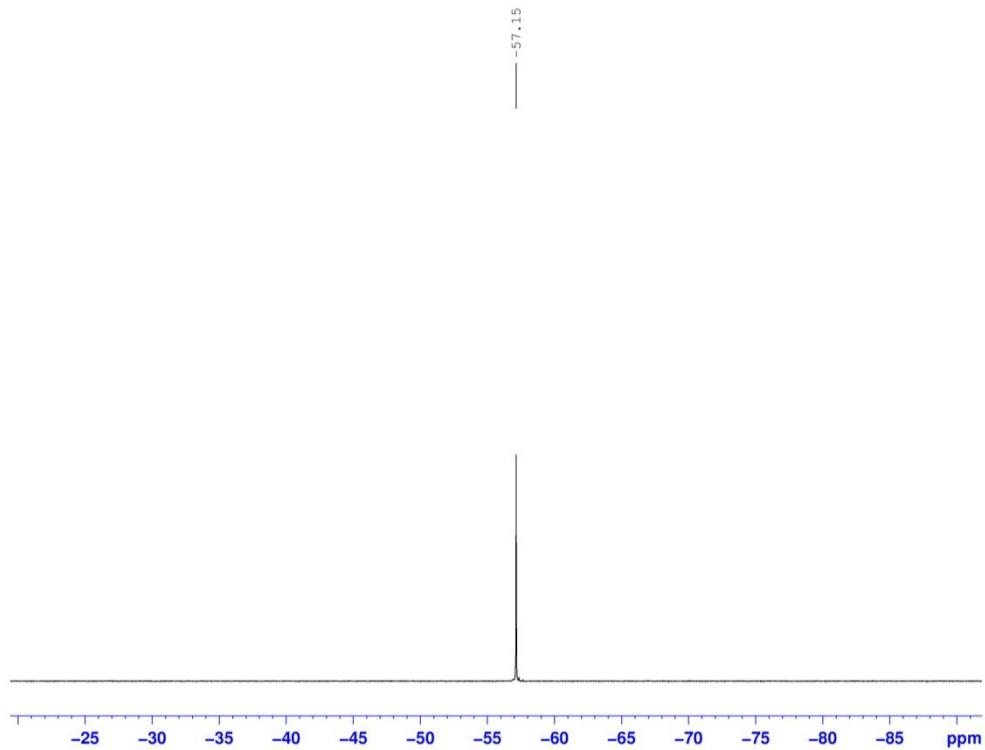
^1H NMR of 3a'4



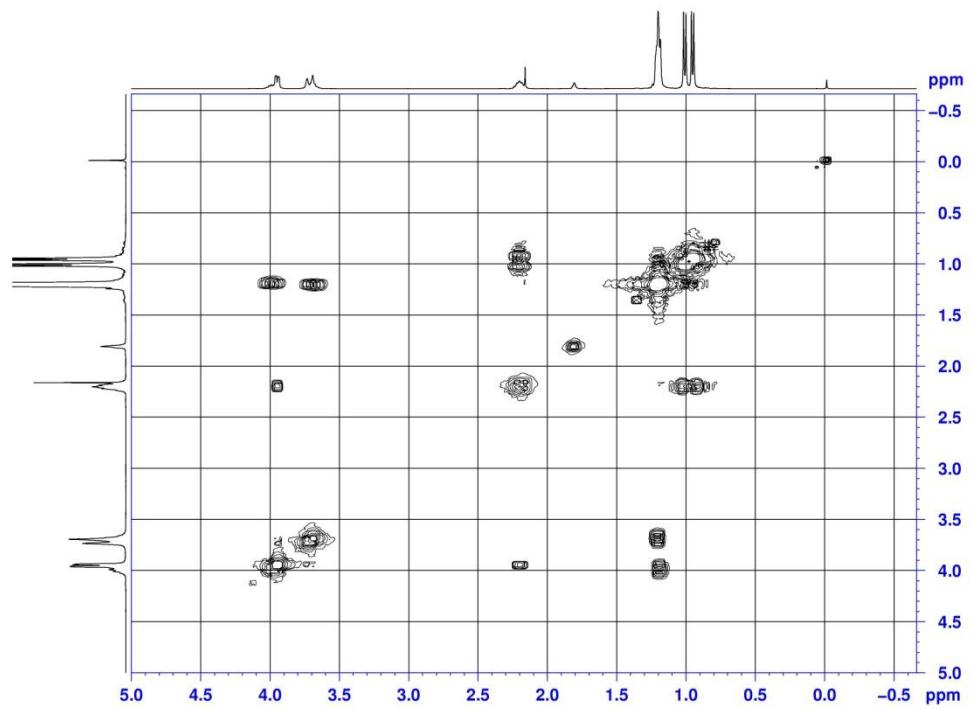
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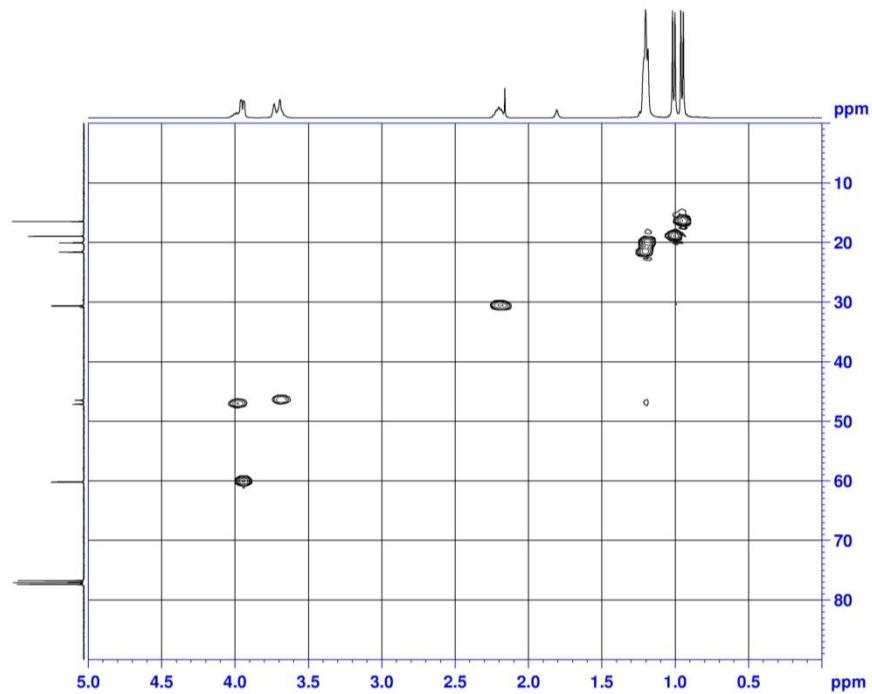
³¹P NMR of 3a'4



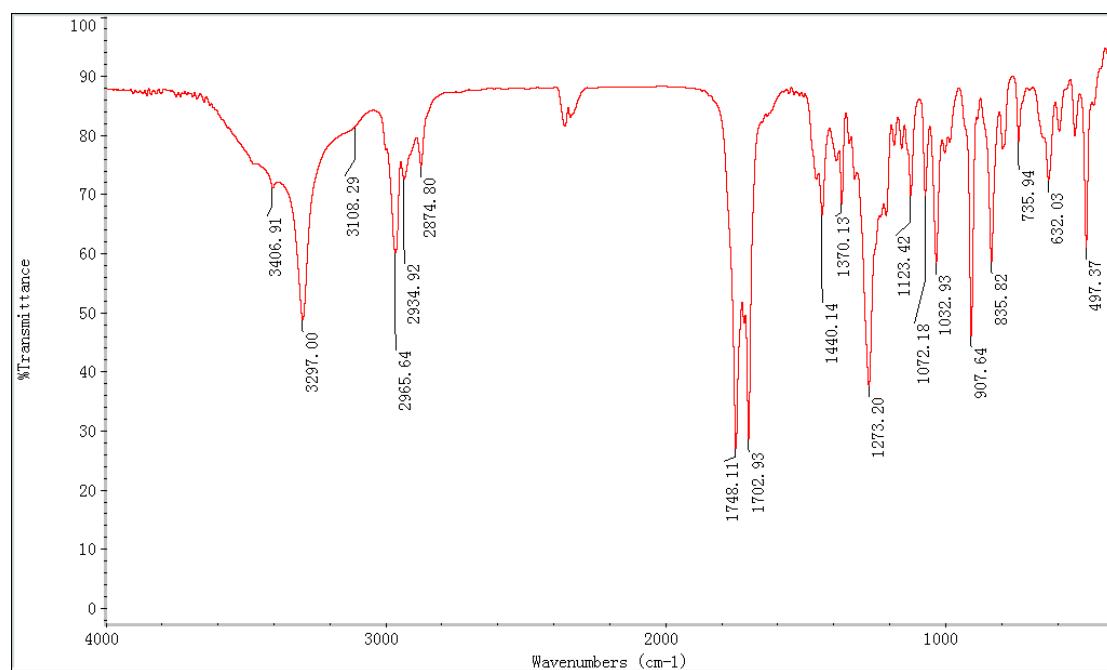
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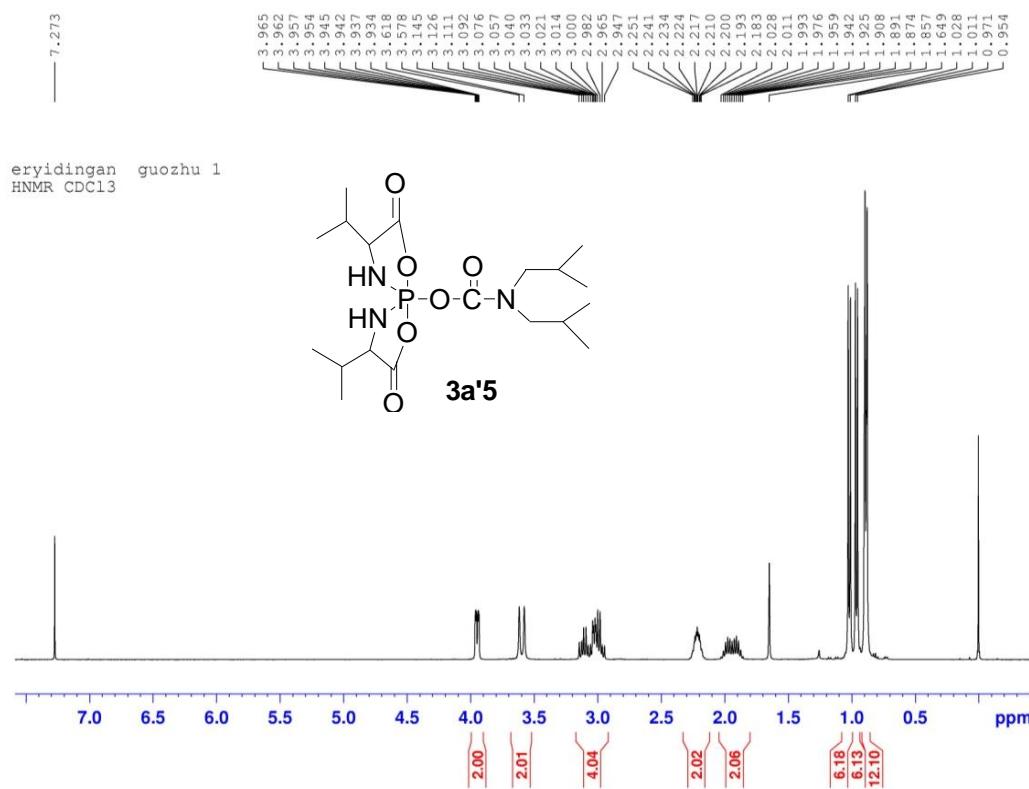
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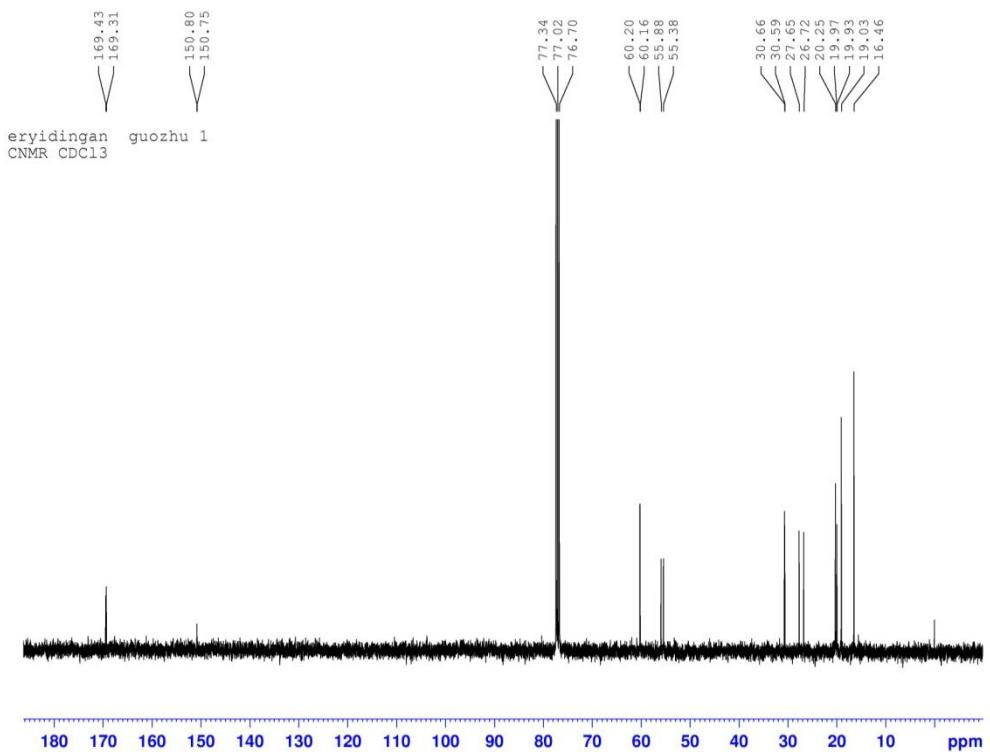
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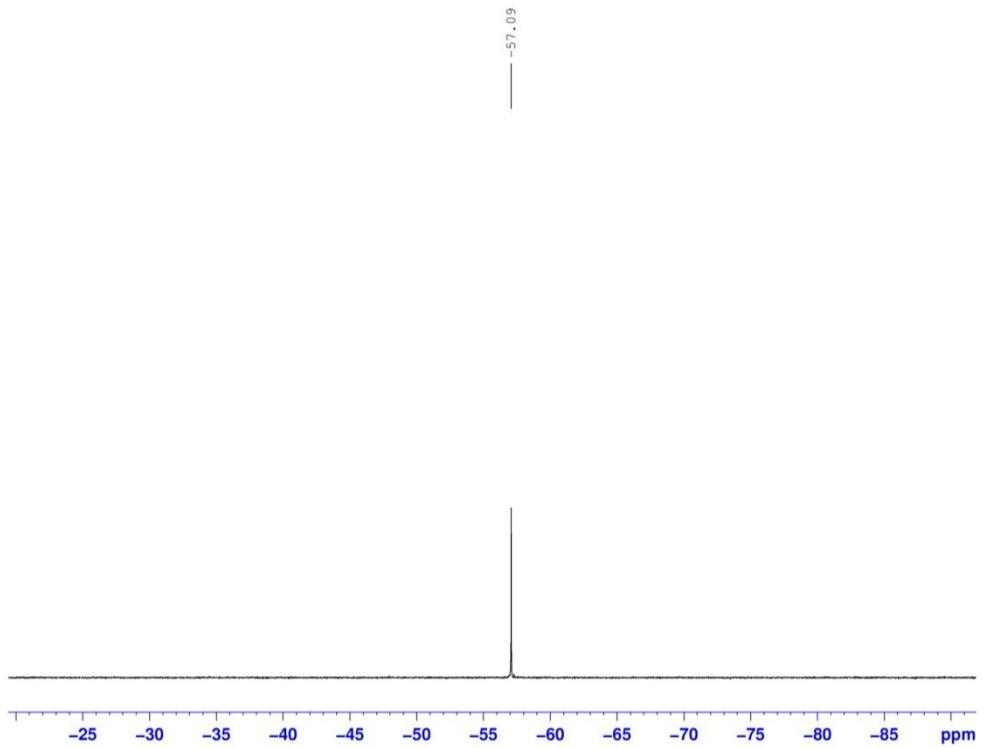
¹ H NMR of 3a'5



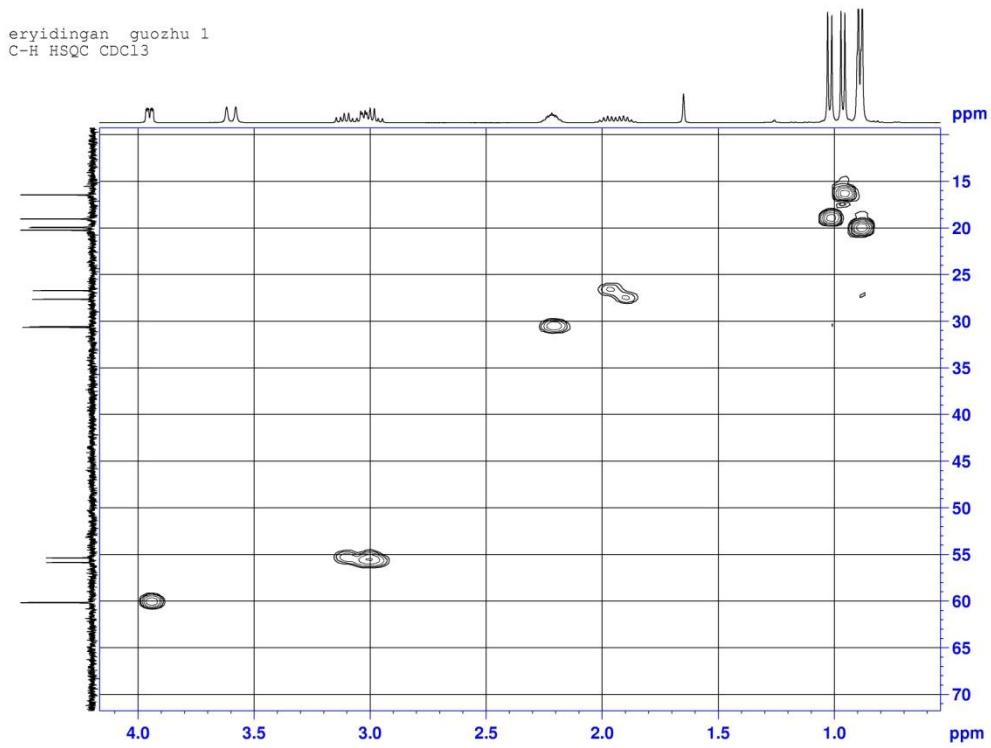
¹³C NMR of 3a'5



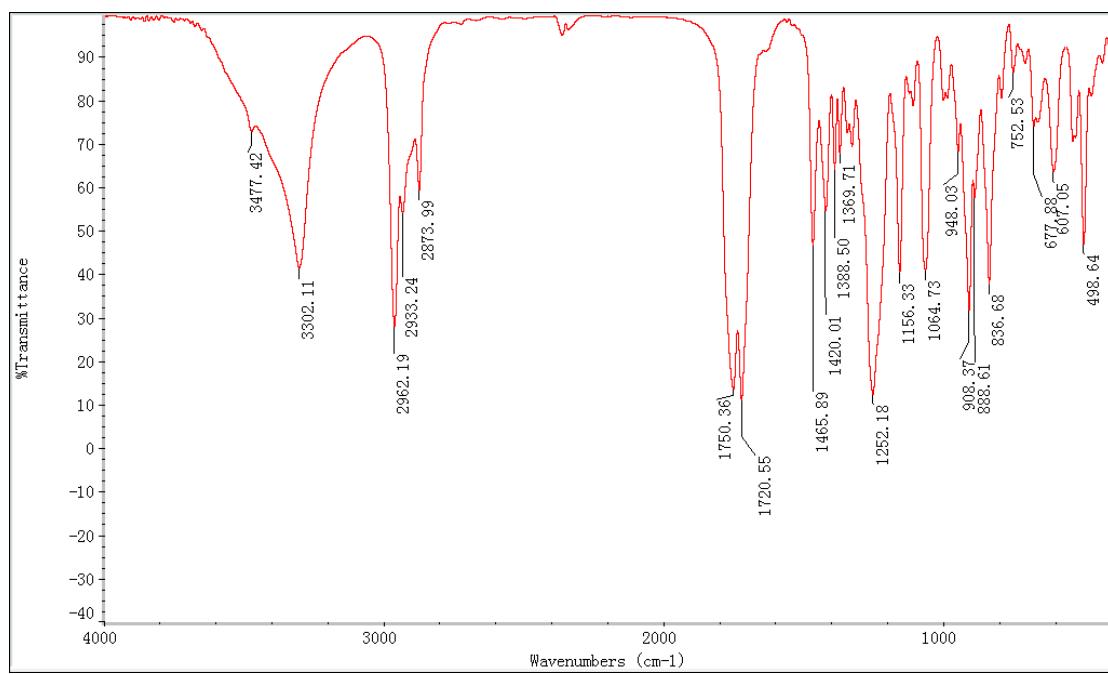
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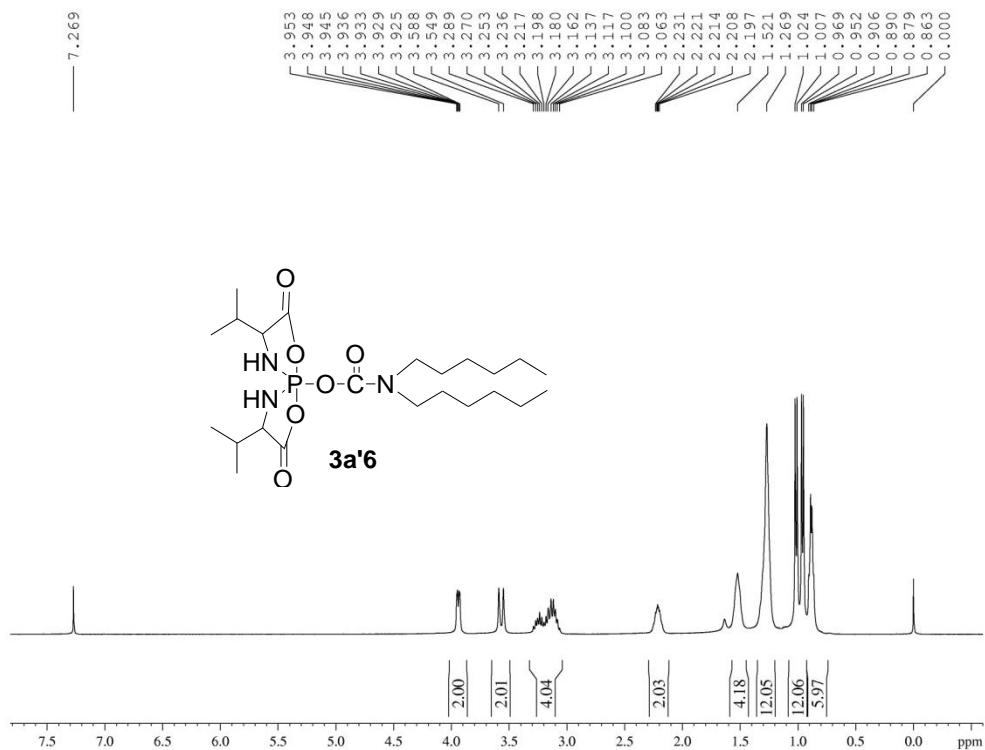
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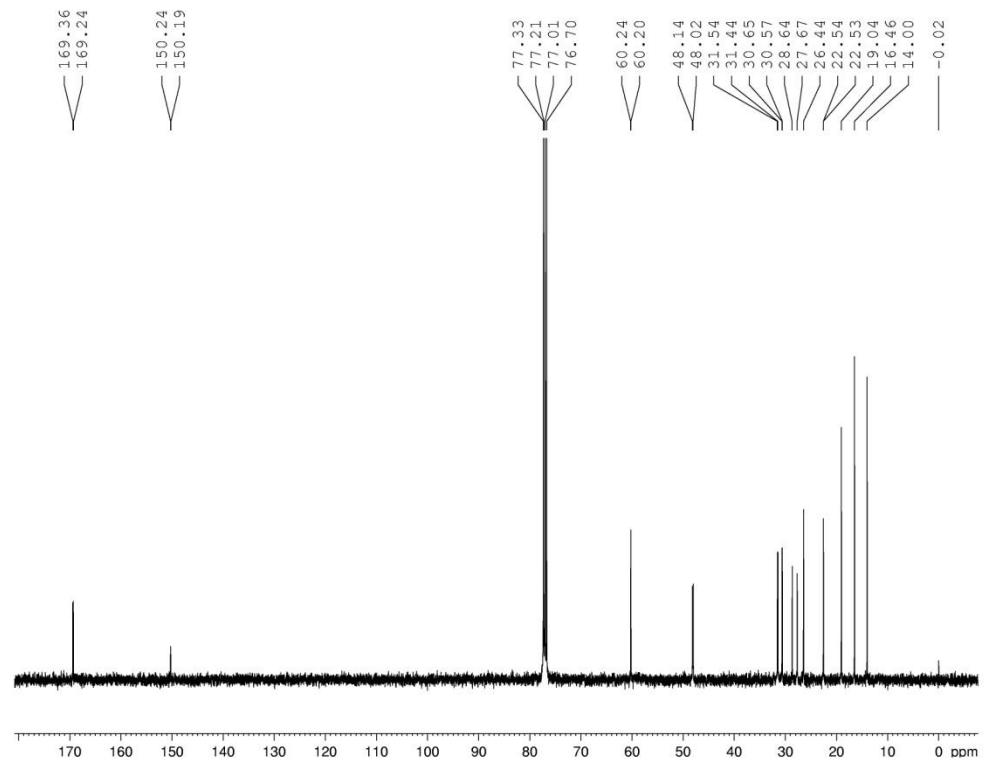
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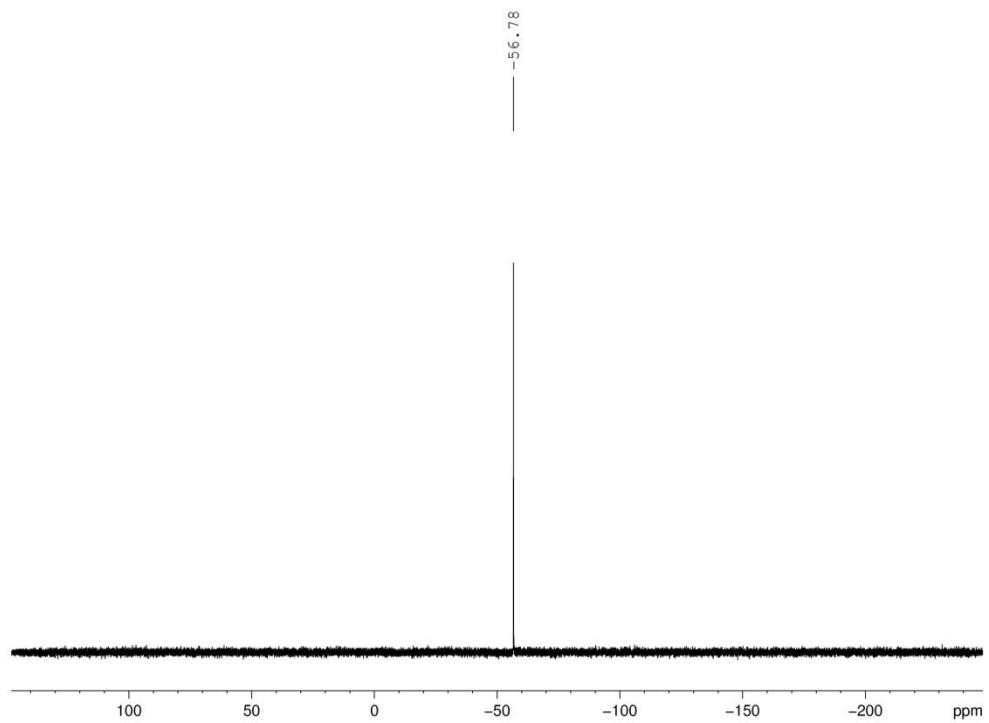
¹H NMR of 3a'6



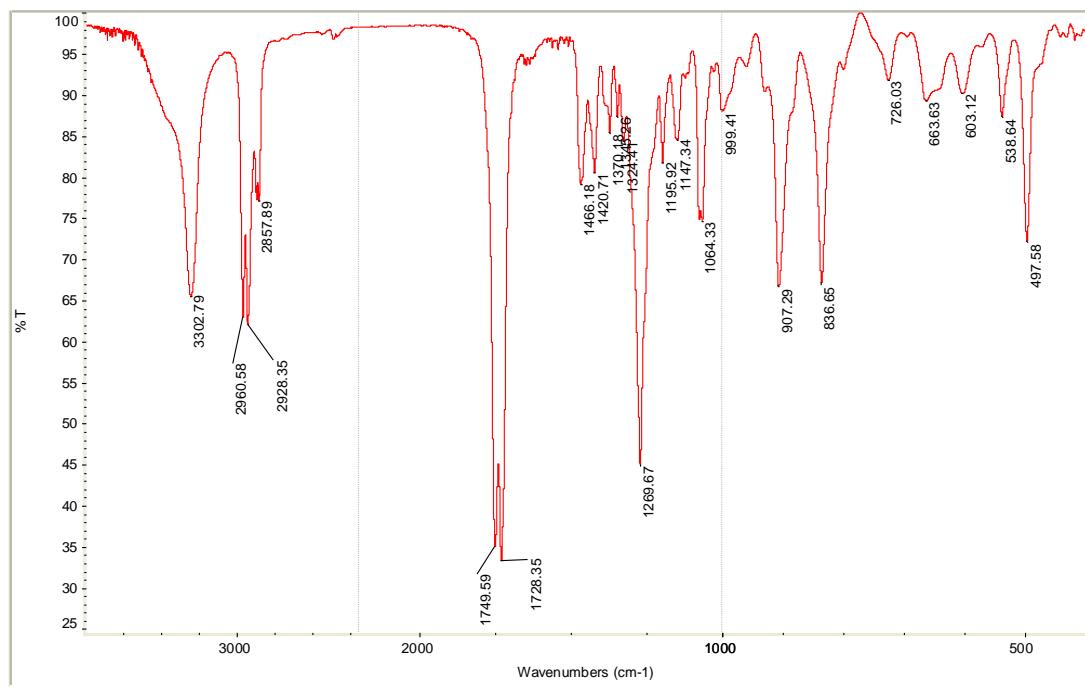
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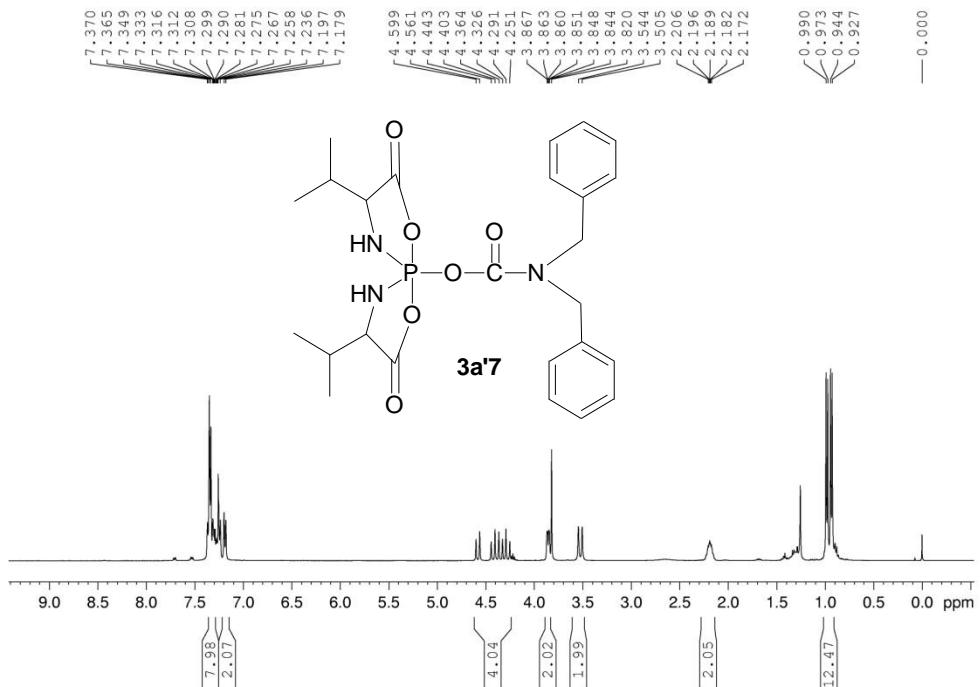
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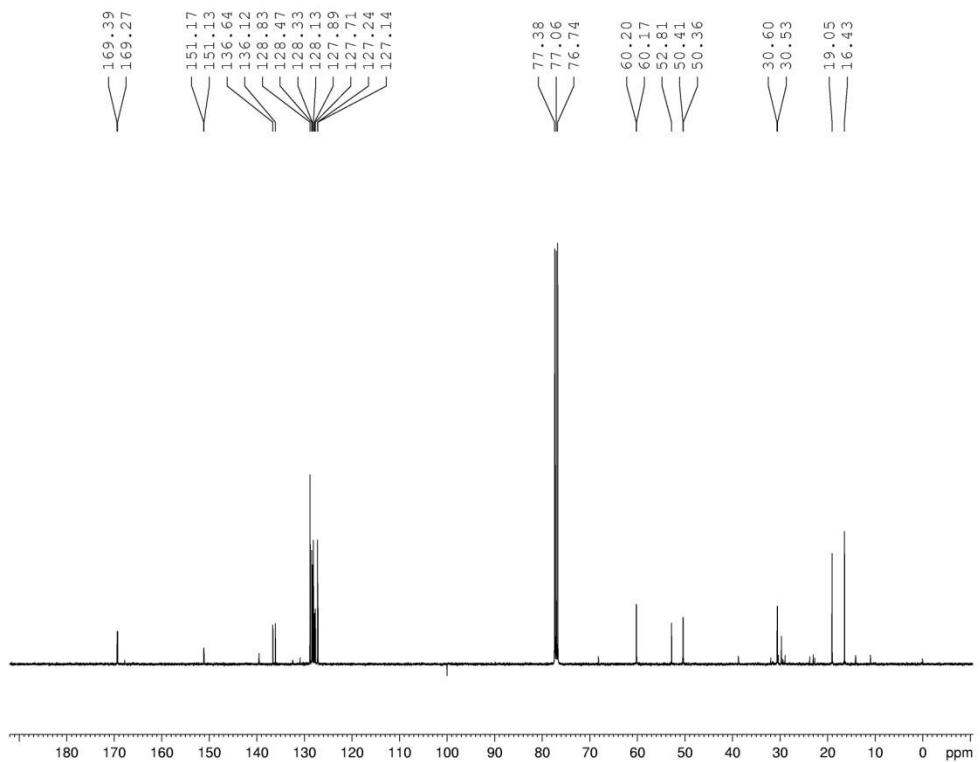
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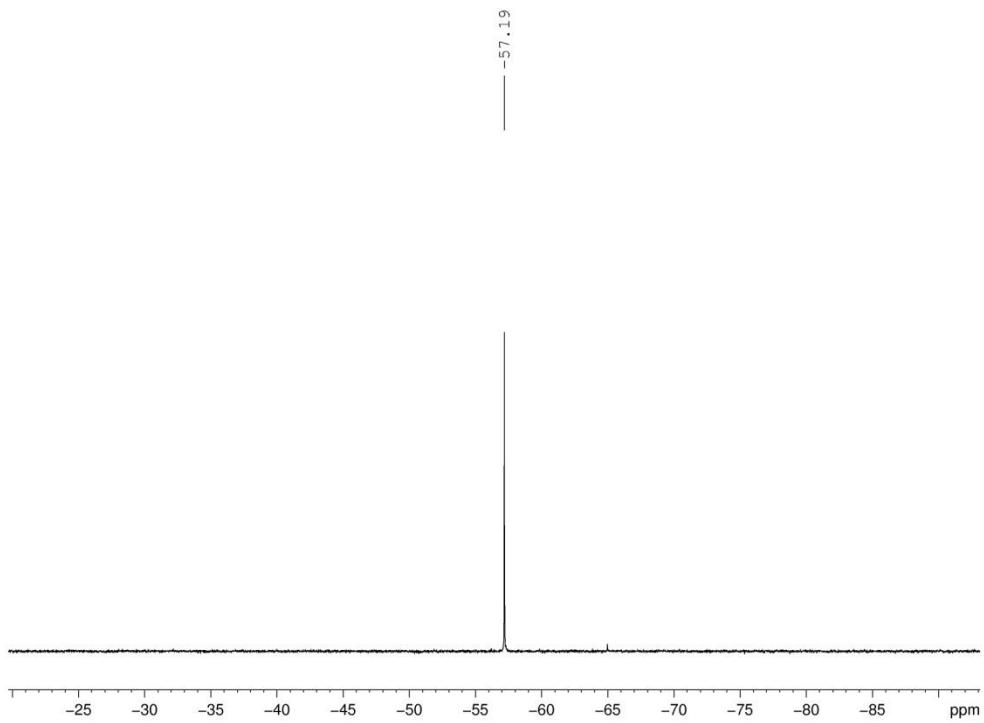
¹ H NMR of 3a'7



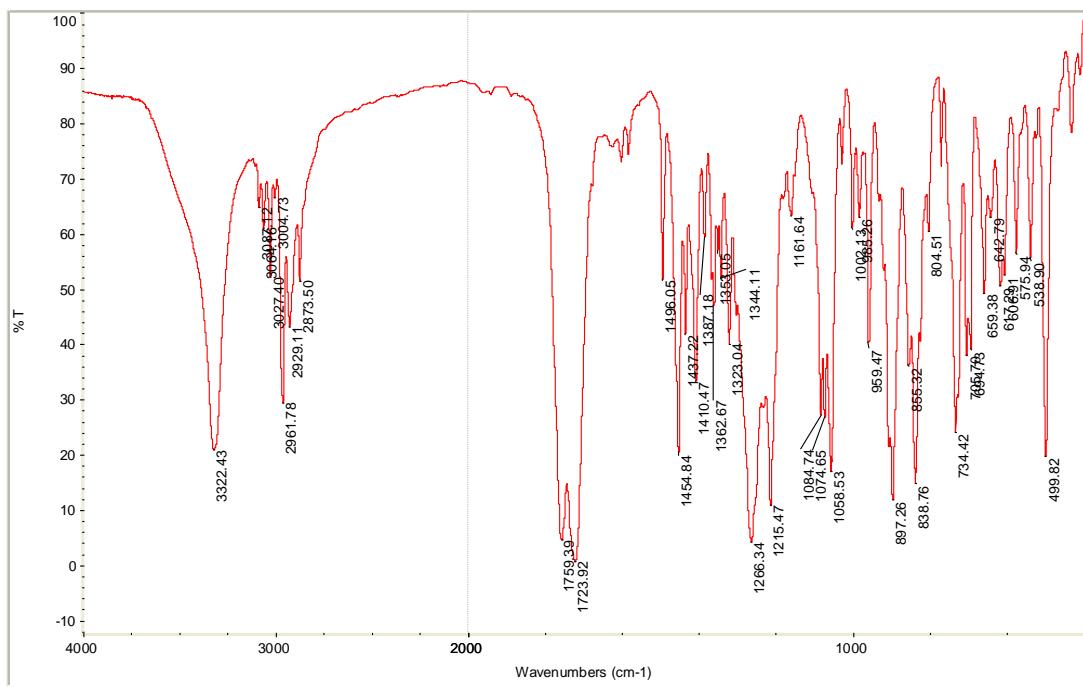
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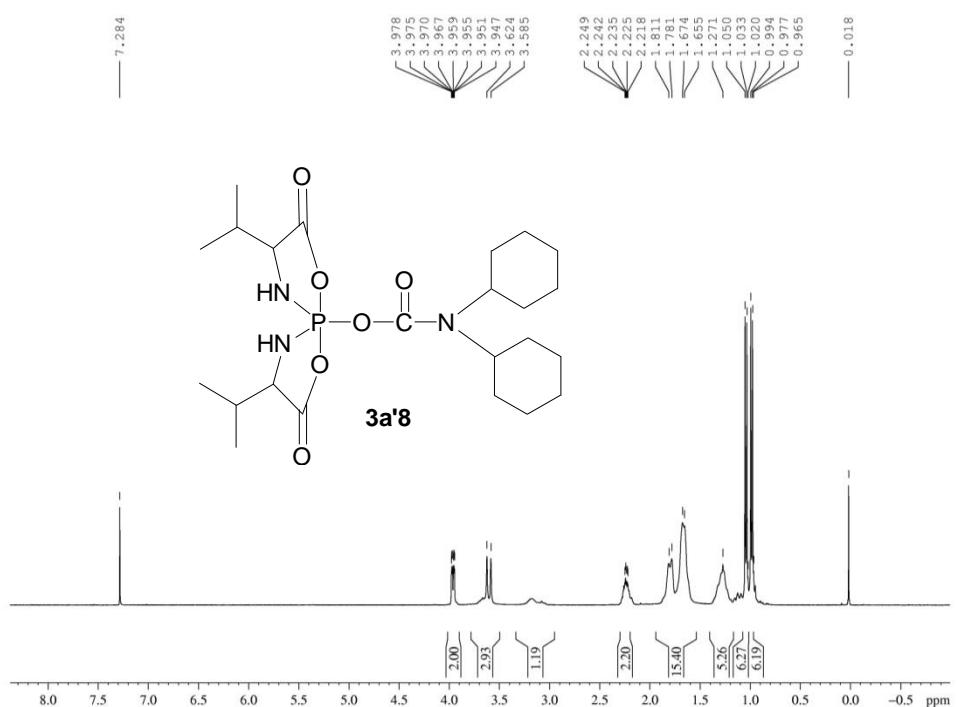
^{31}P NMR of 3a'7



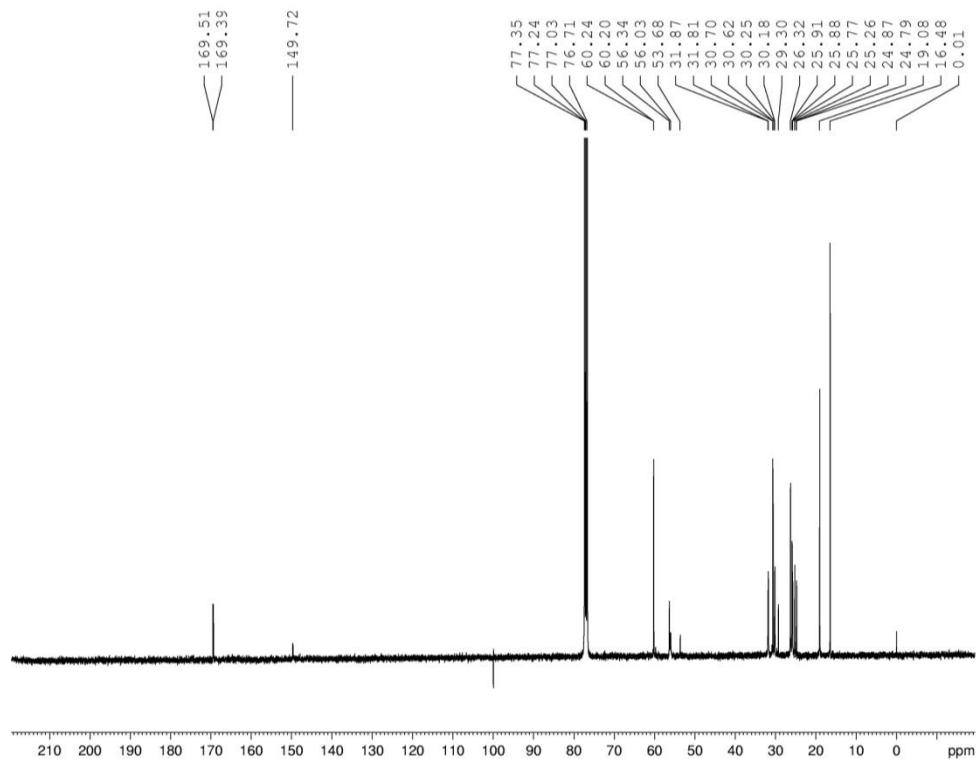
IR of 3a'7



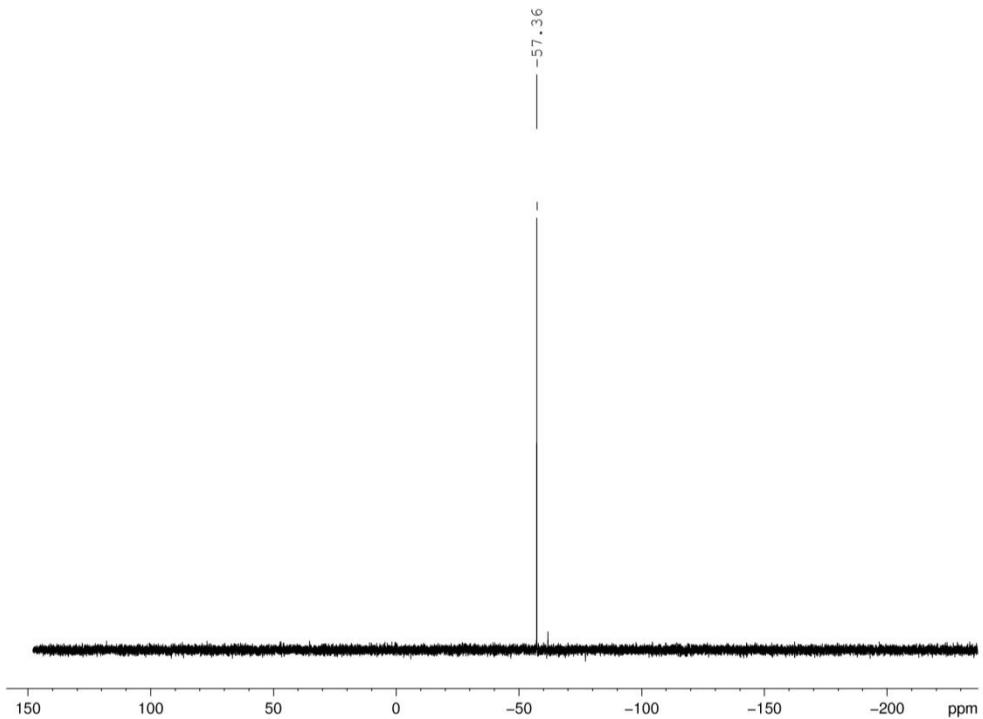
¹H NMR of 3a'8



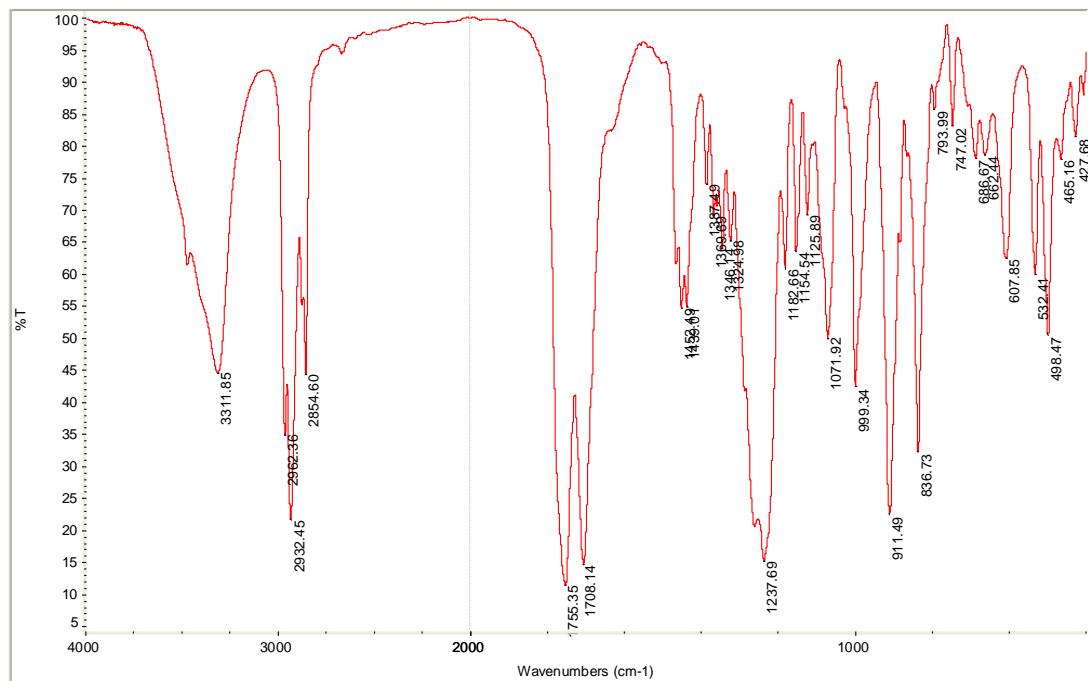
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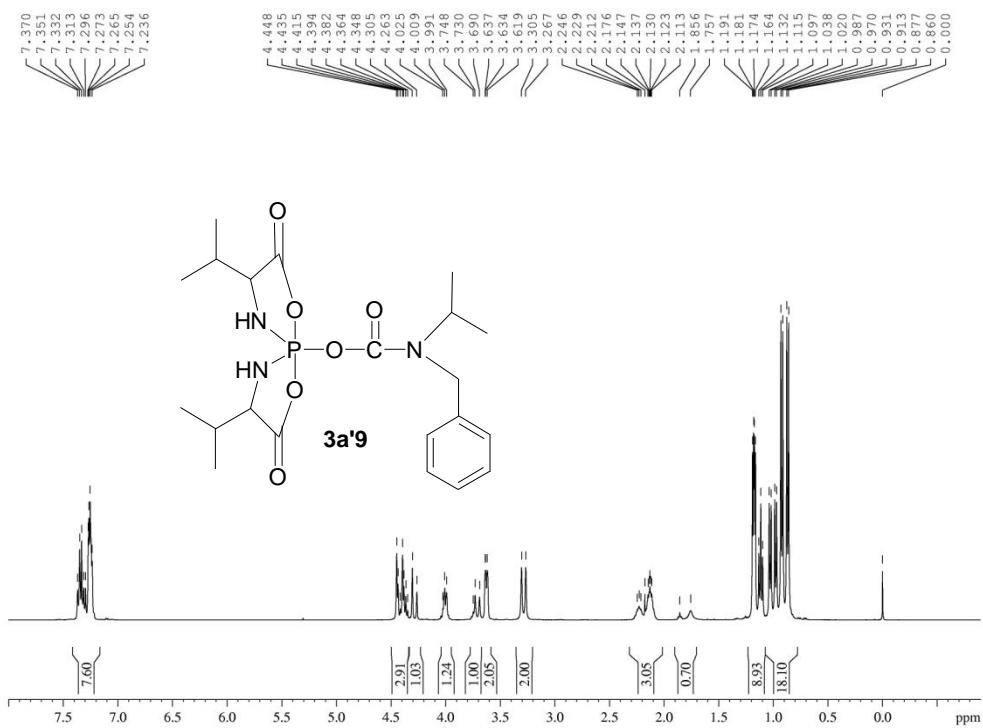
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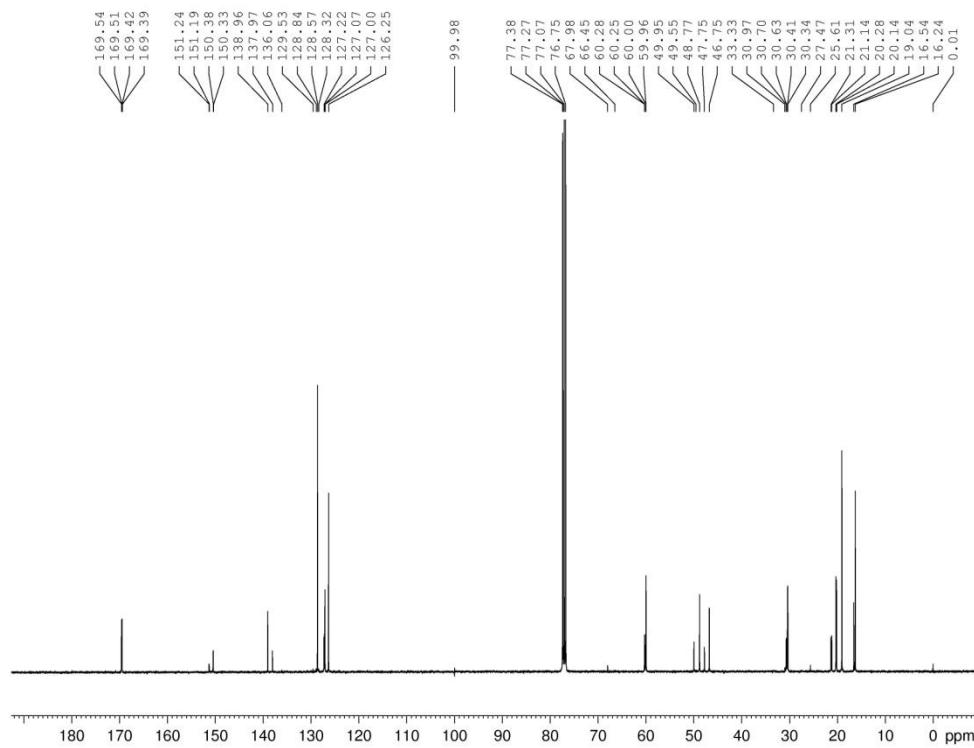
IR of 3a'8



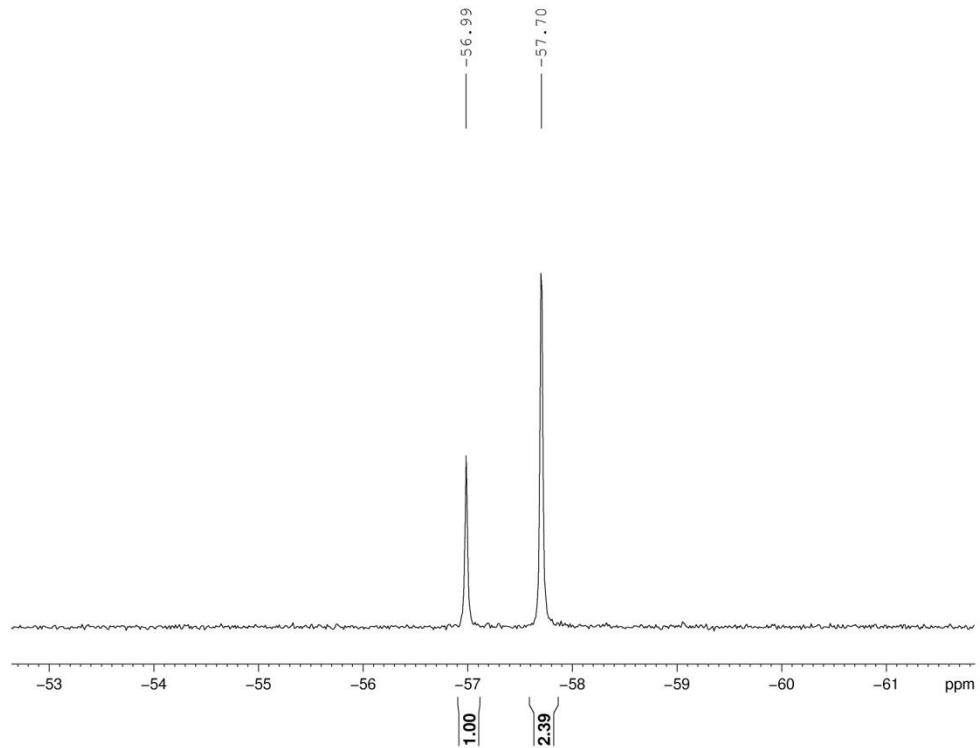
¹H NMR of 3a'9 (cis-trans isomers since the restricted rotation of C(O)–N bond)



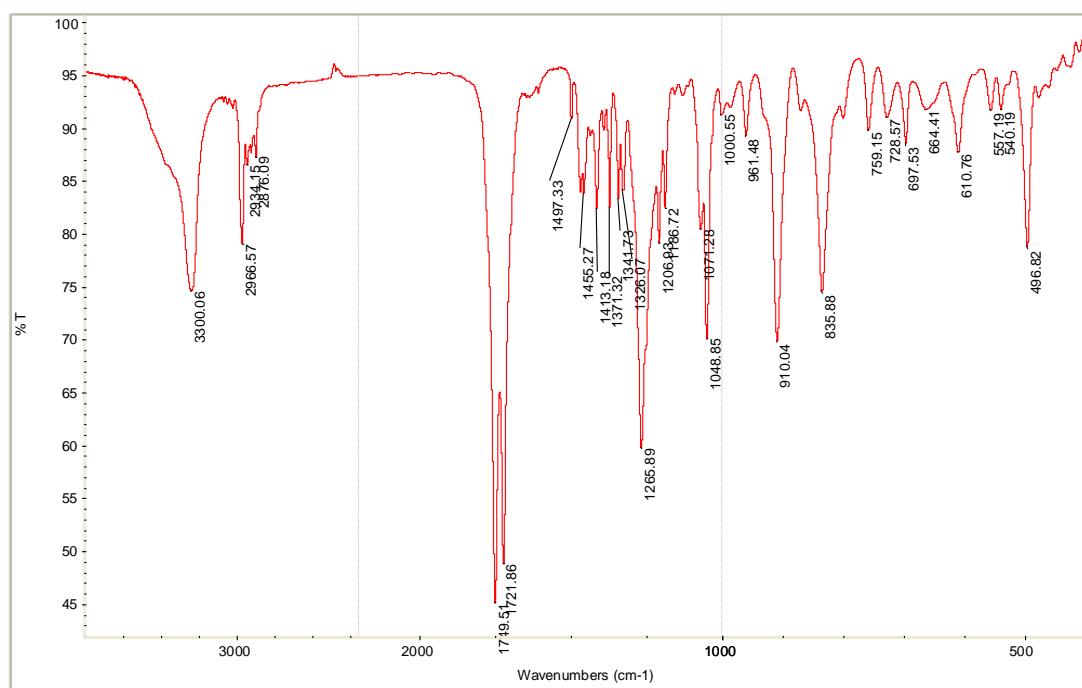
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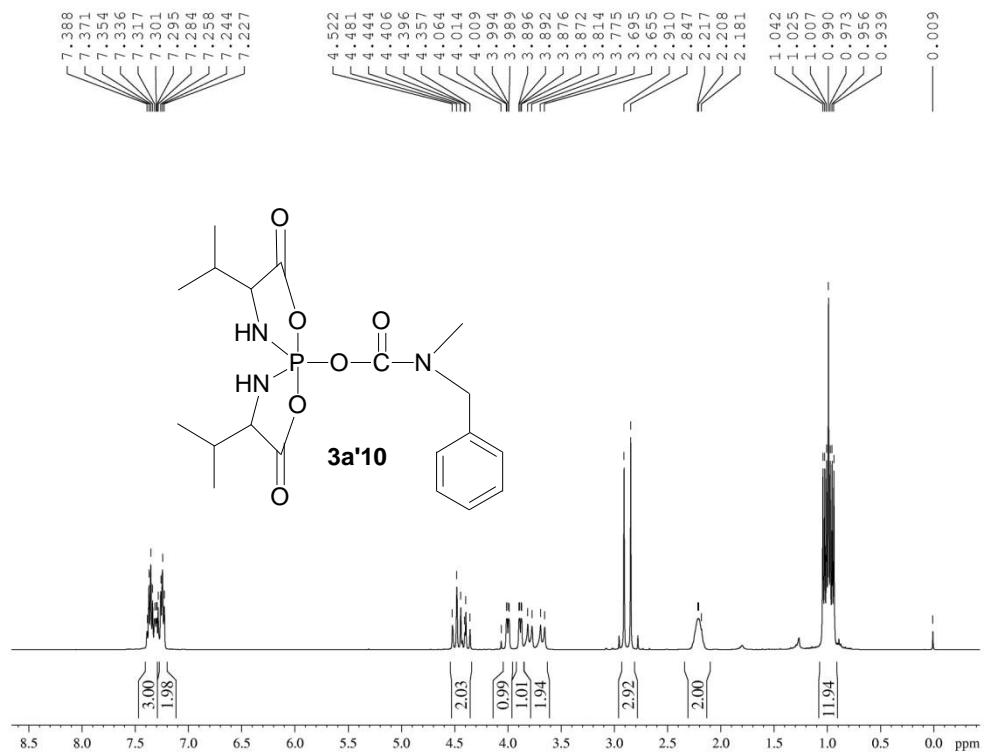
^{31}P NMR of 3a'9



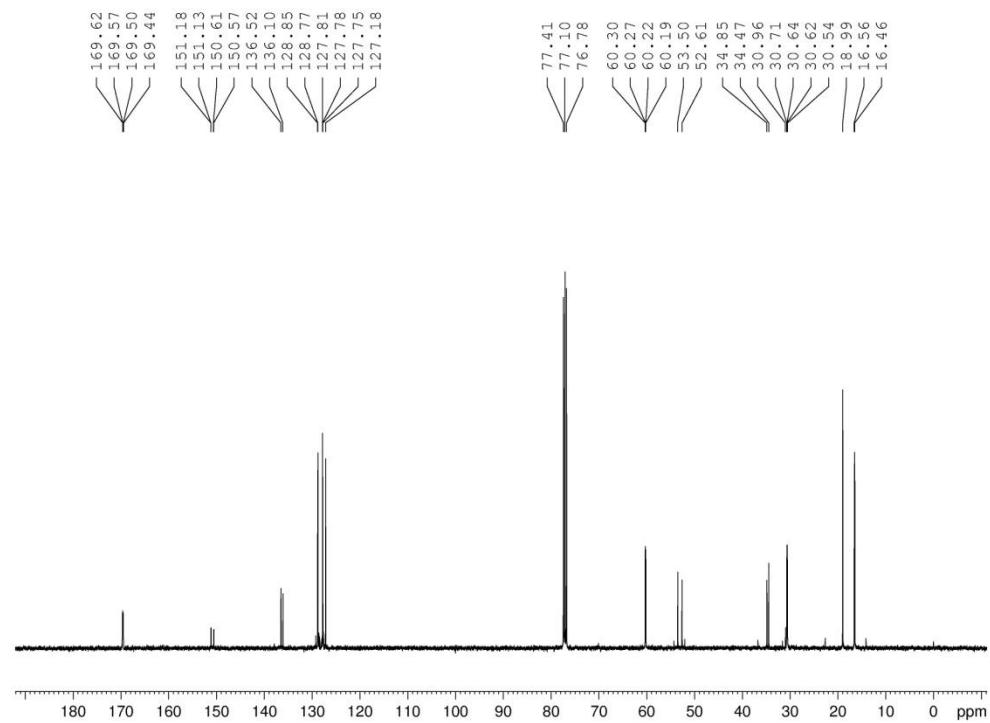
IR of 3a'9



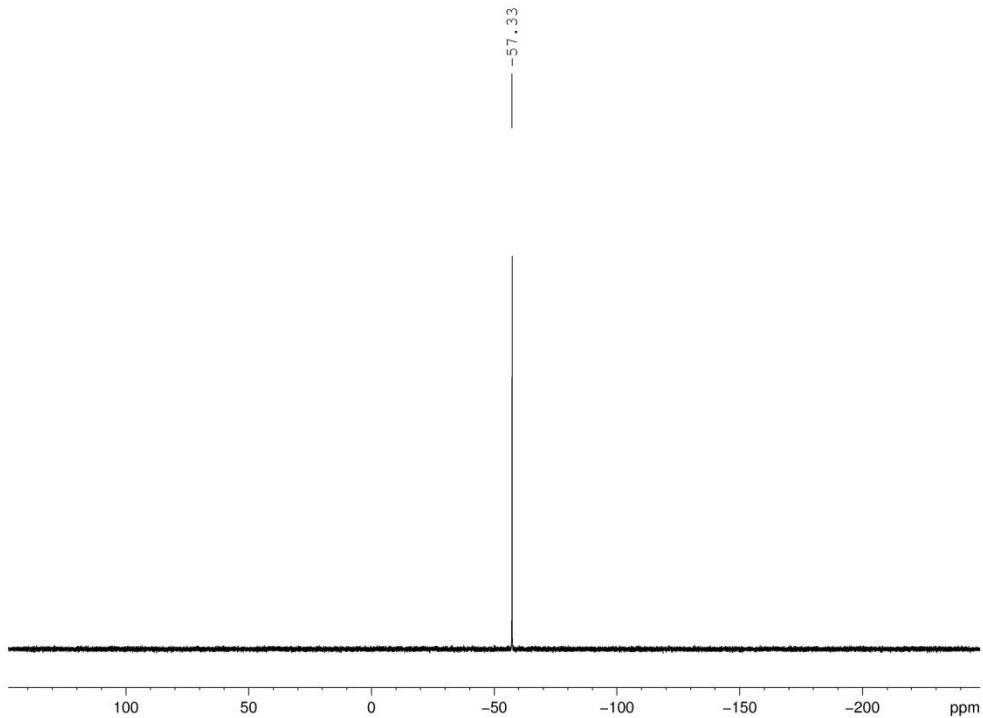
¹H NMR of 3a'10 (cis-trans isomers since the restricted rotation of C(O)–N bond)



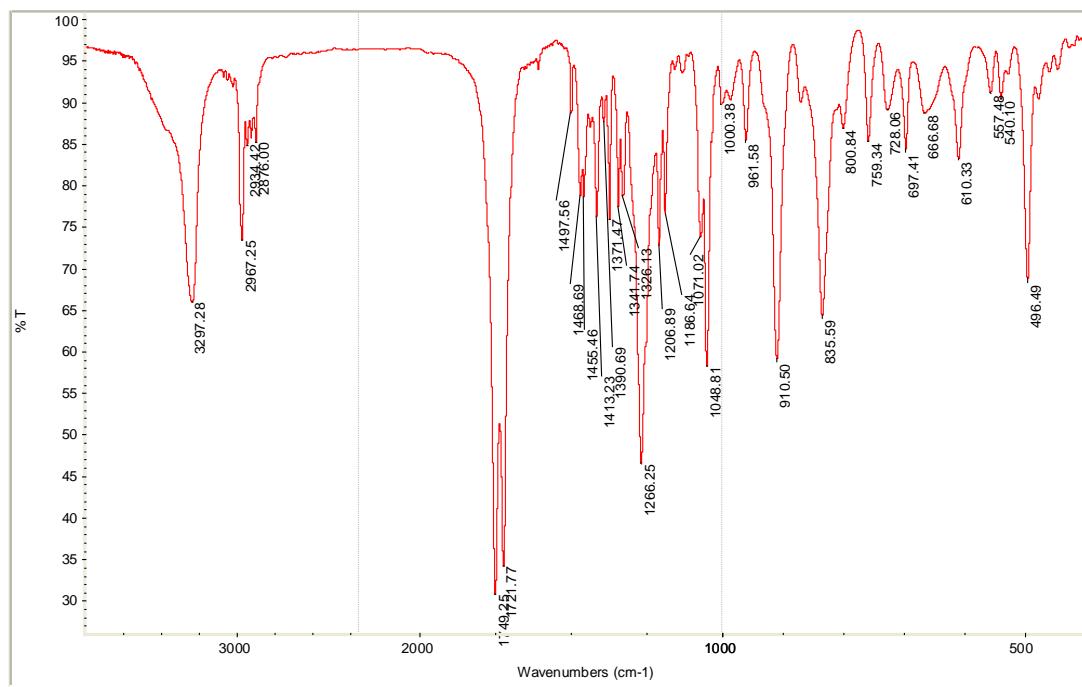
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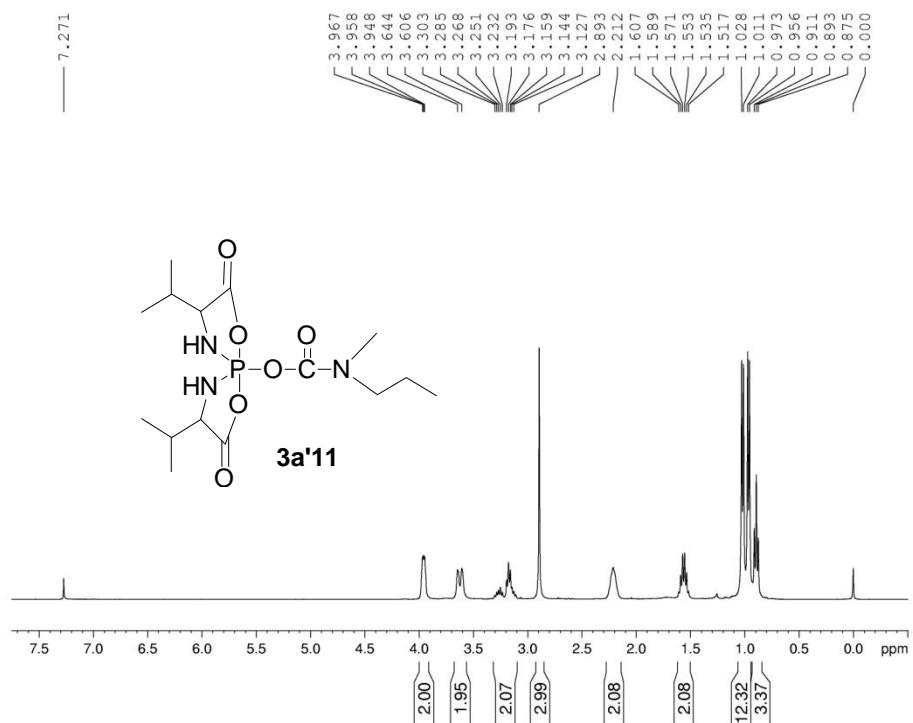
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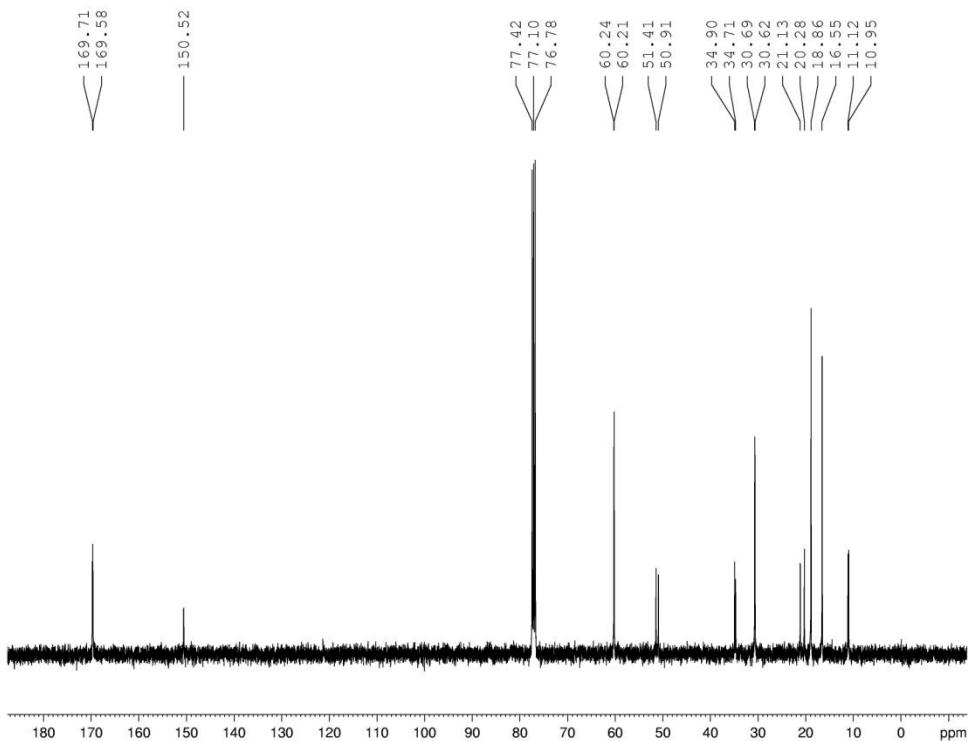
IR of 3a'10



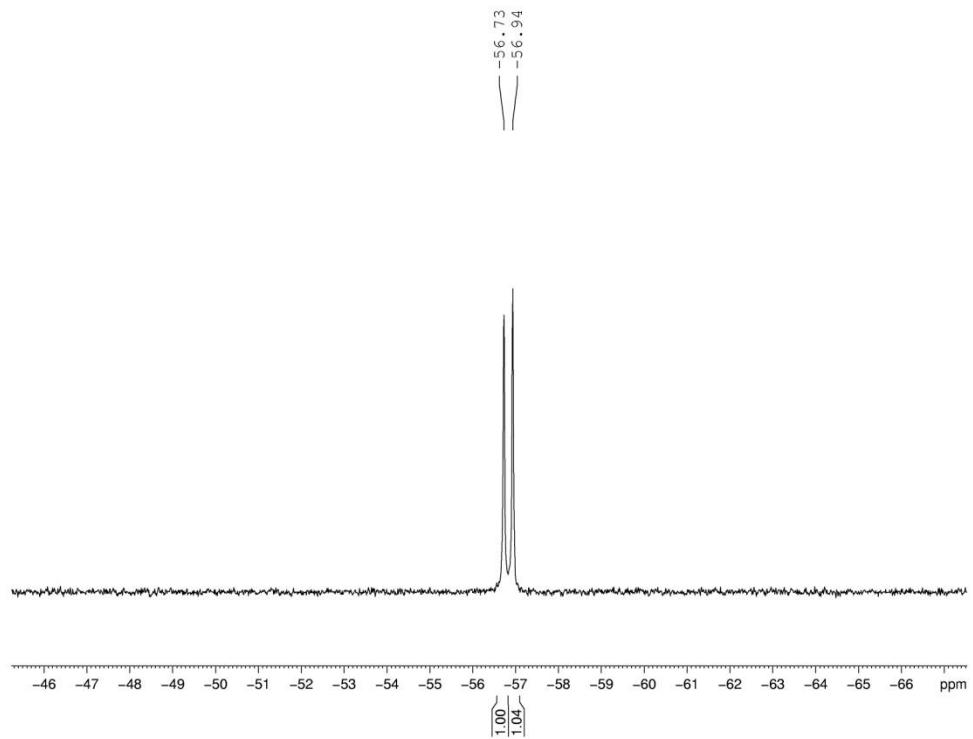
¹H NMR of 3a'11 (cis-trans isomers since the restricted rotation of C(O)–N bond)



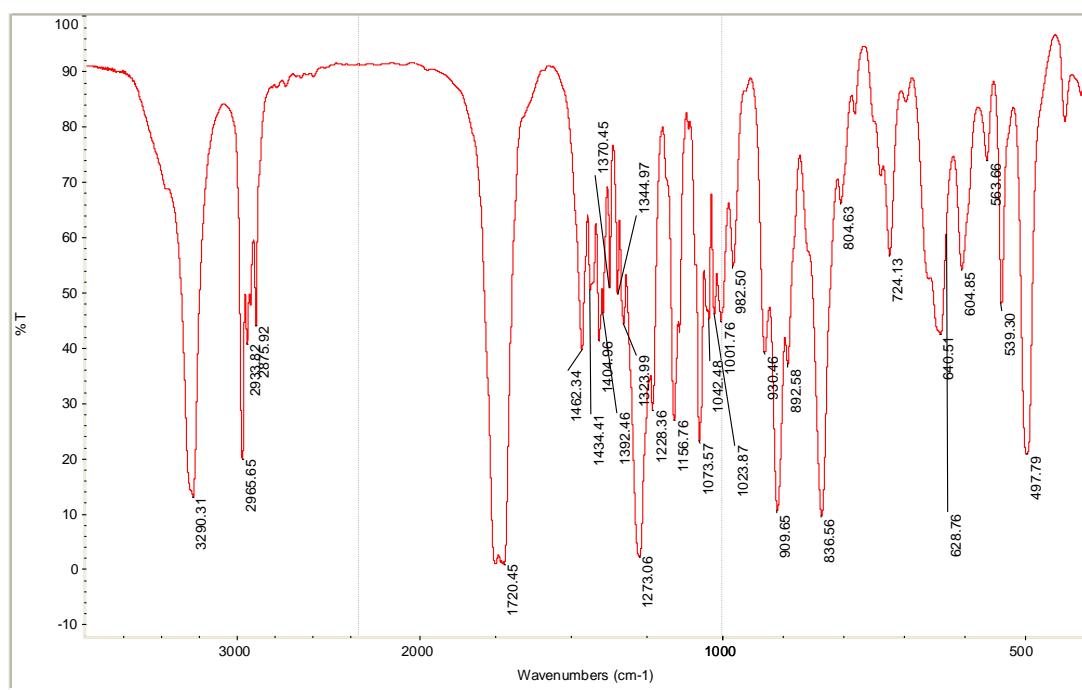
¹³C NMR of 3a'11



³¹P NMR of 3a'11

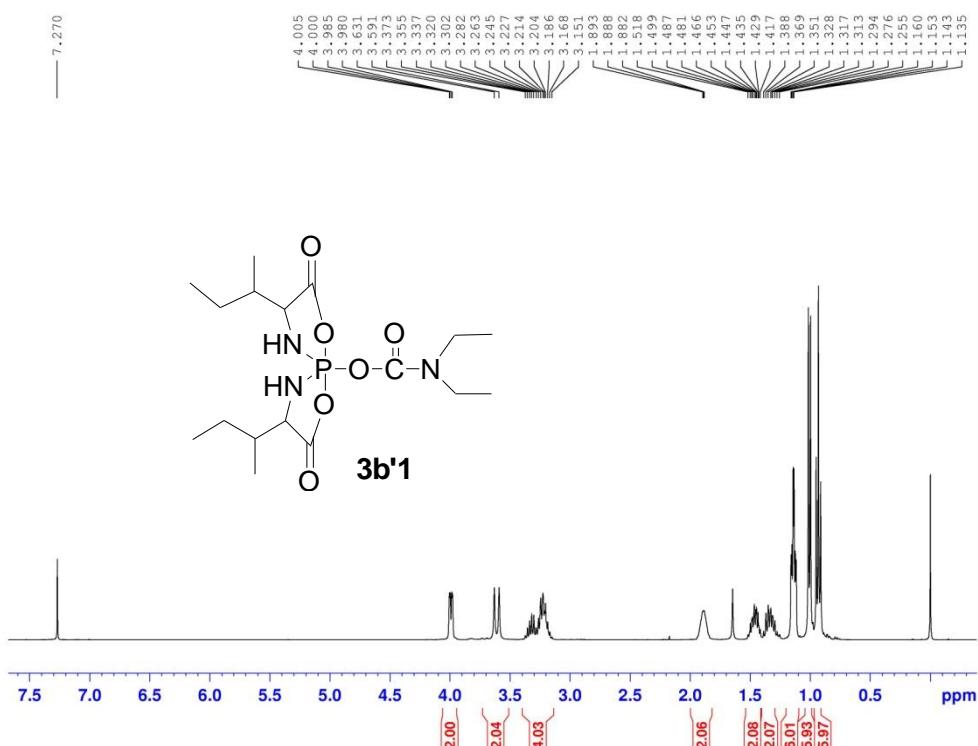


IR of 3a'11

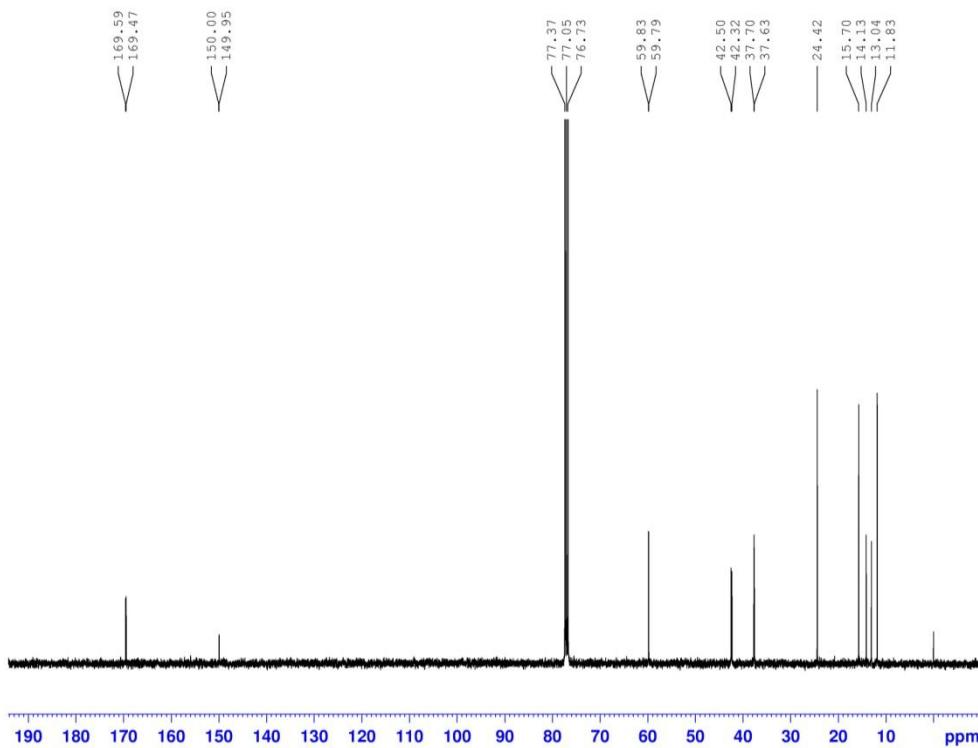


6. NMR and IR Spectra for compounds 3b'1-3b'5

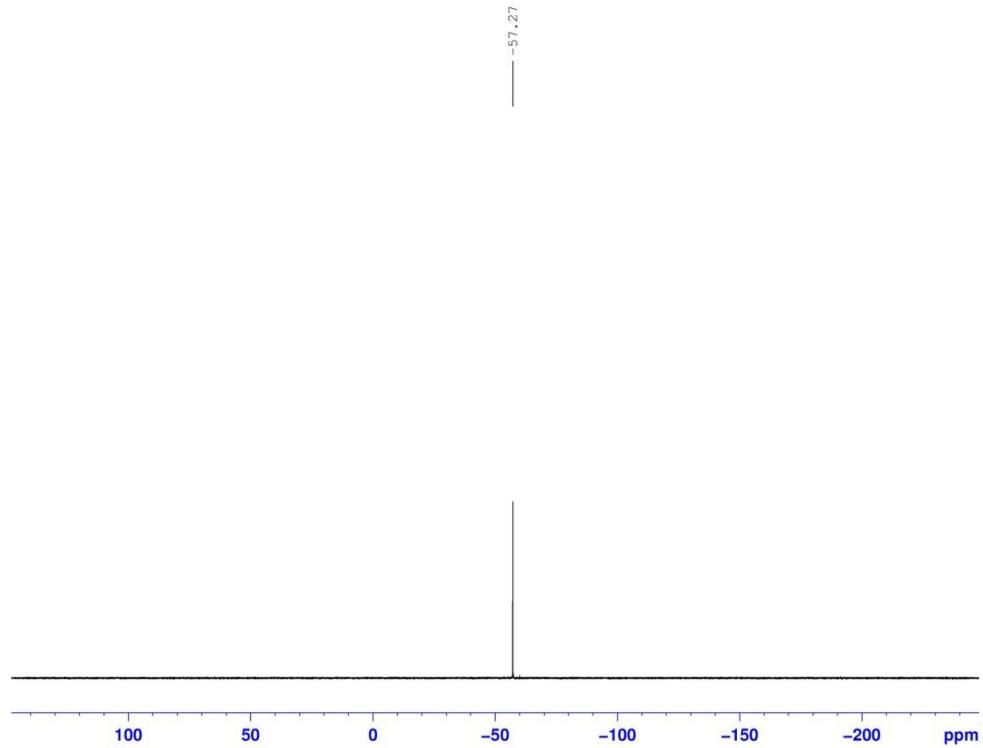
¹ H NMR of 3b'1



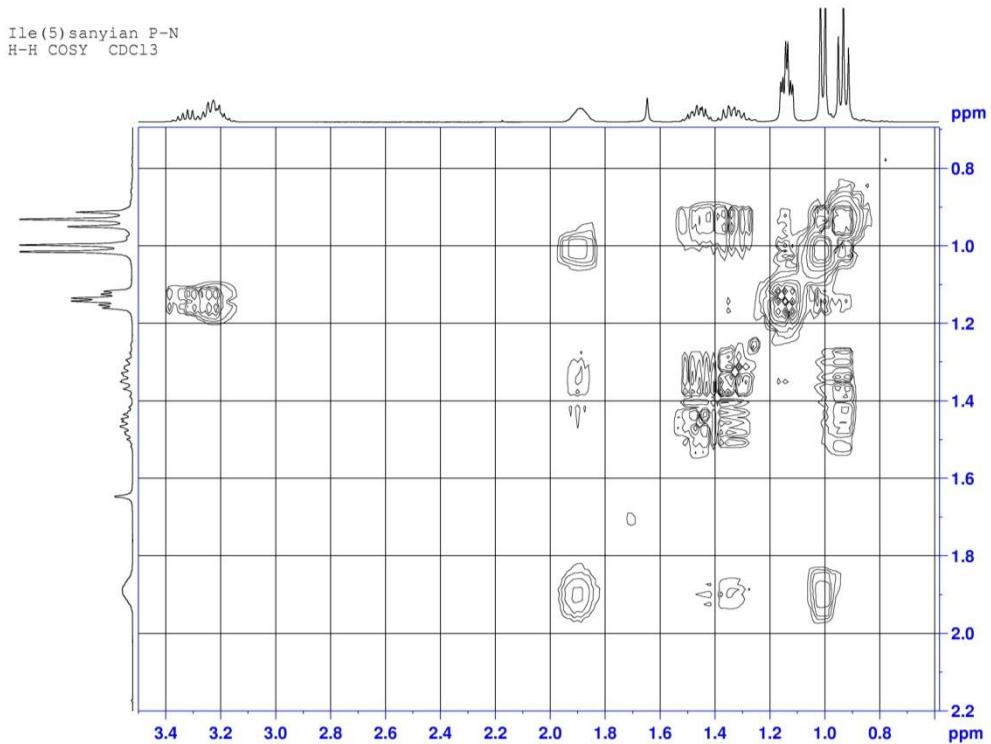
¹³ C NMR of 3b'1



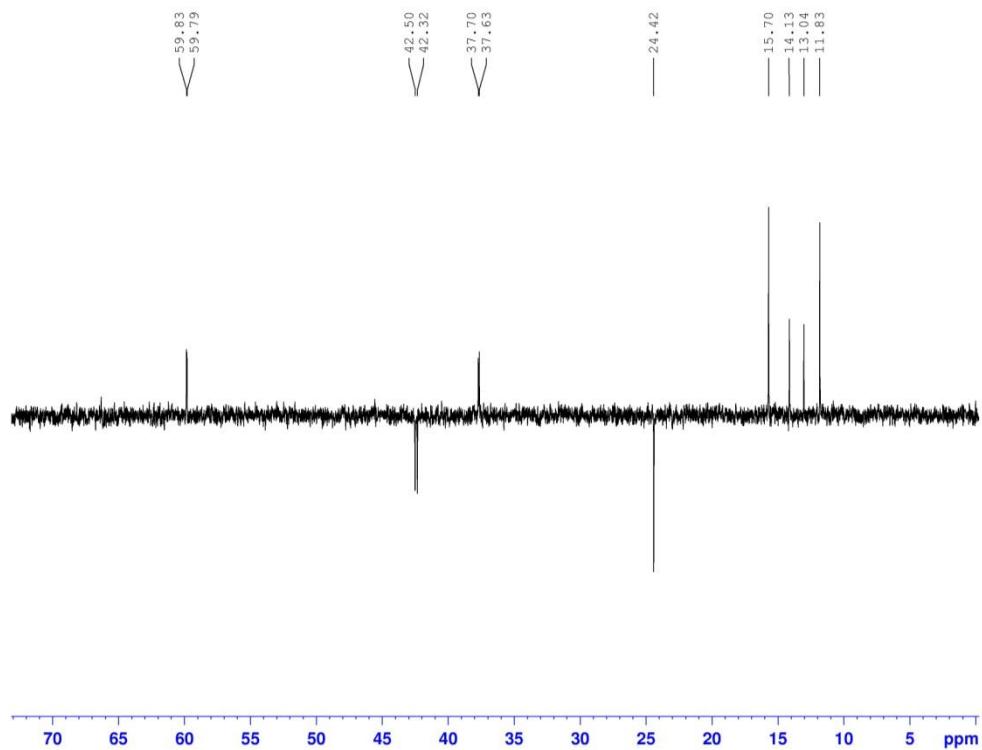
^{31}P NMR of 3b'1



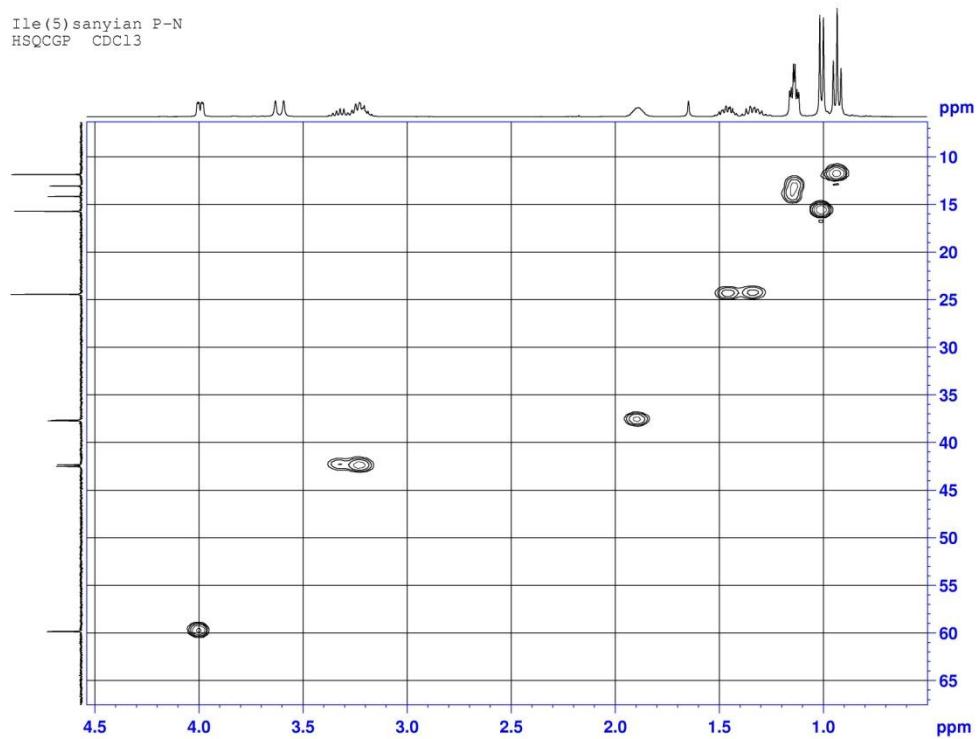
H-H COSY of 3b'1



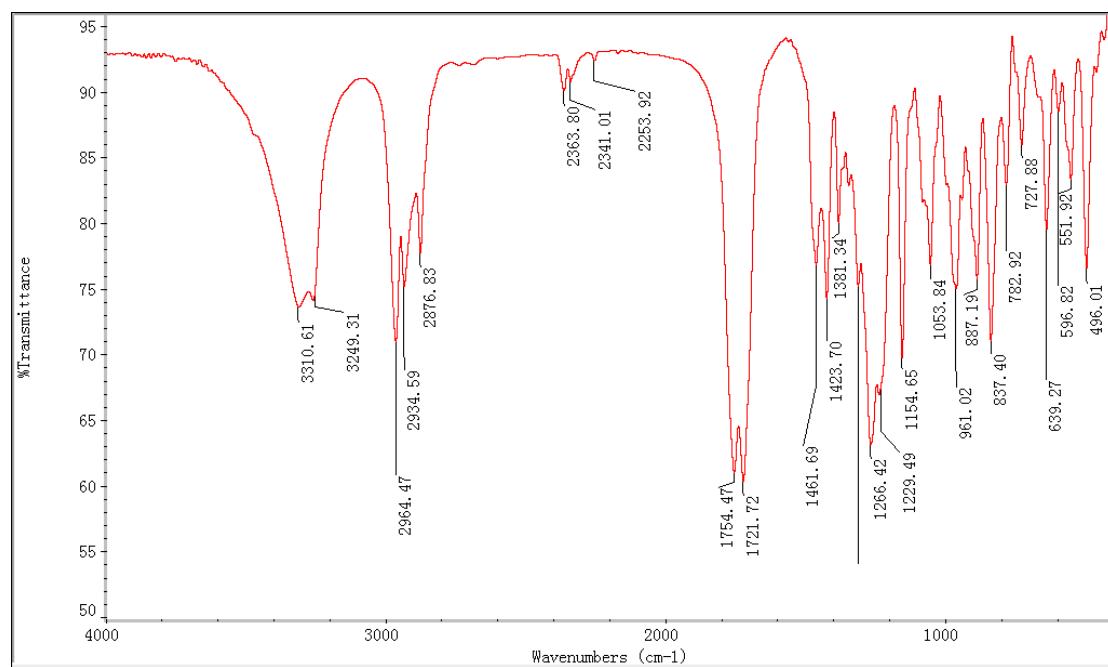
DEPT 135 of 3b'1



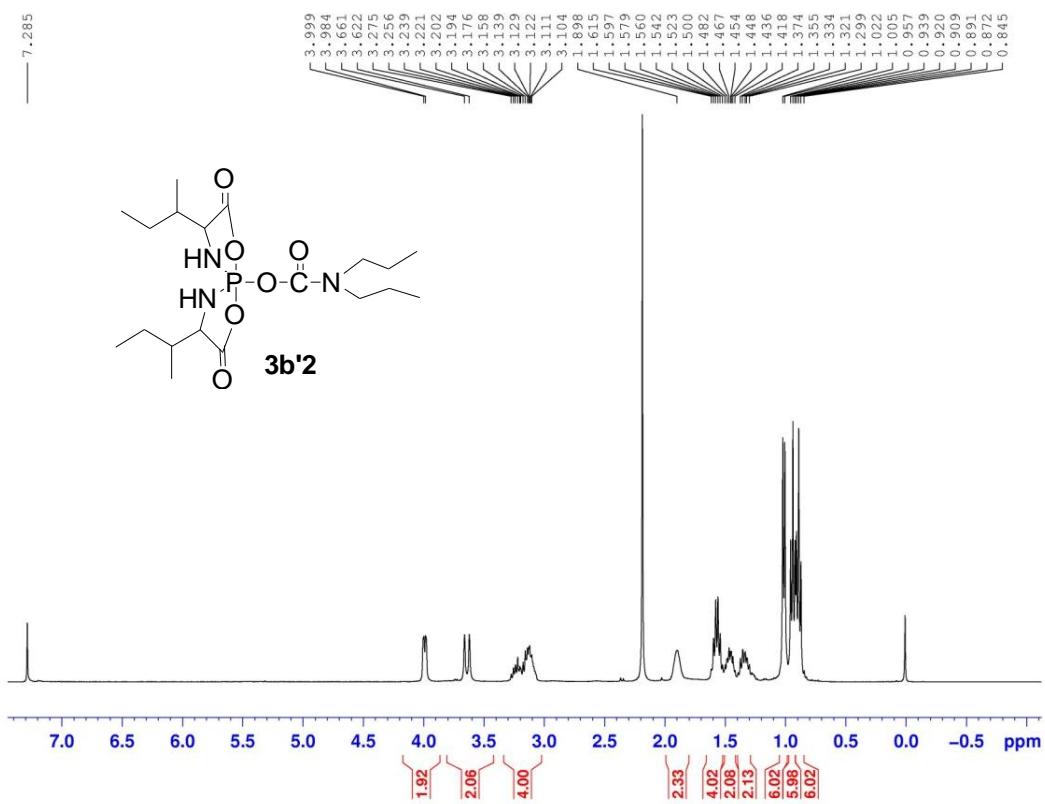
HSQC of 3b'1



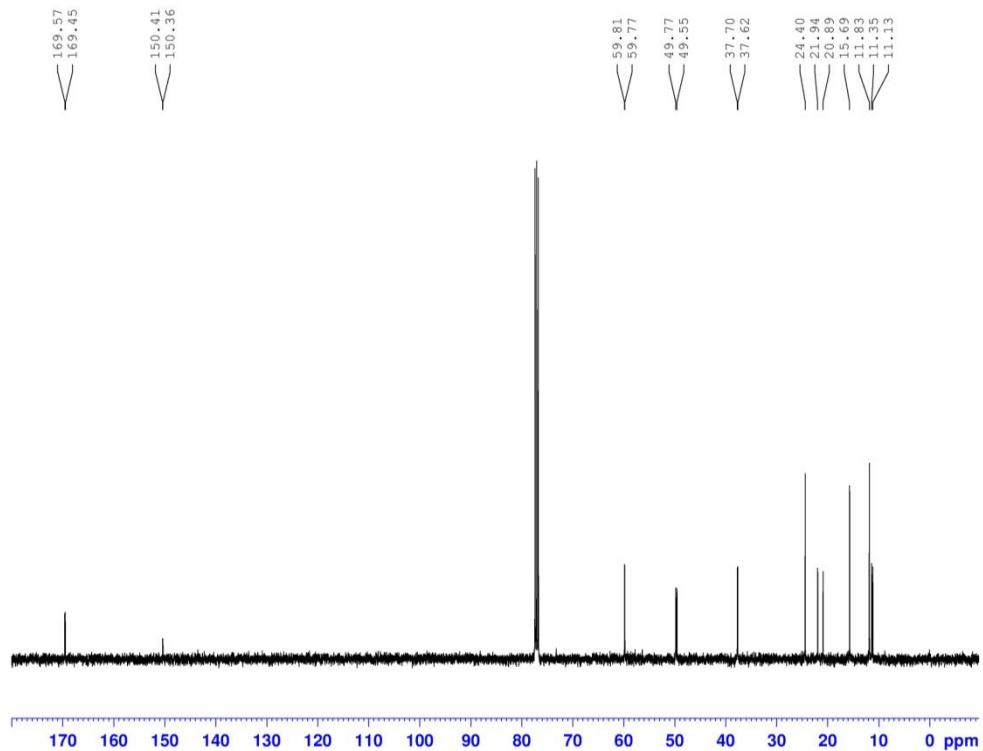
IR of 3b'1



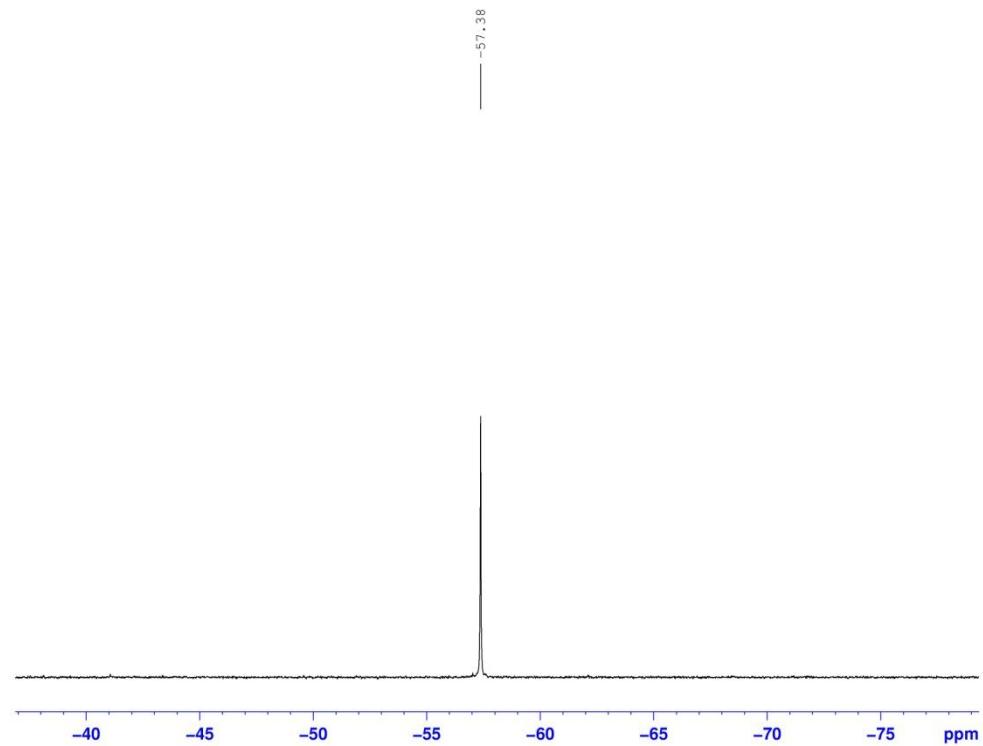
¹ H NMR of 3b'2



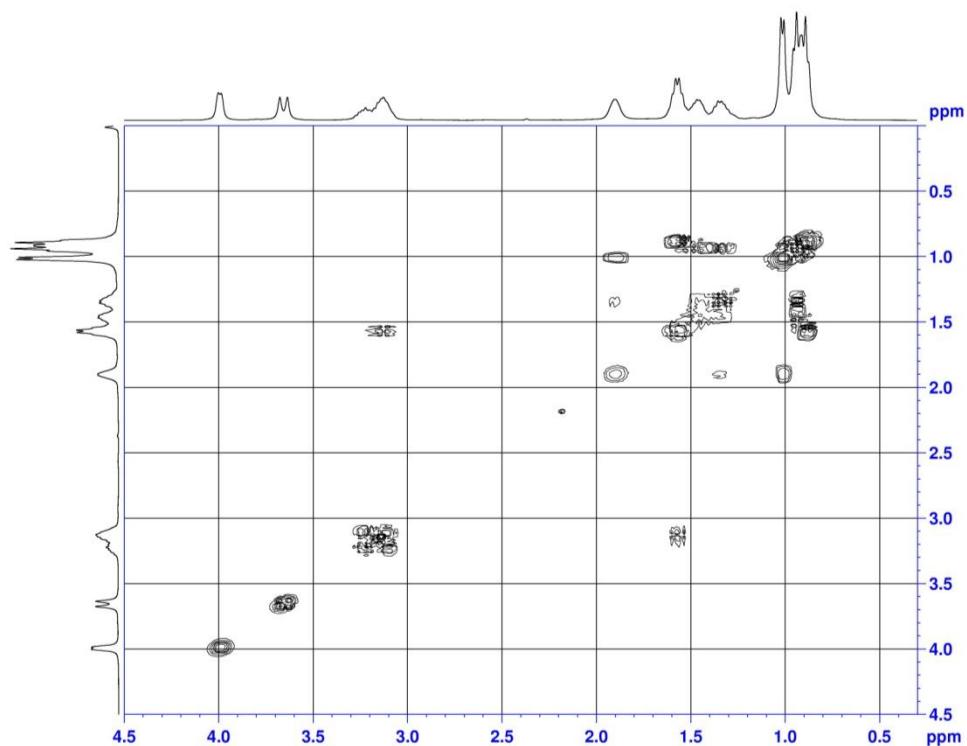
^{13}C NMR of 3b'2



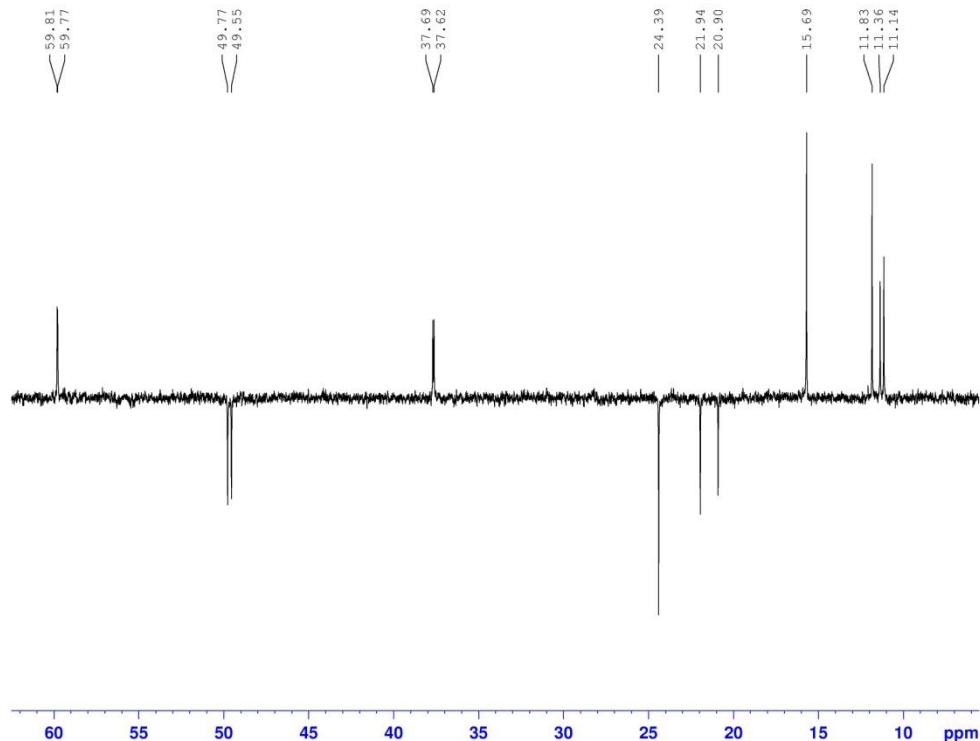
^{31}P NMR of 3b'2



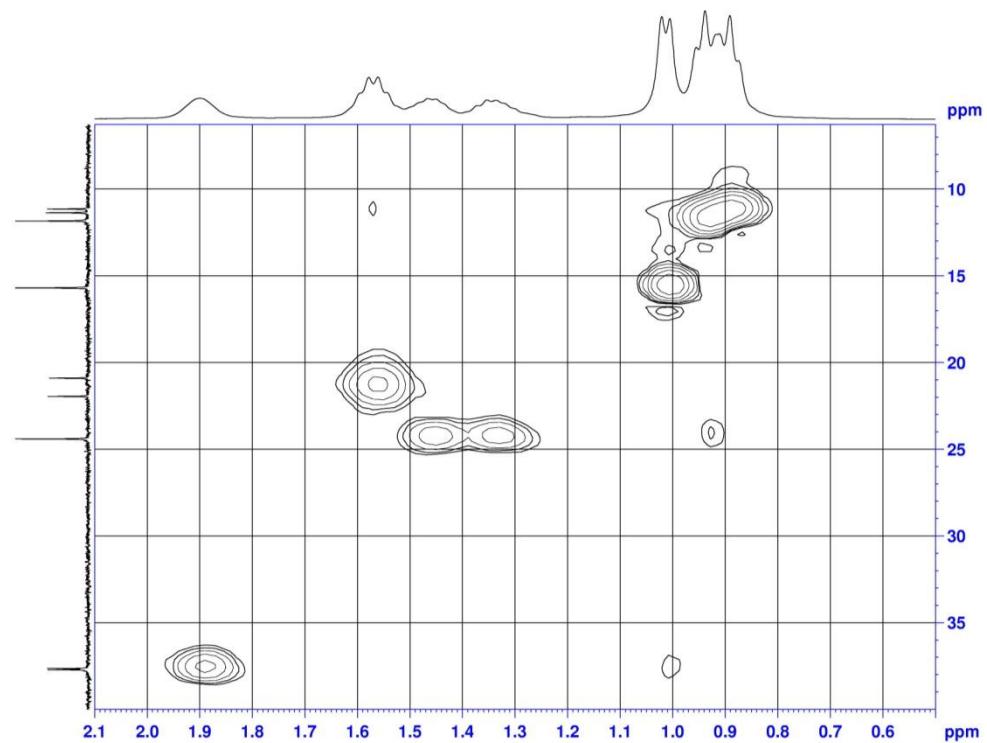
H-H COSY of 3b'2



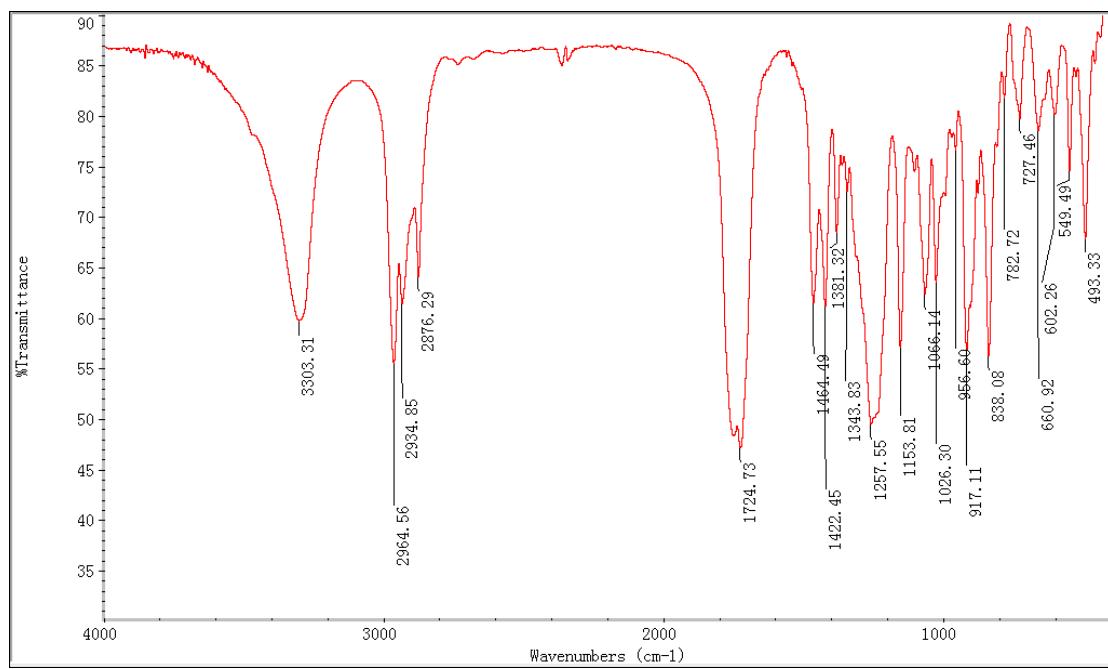
DEPT 135 of 3b'2



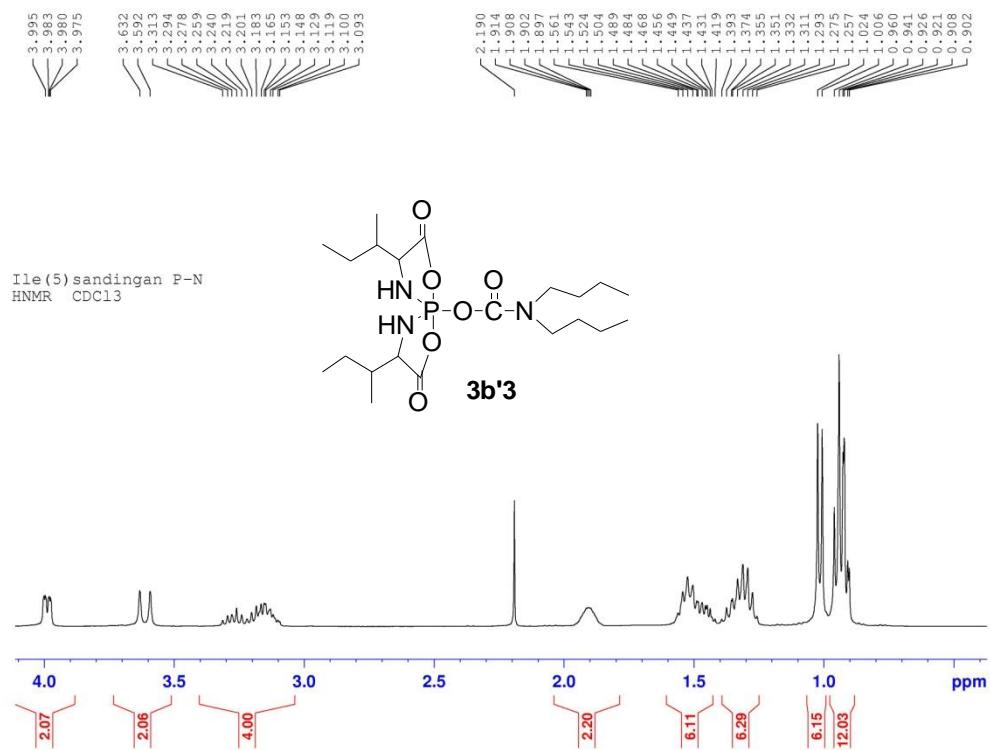
HSQC of 3b'2



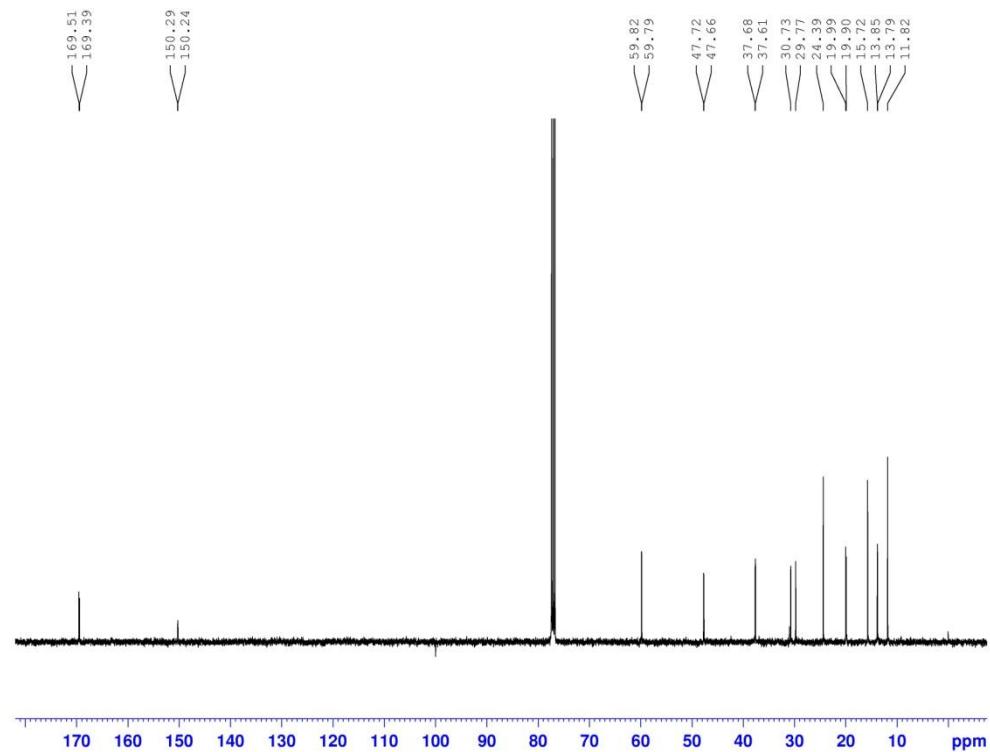
IR of 3b'2



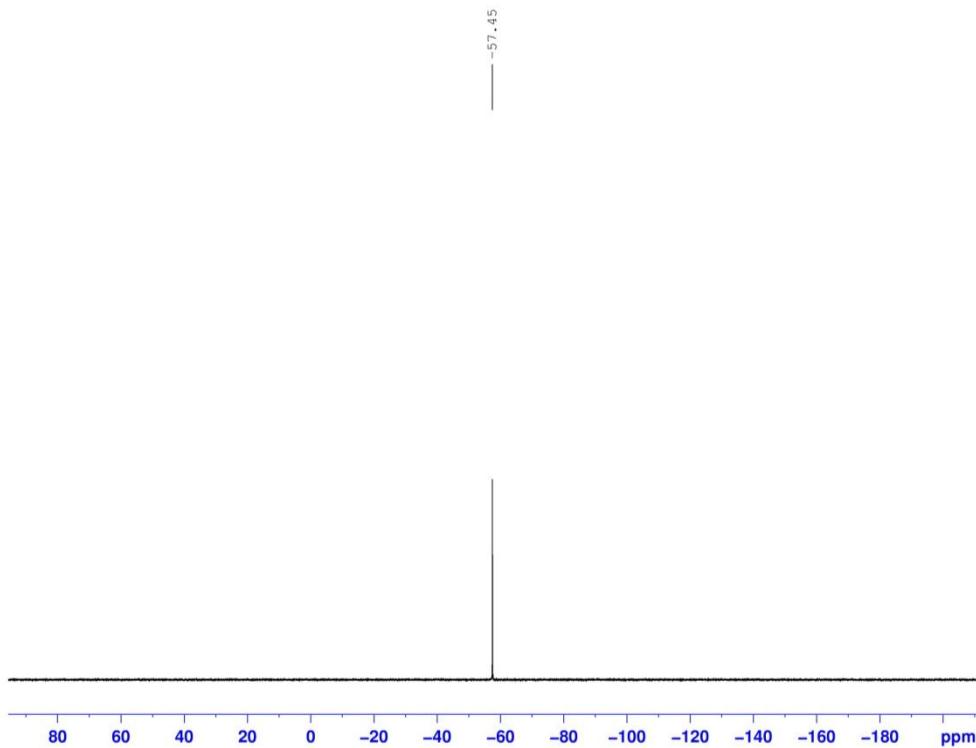
¹H NMR of 3b'3



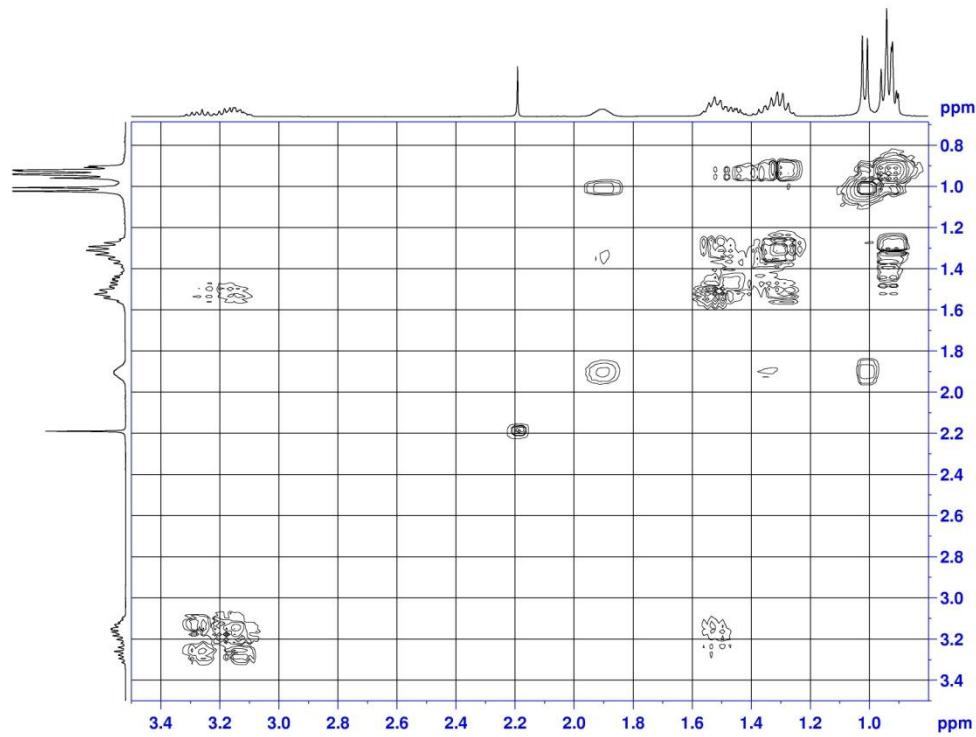
¹³C NMR of 3b'3



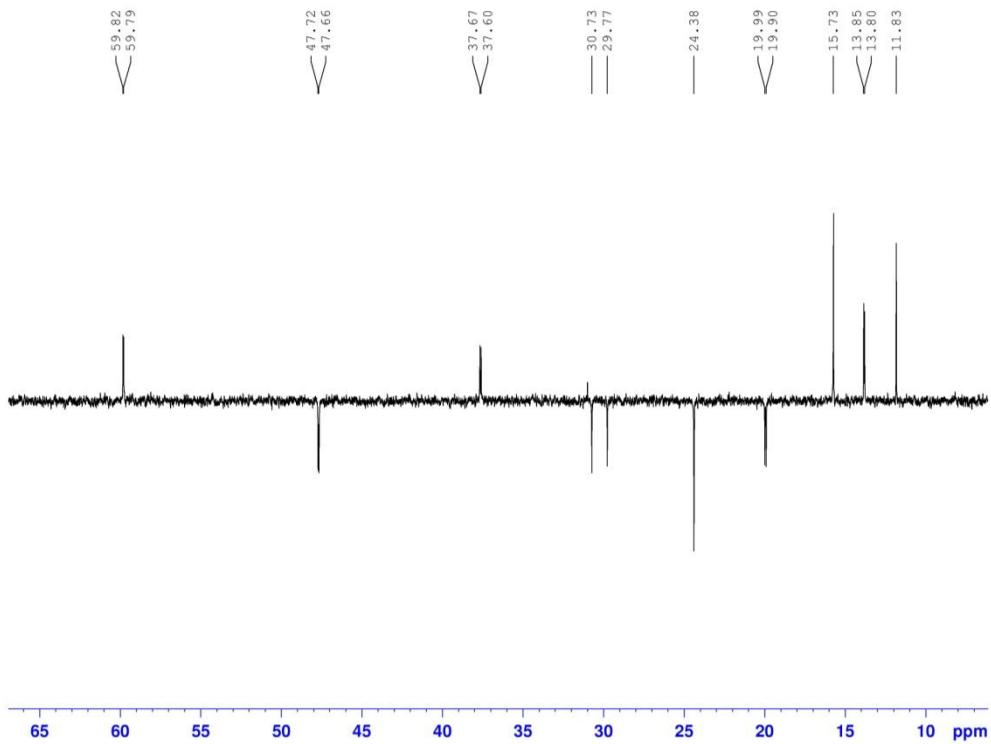
^{31}P NMR of 3b'3



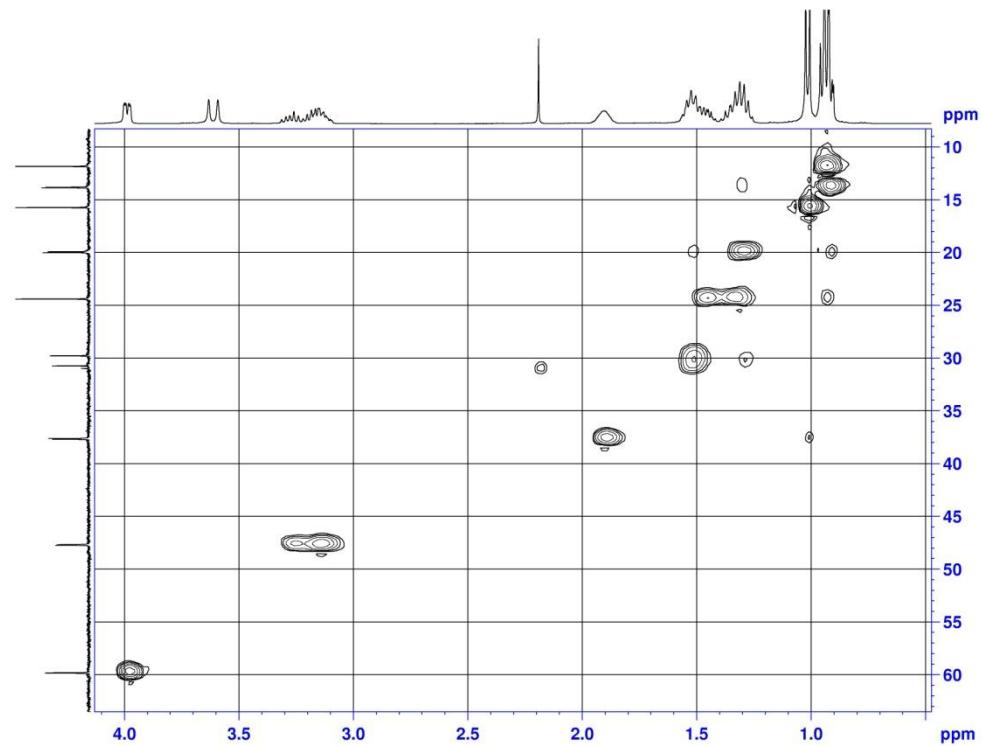
H-H COSY of 3b'3



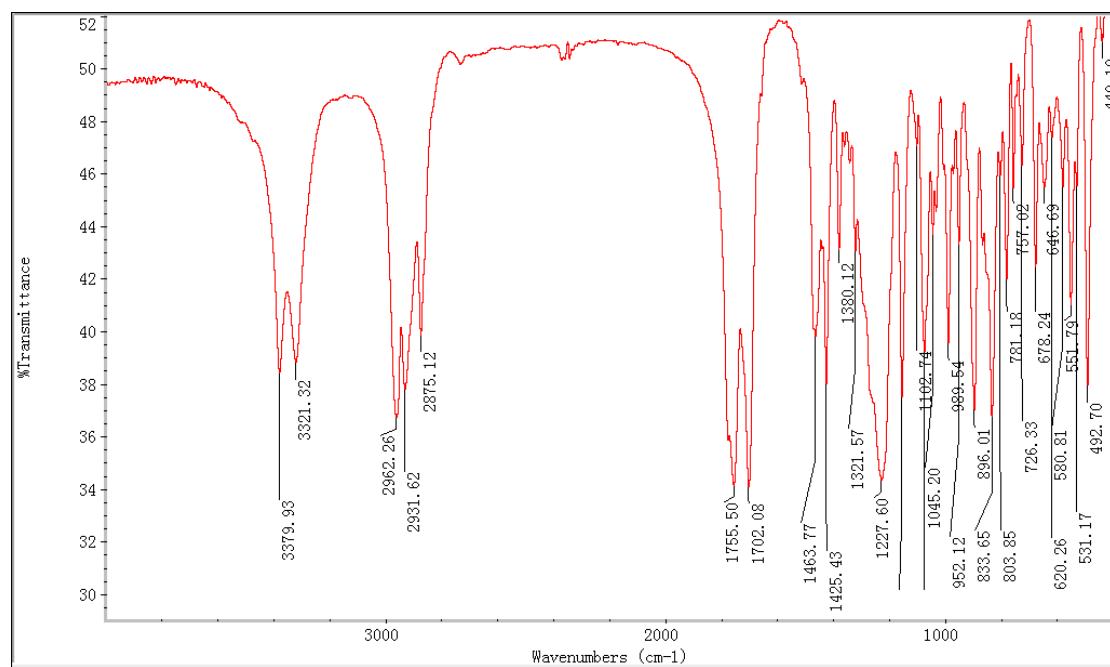
DEPT 135 of 3b'3



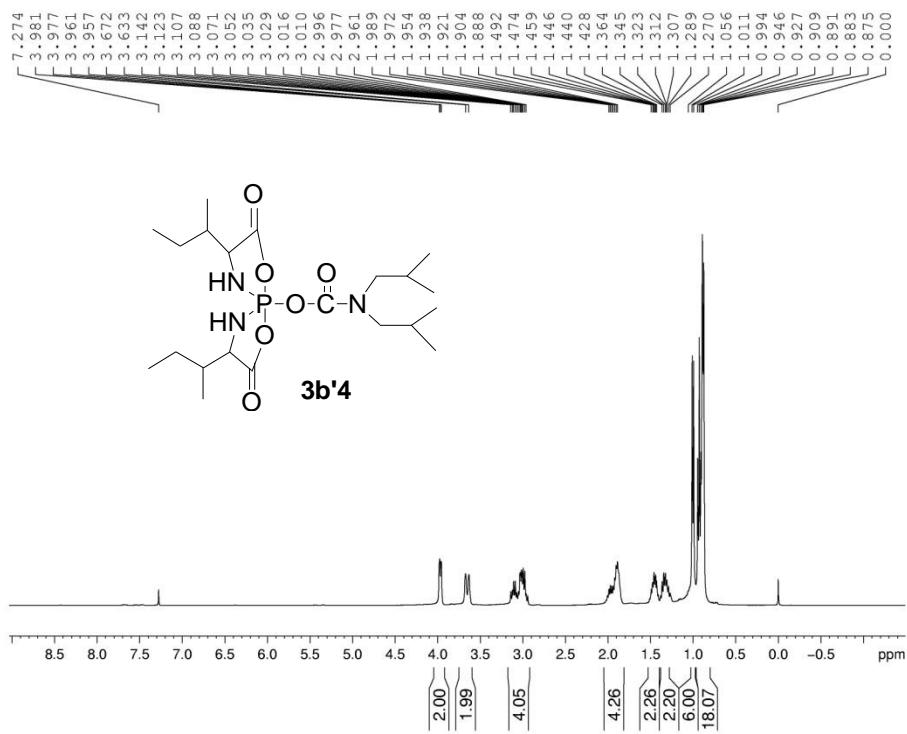
HSQC of 3b'3



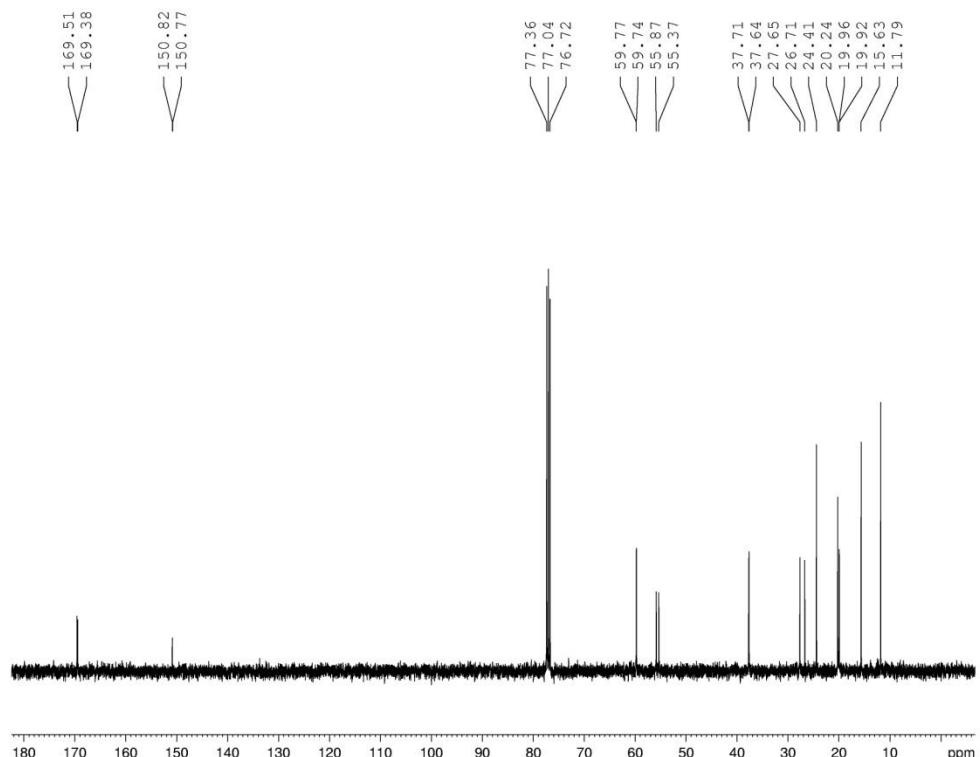
IR of 3b'3



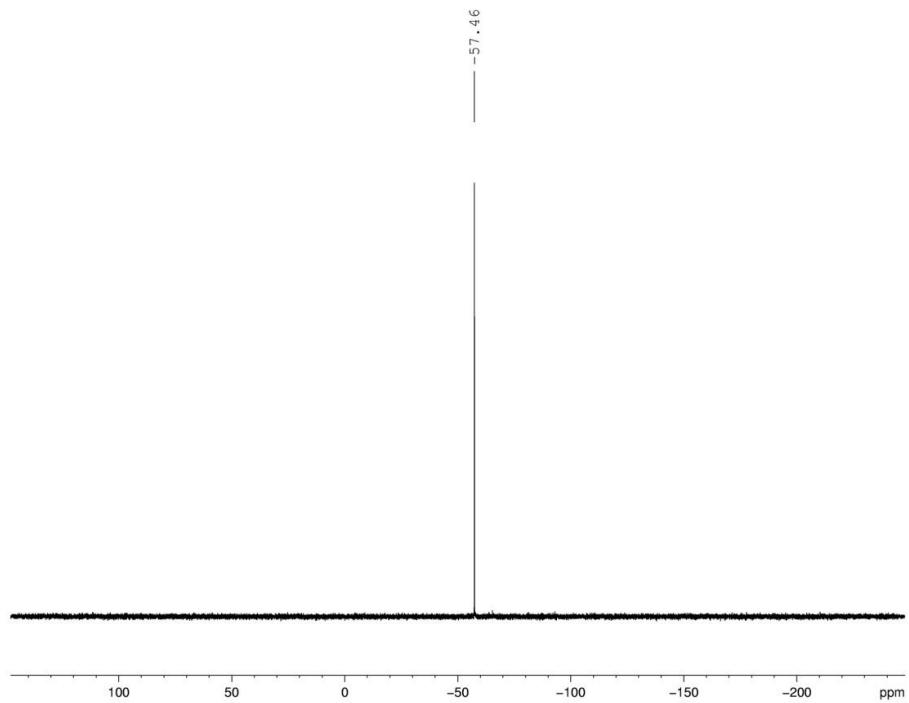
¹ H NMR of 3b'4



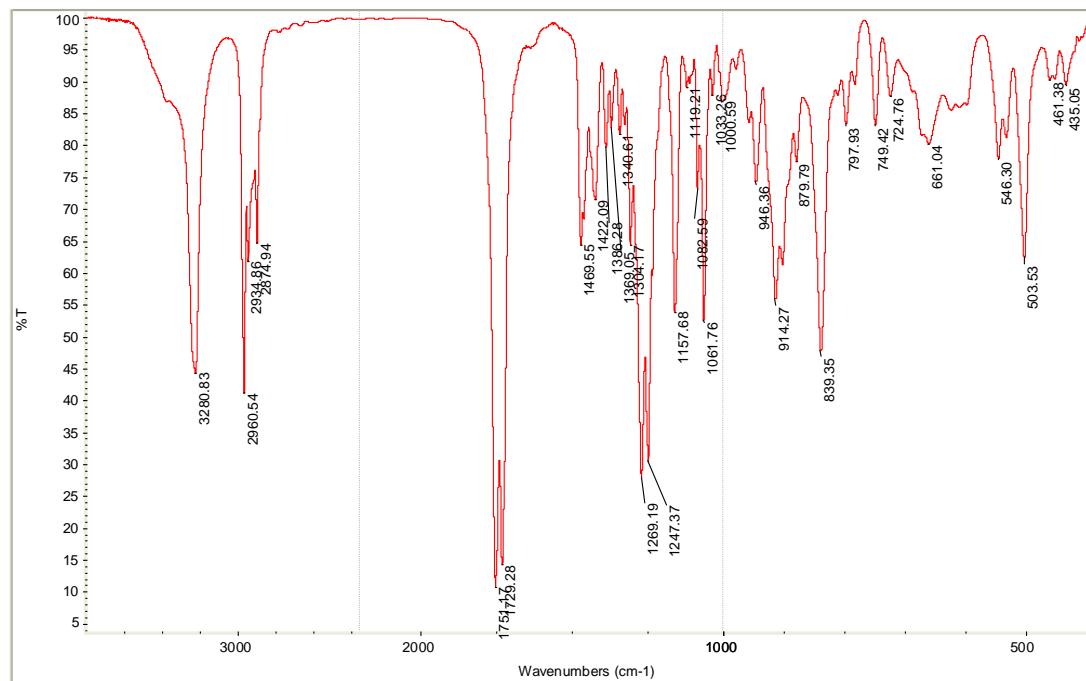
^{13}C NMR of 3b'4



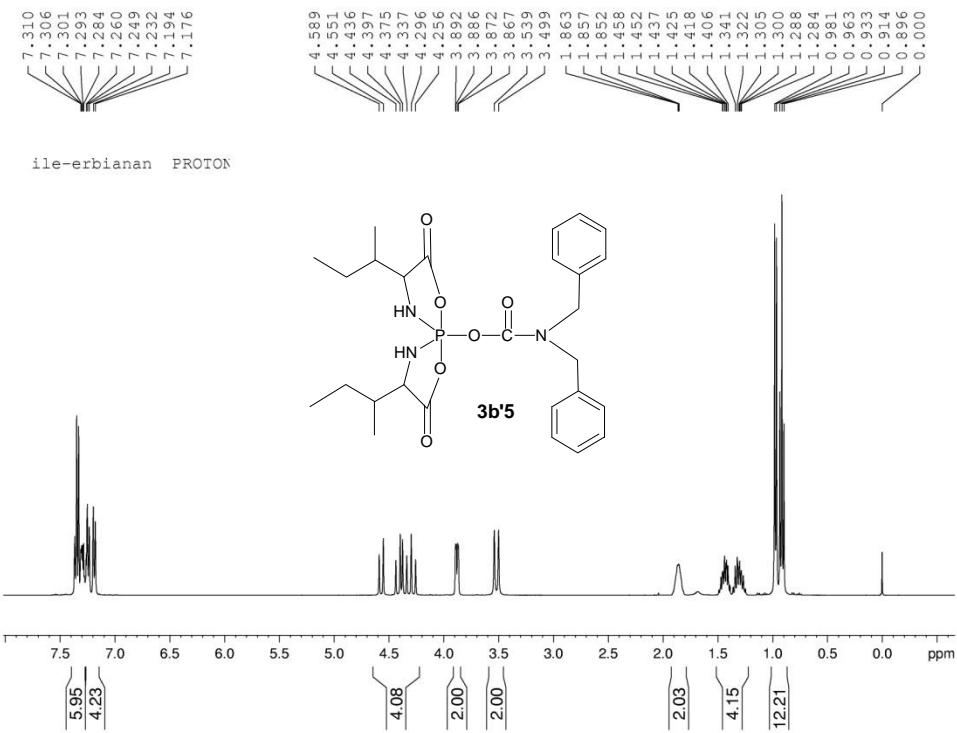
^{31}P NMR of 3b'4



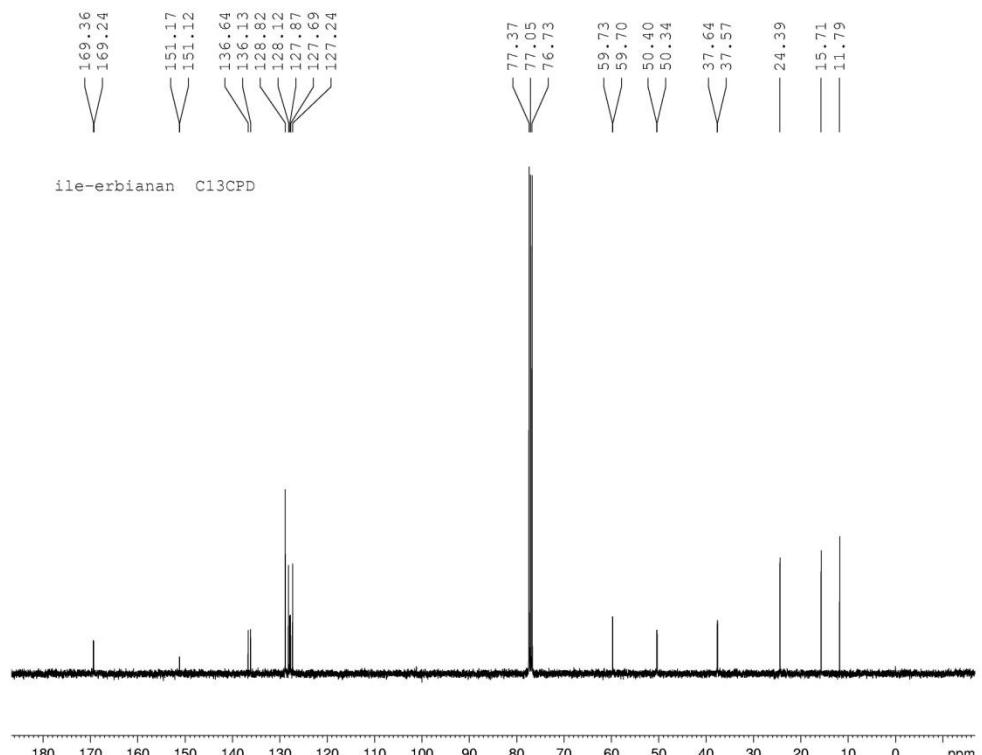
IR of 3b'4



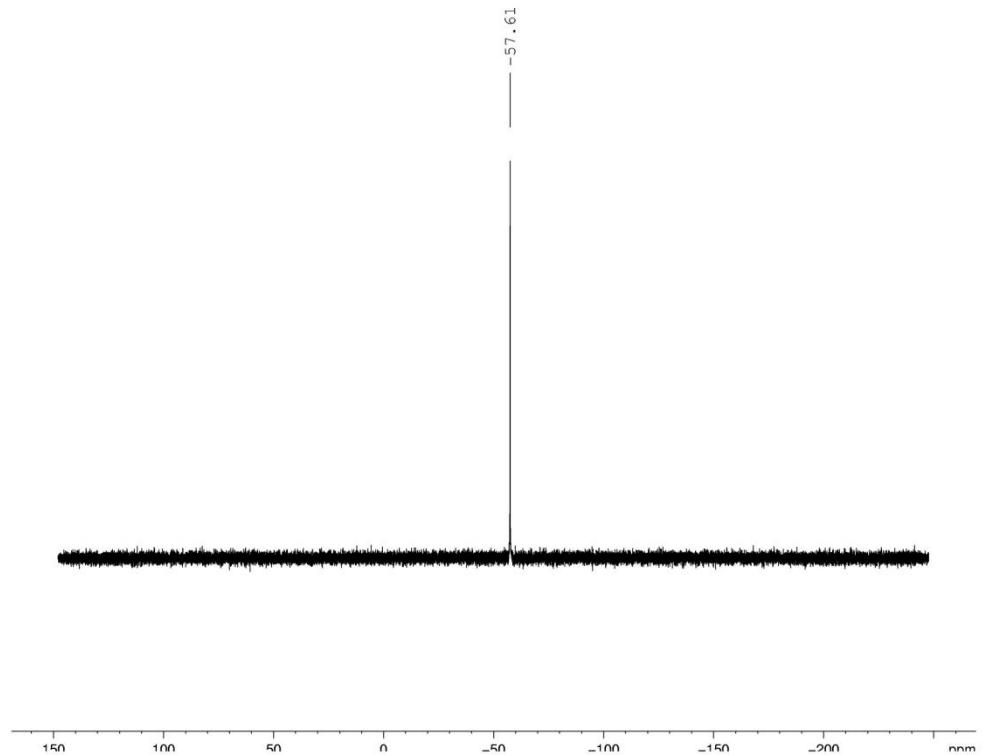
¹ H NMR of 3b'5



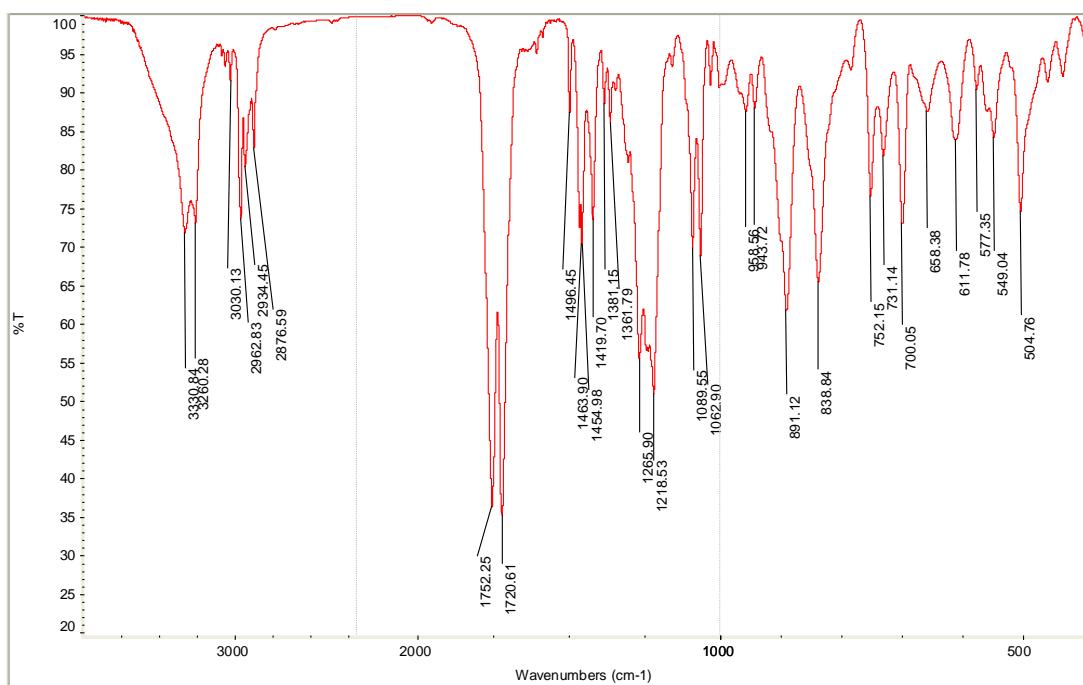
^{13}C NMR of 3b'5



^{31}P NMR of 3b'5

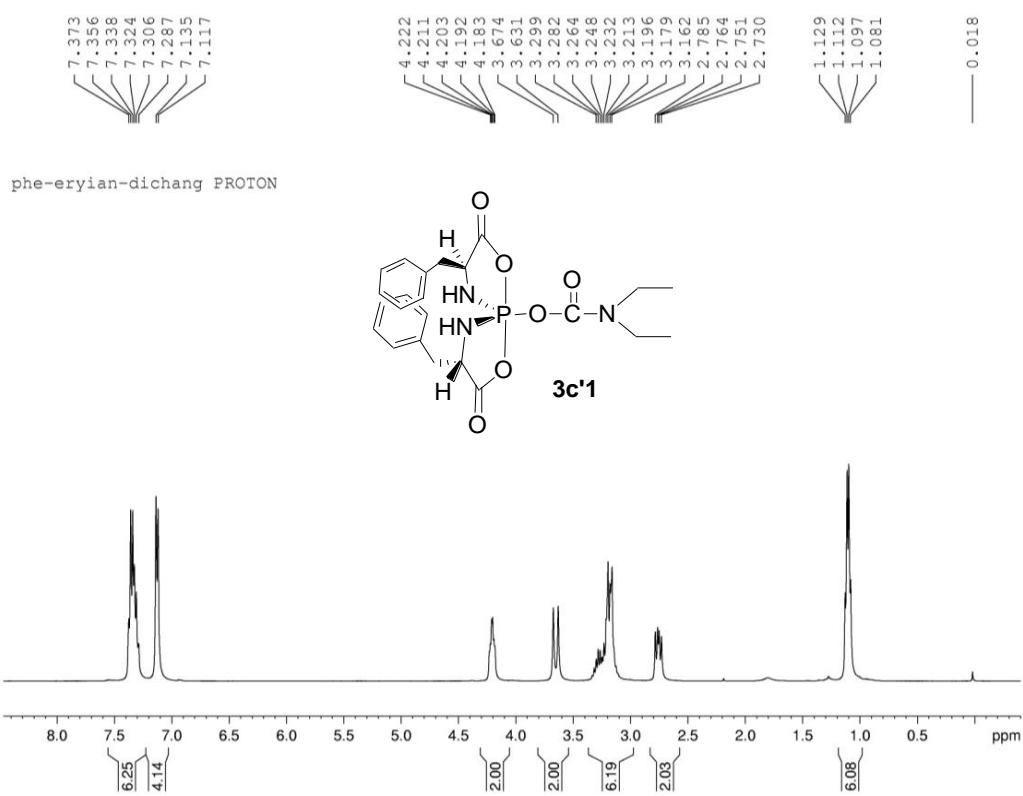


IR of 3b'5

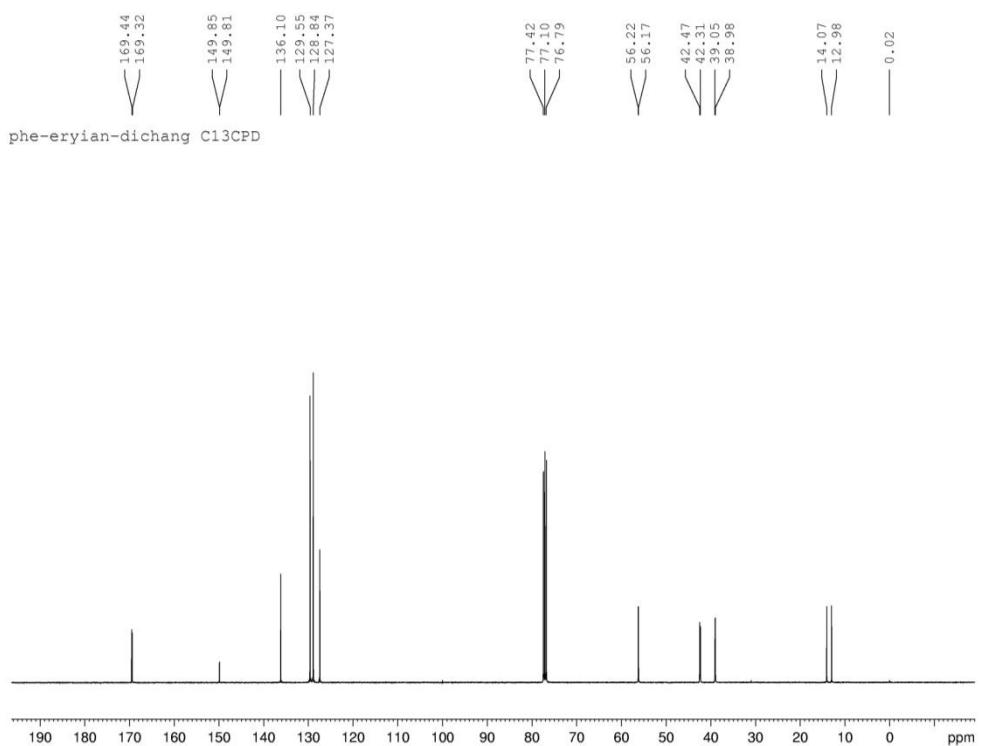


7. NMR and IR Spectra for compounds 3c'1-3c'5 and 3c1-3c3

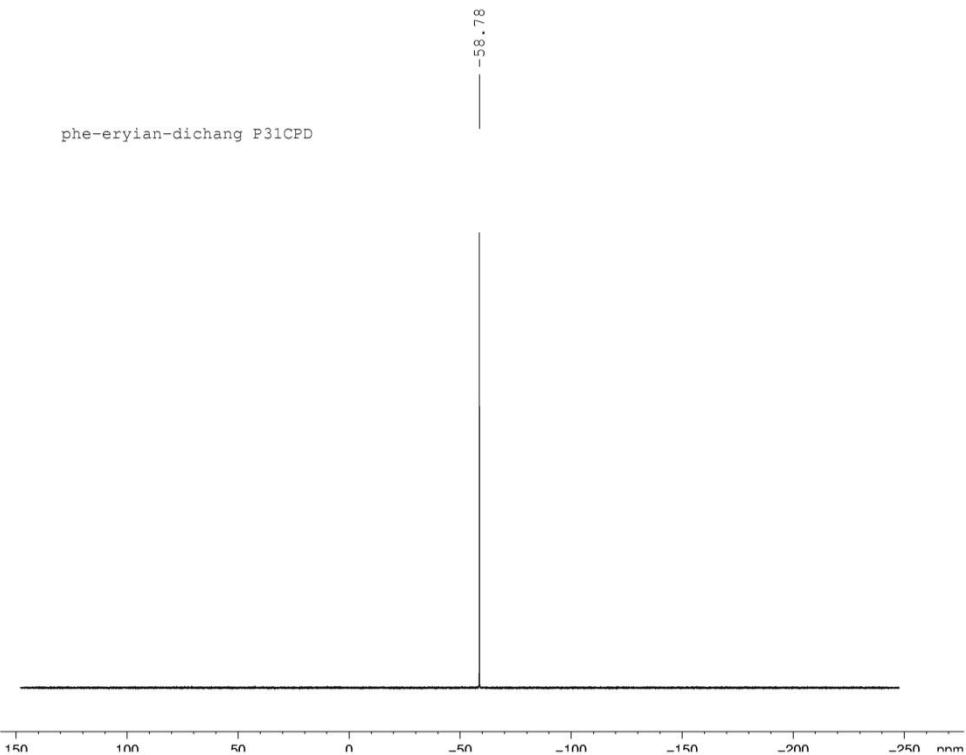
¹ H NMR of 3c'1



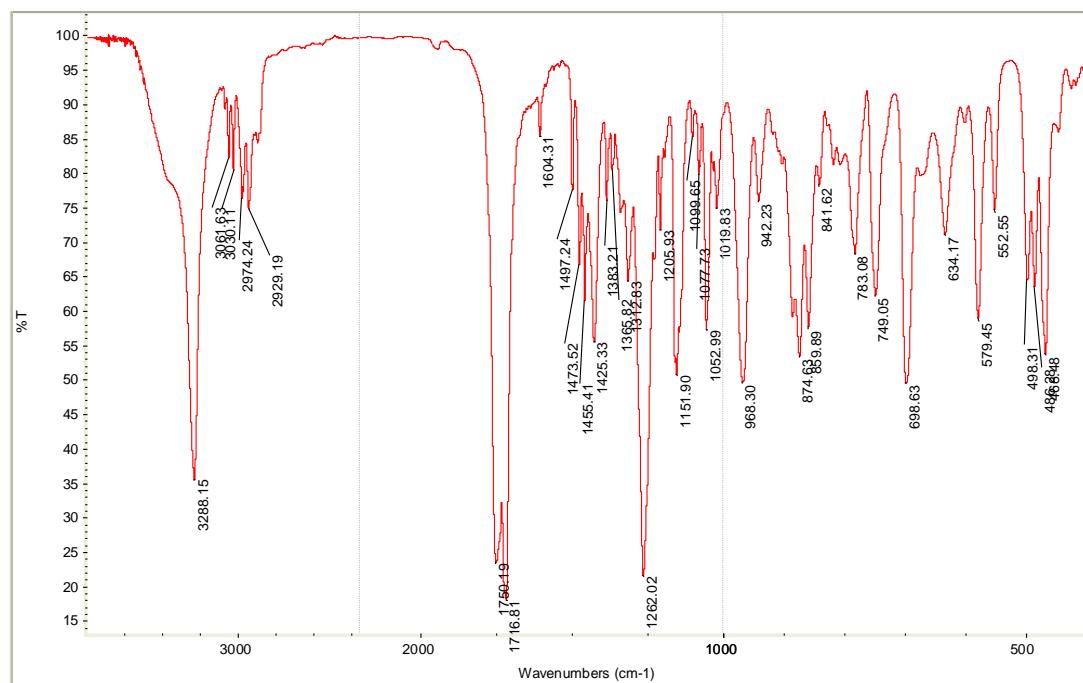
¹³C NMR of 3c'1



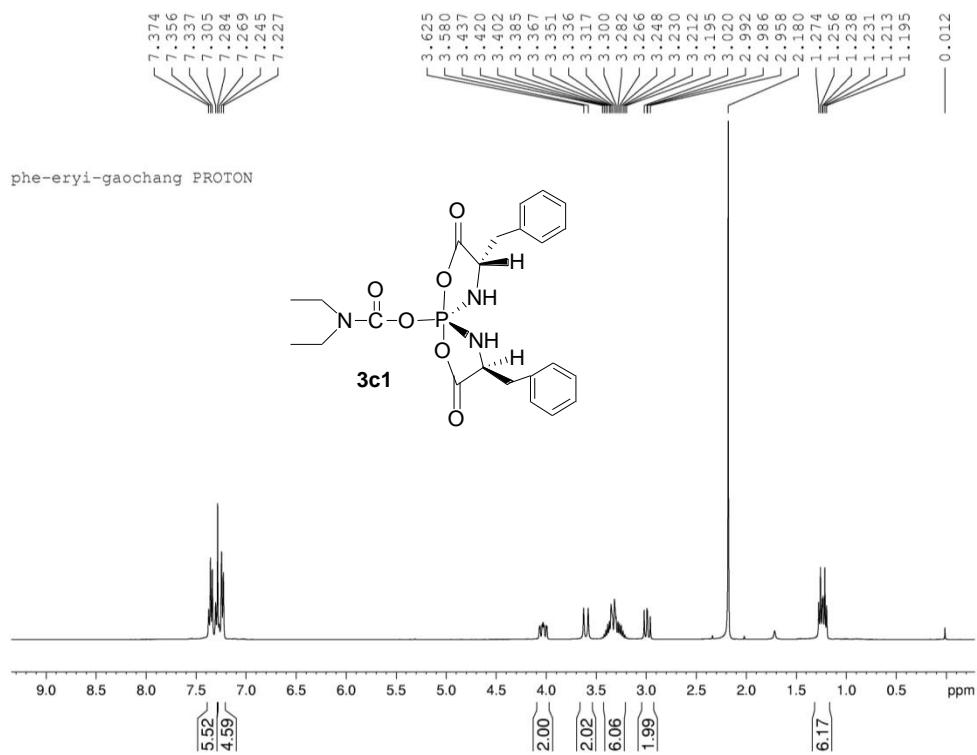
³¹P NMR of 3c'1



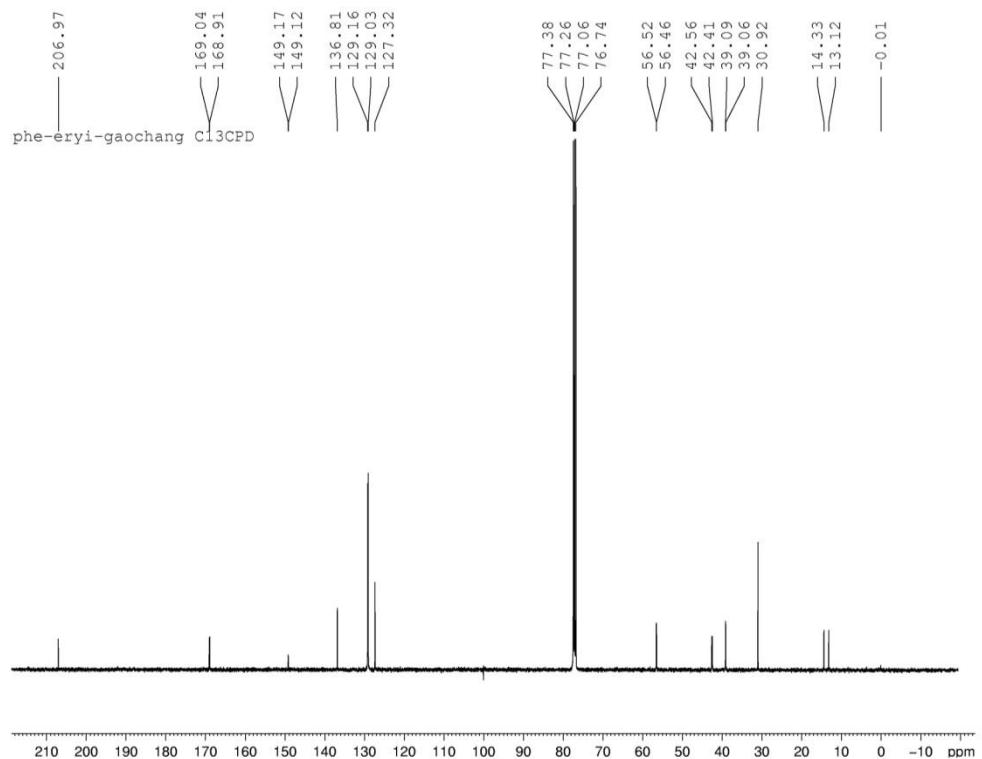
IR of 3c'1



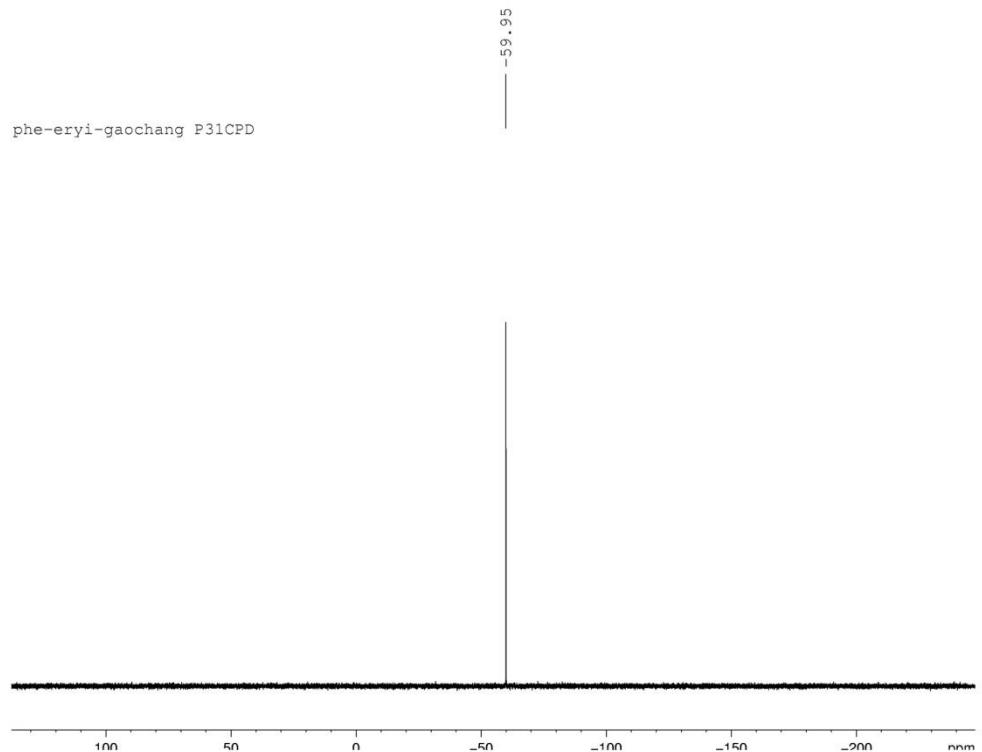
¹H NMR of 3c1



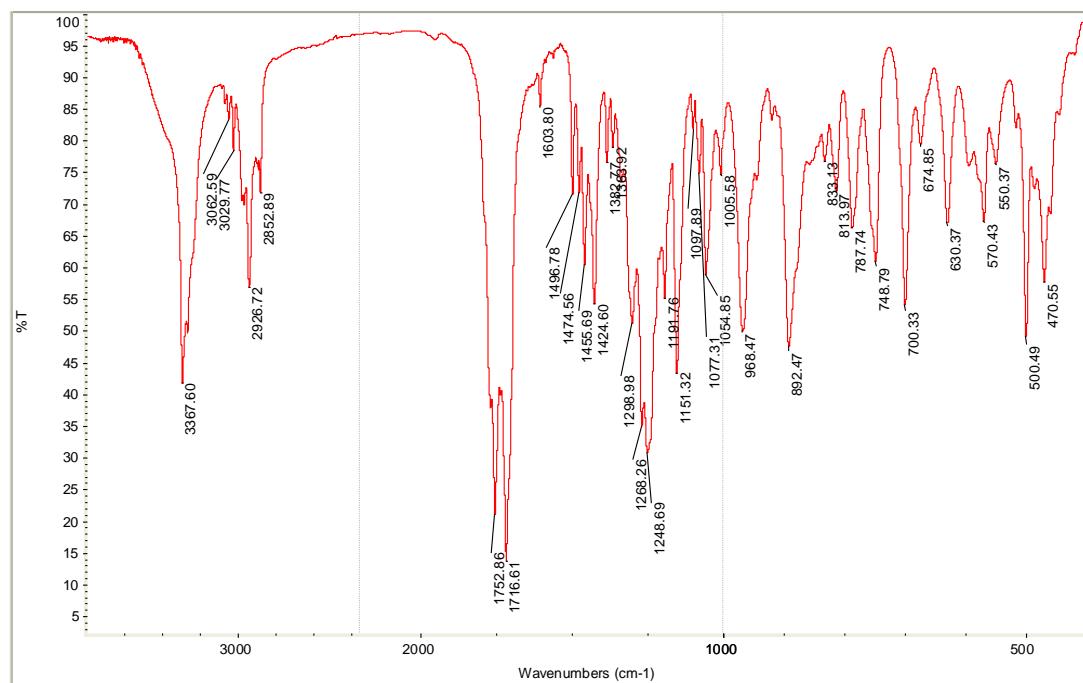
¹³C NMR of 3c1



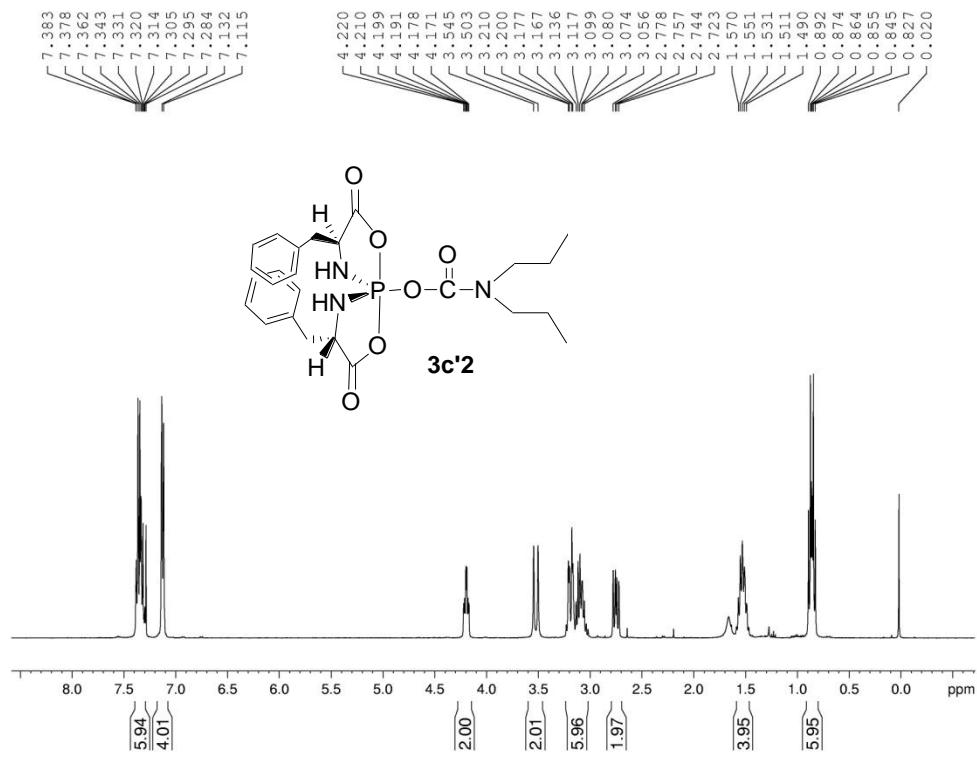
³¹P NMR of 3c1



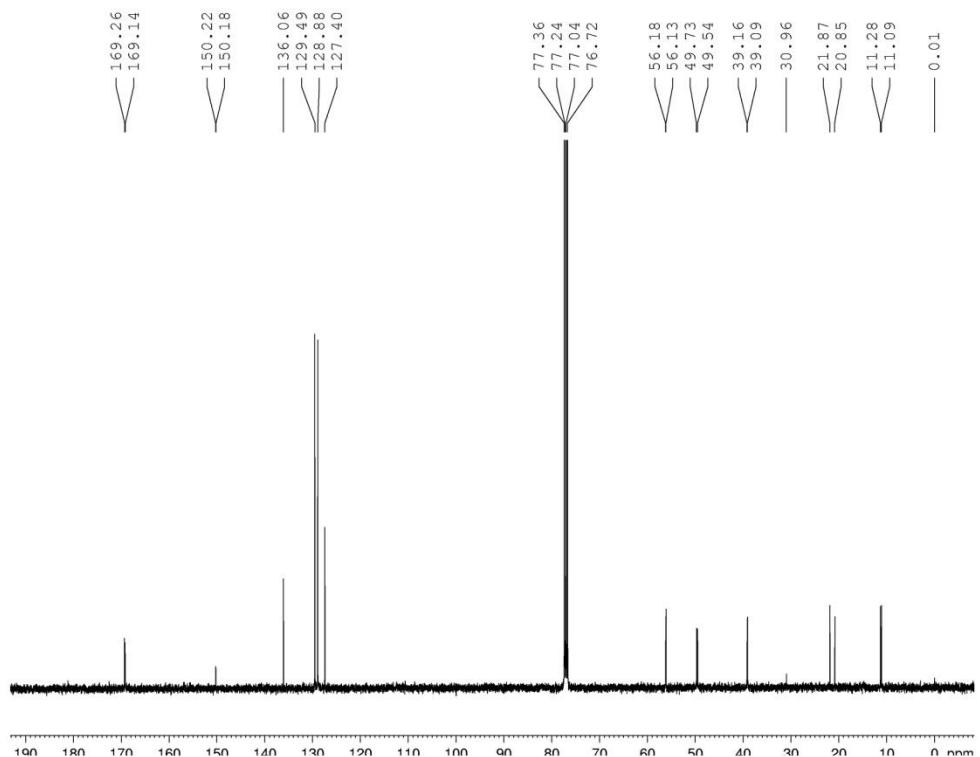
IR of 3c1



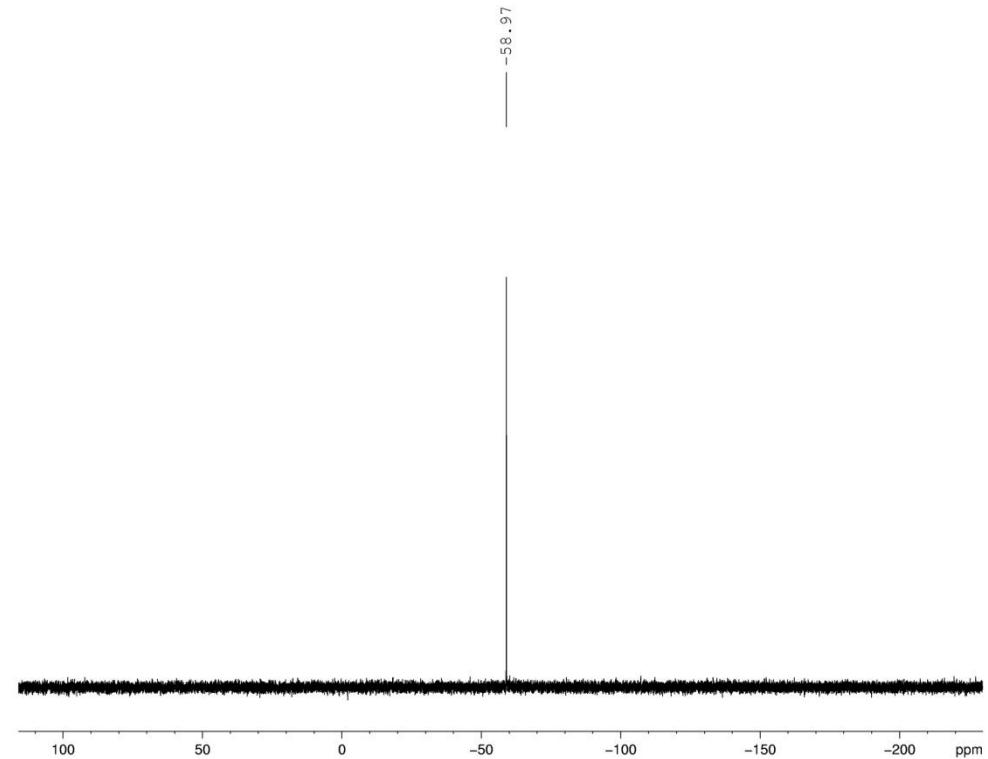
¹ H NMR of 3c'2



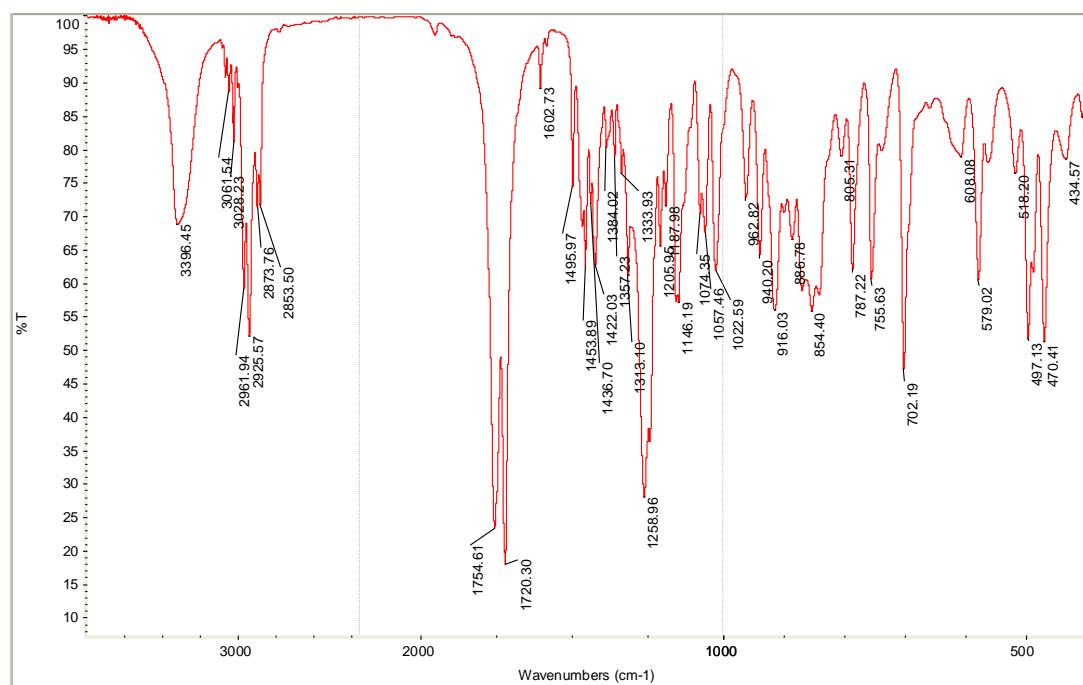
¹³C NMR of 3c'2



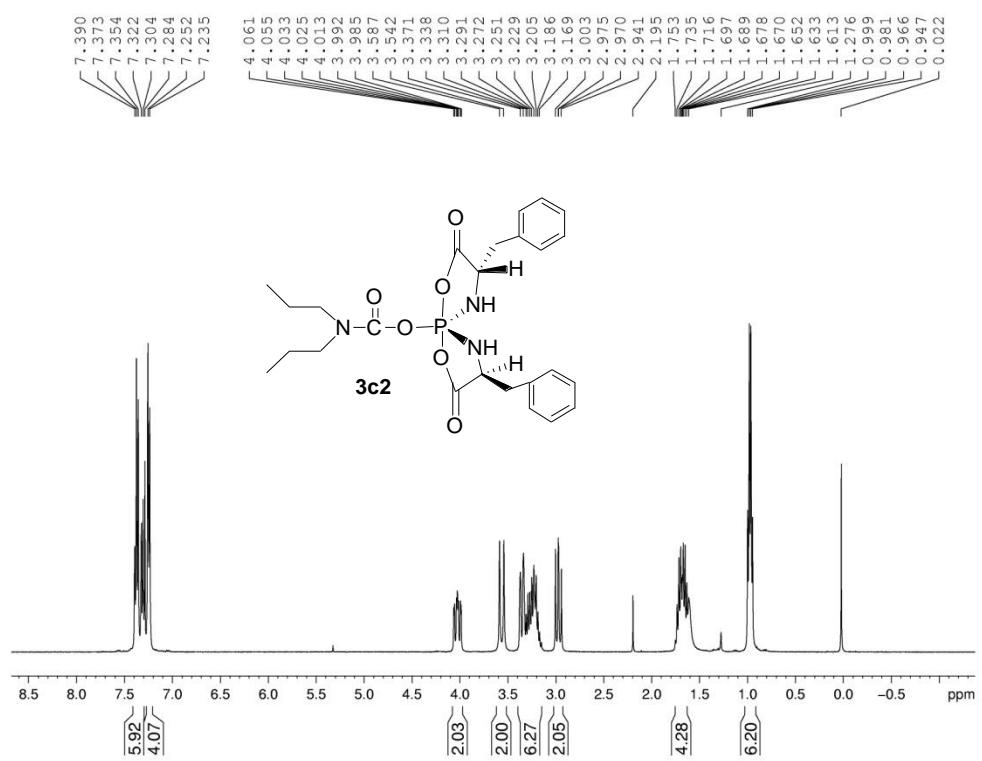
³¹P NMR of 3c'2



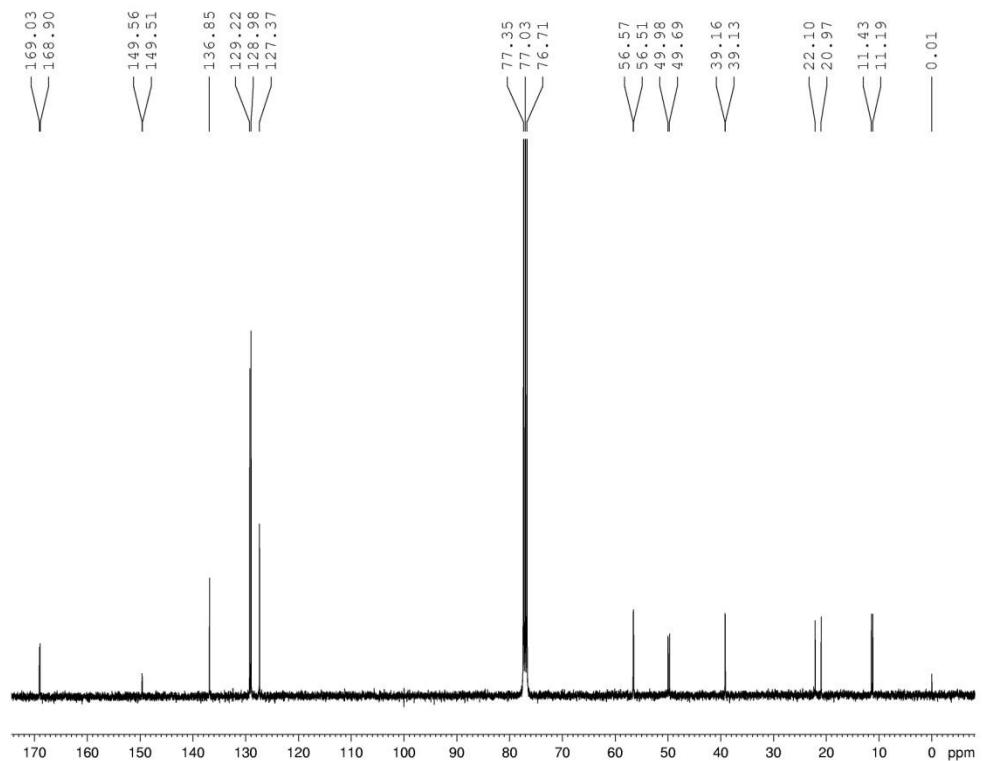
IR of 3c'2



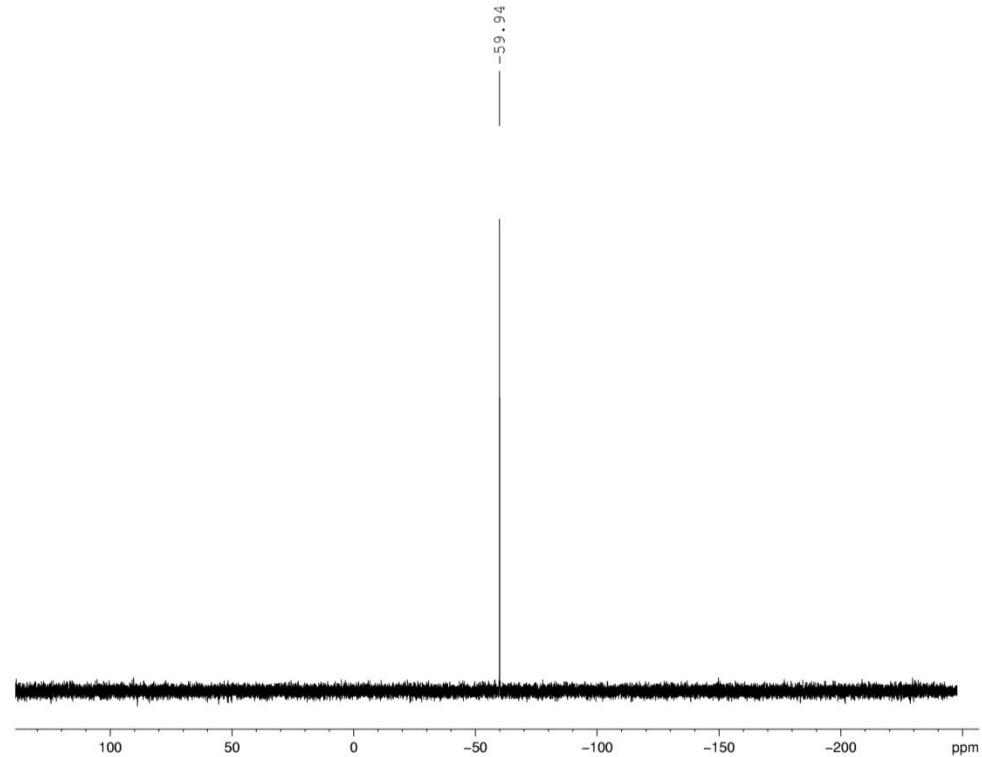
¹ H NMR of 3c2



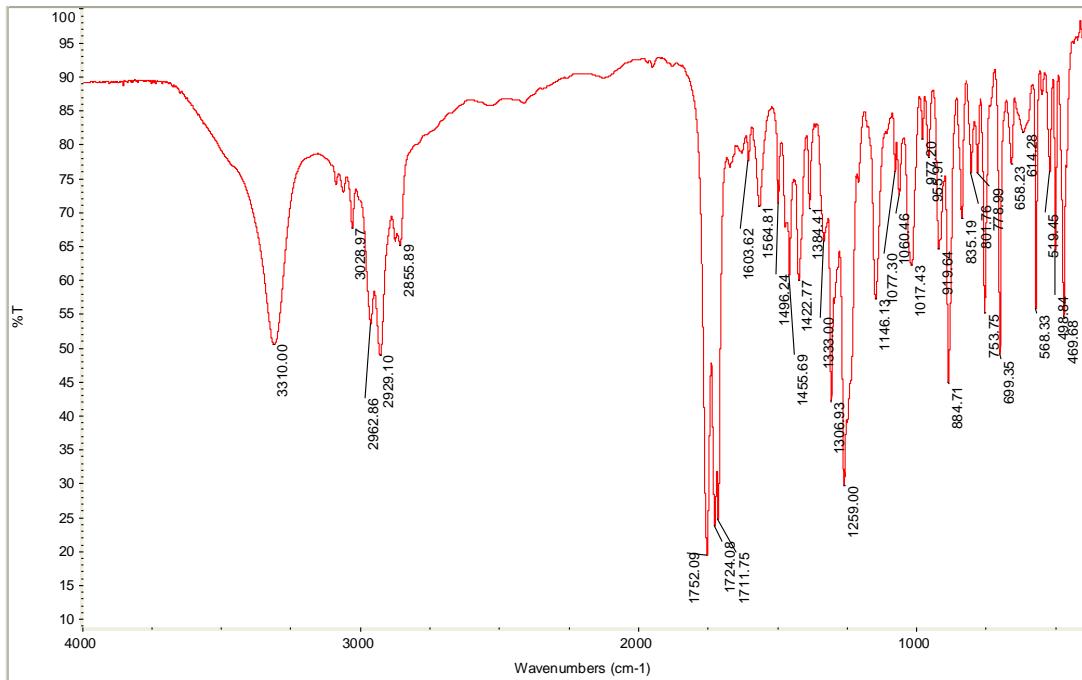
¹³C NMR of 3c2



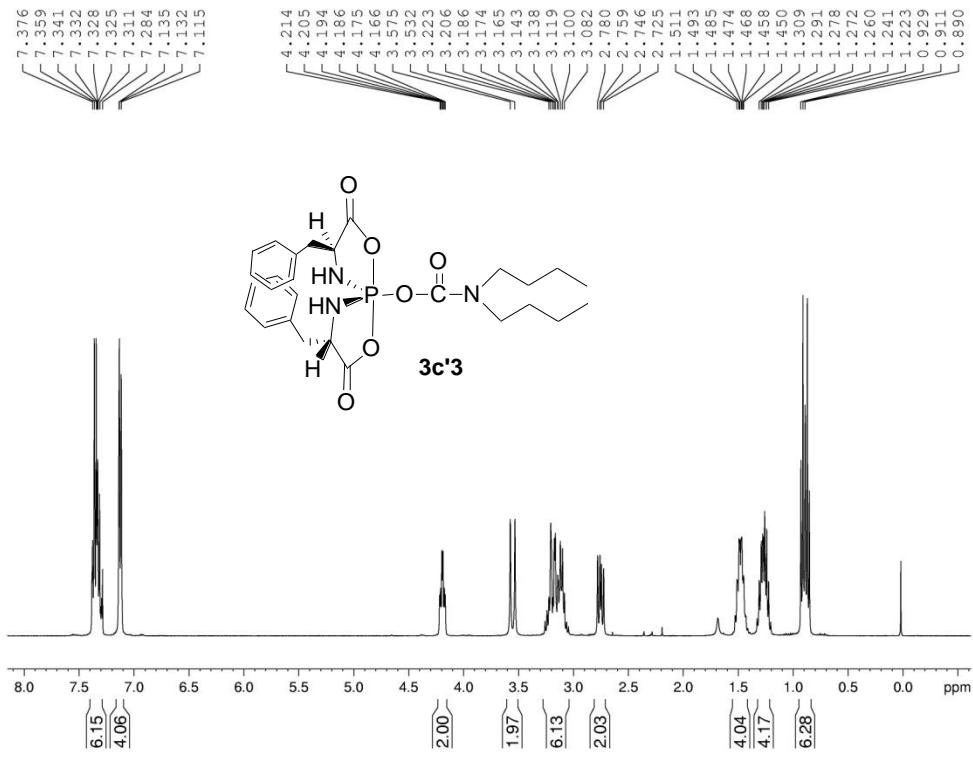
³¹P NMR of 3c2



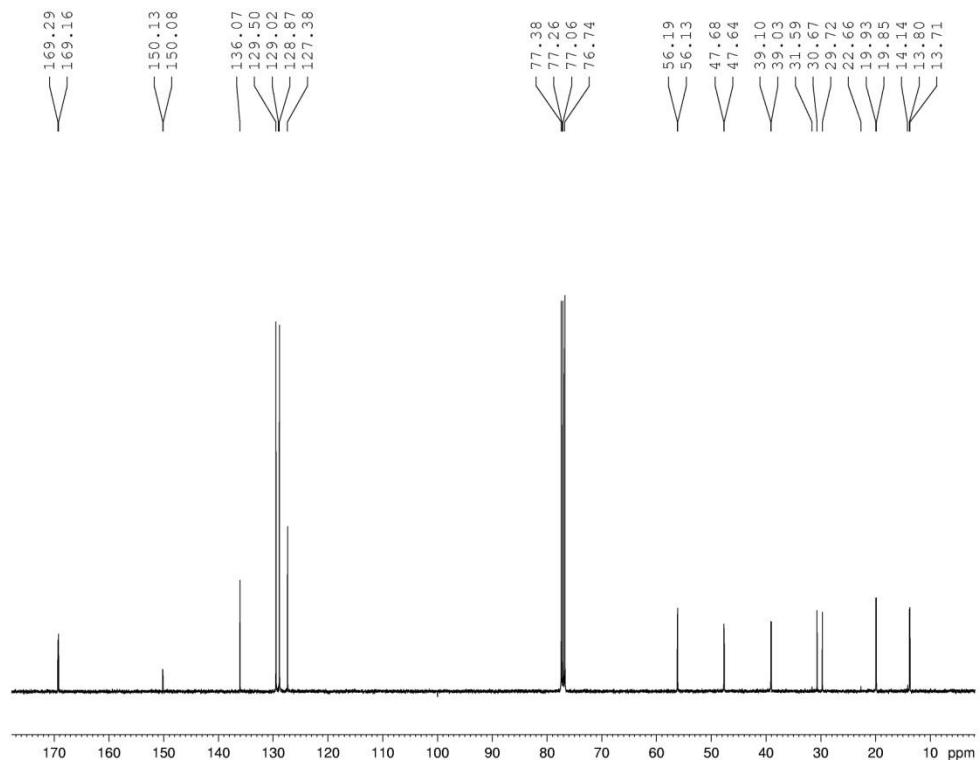
IR of 3c2



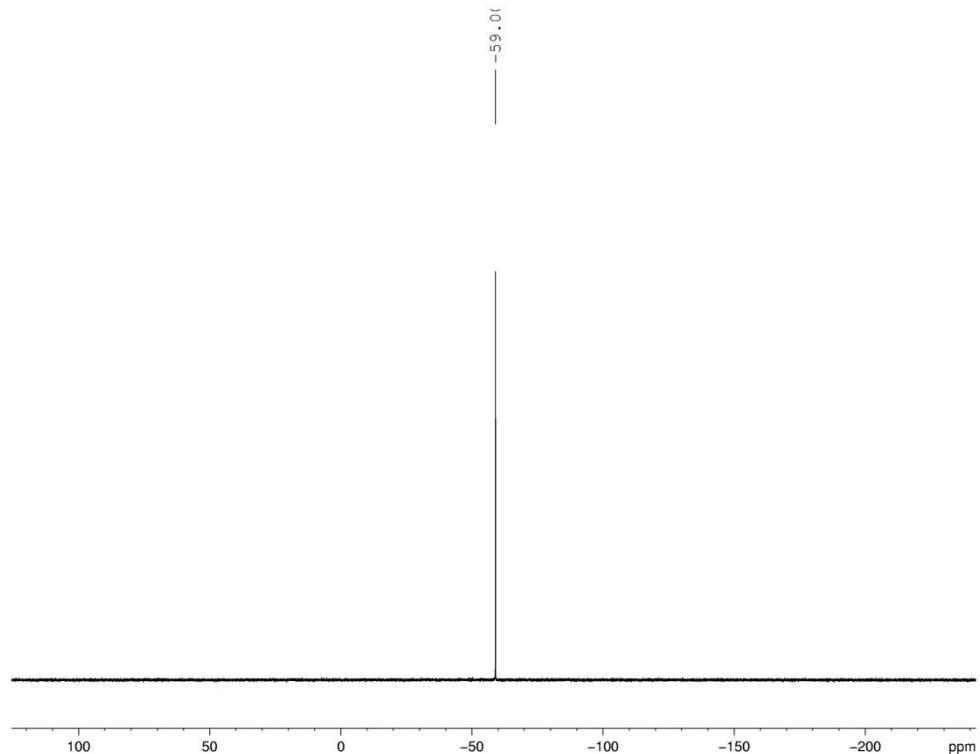
¹ H NMR of 3c'3



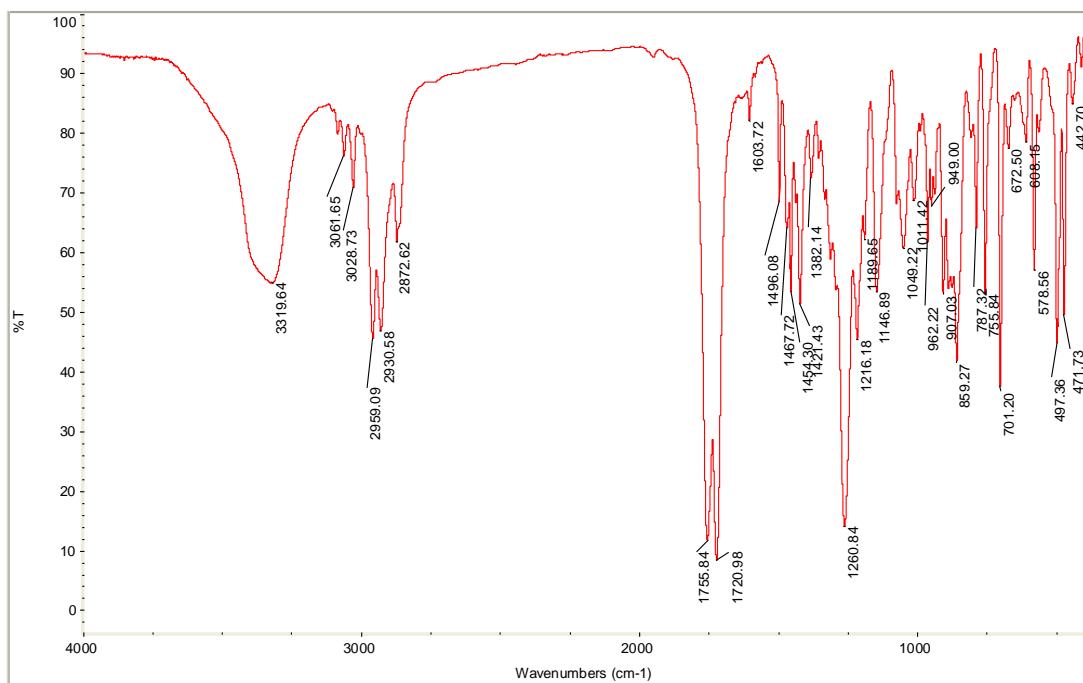
¹³C NMR of 3c'3



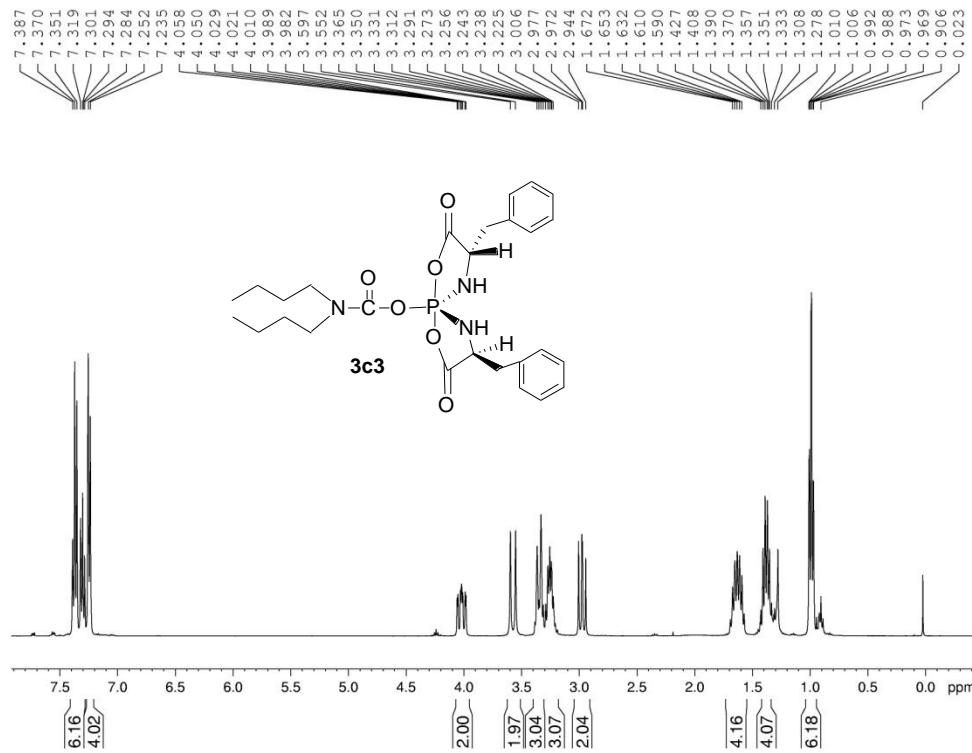
³¹P NMR of 3c'3



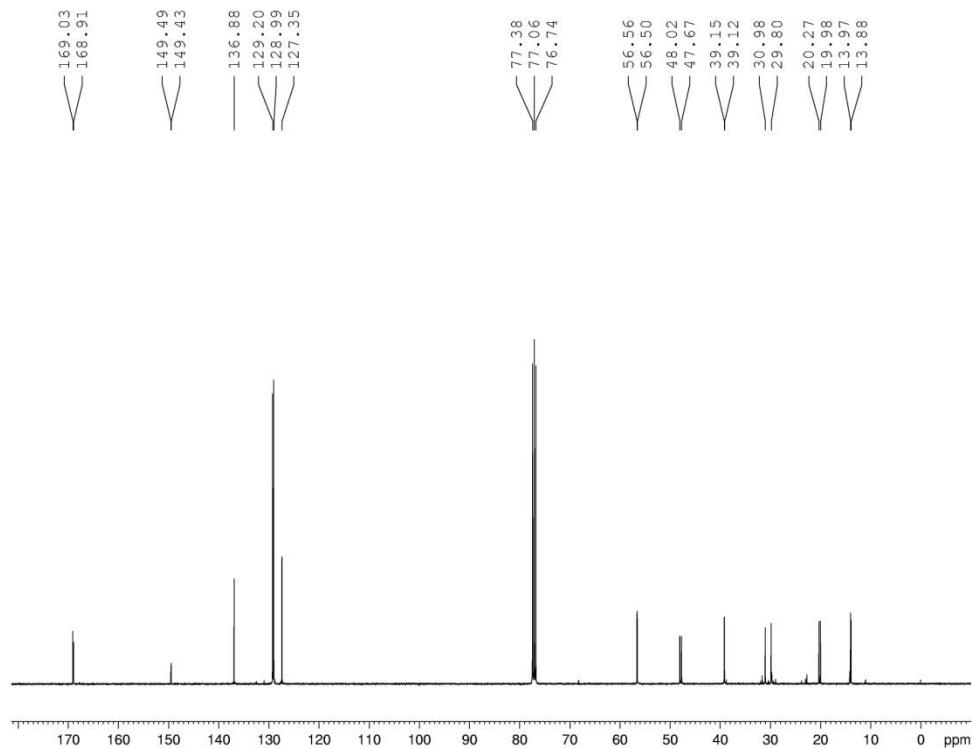
IR of 3c'3



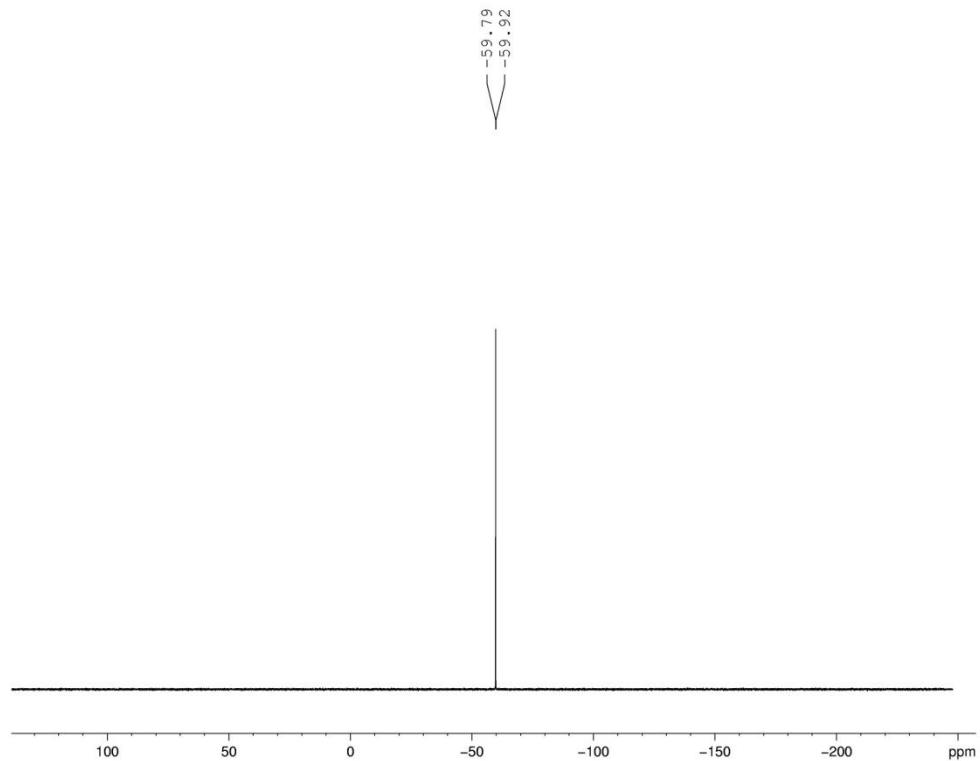
¹ H NMR of 3c3



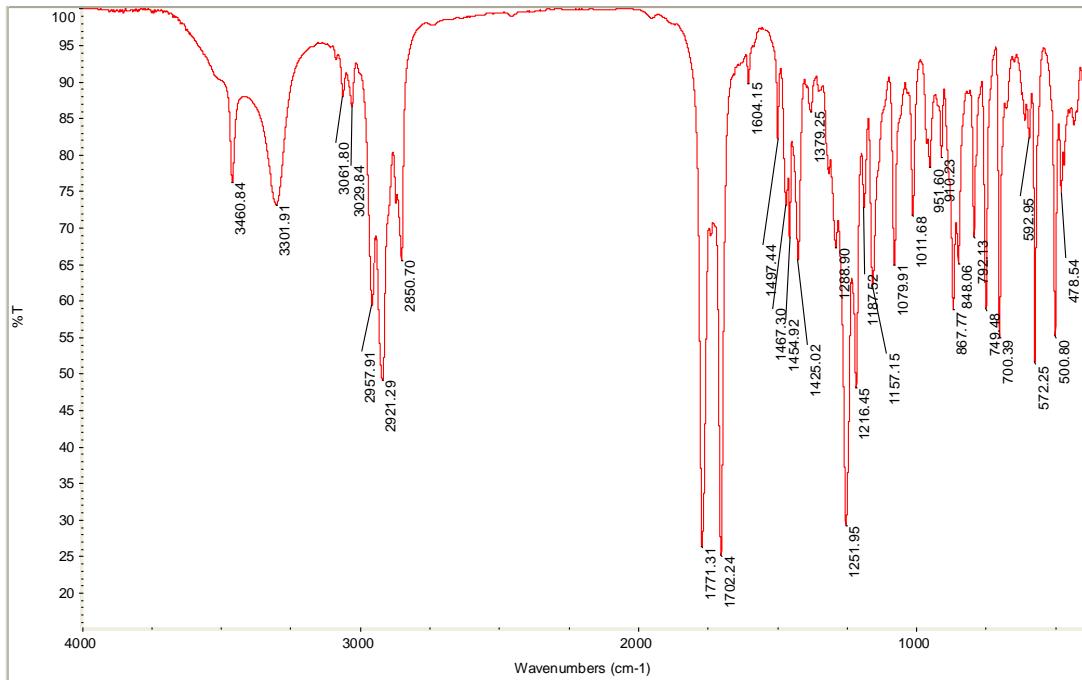
¹³C NMR of 3c3



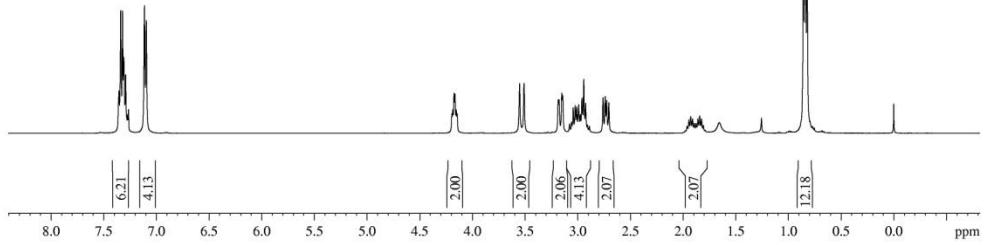
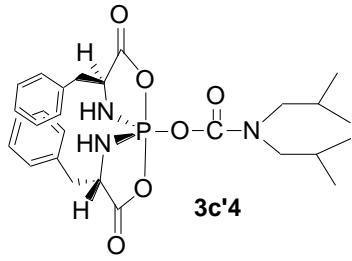
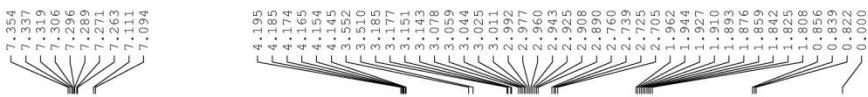
³¹P NMR of 3c3



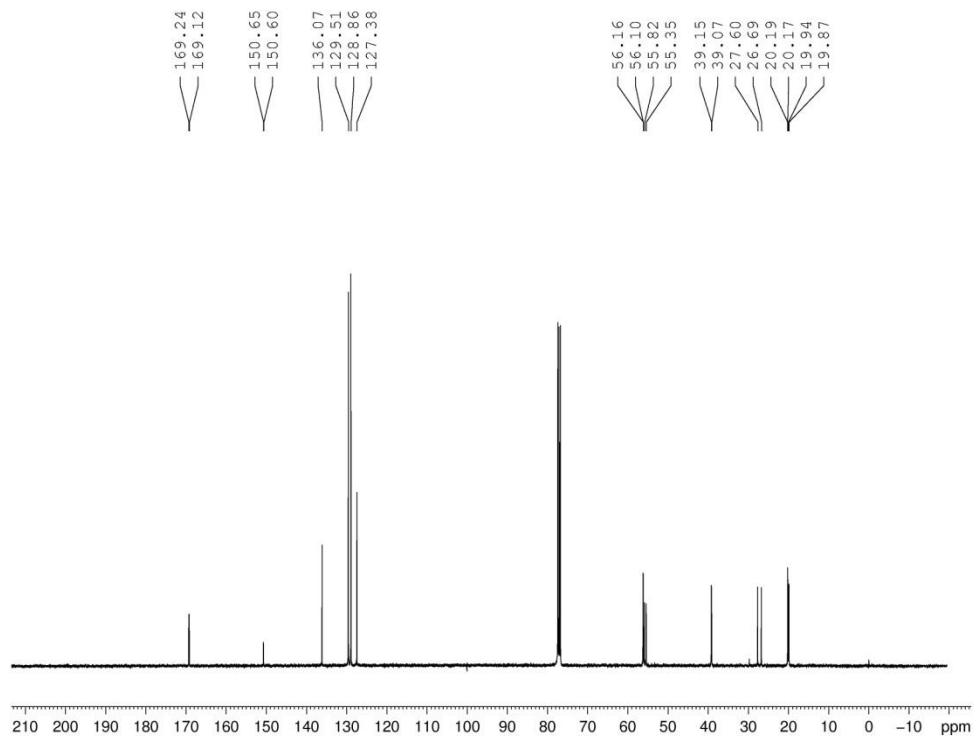
IR of 3c3



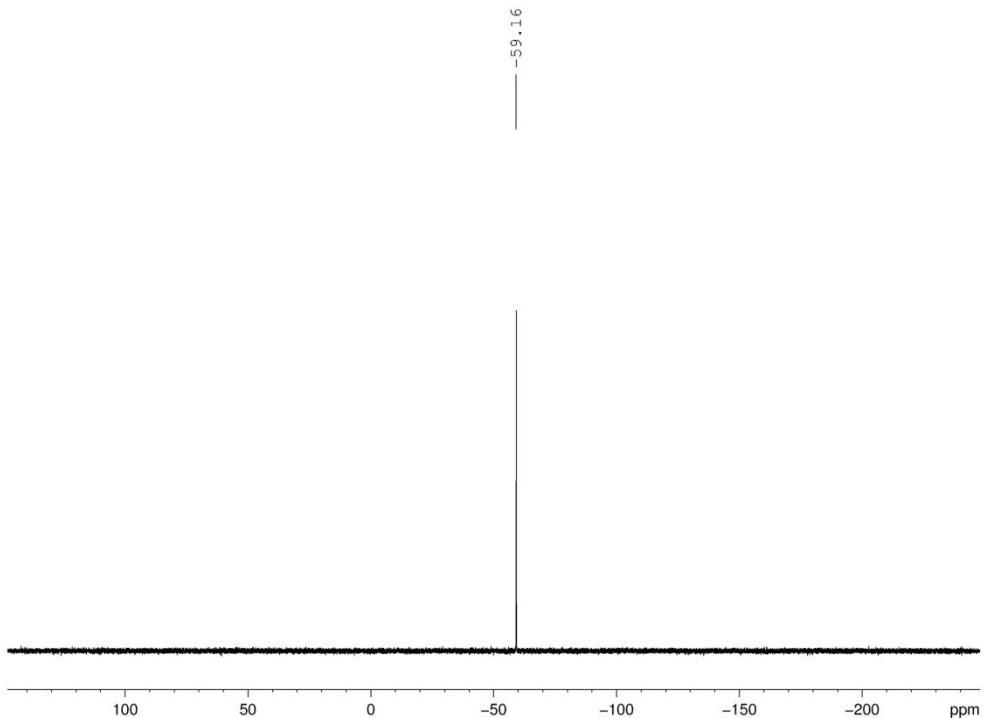
¹ H NMR of 3c'4



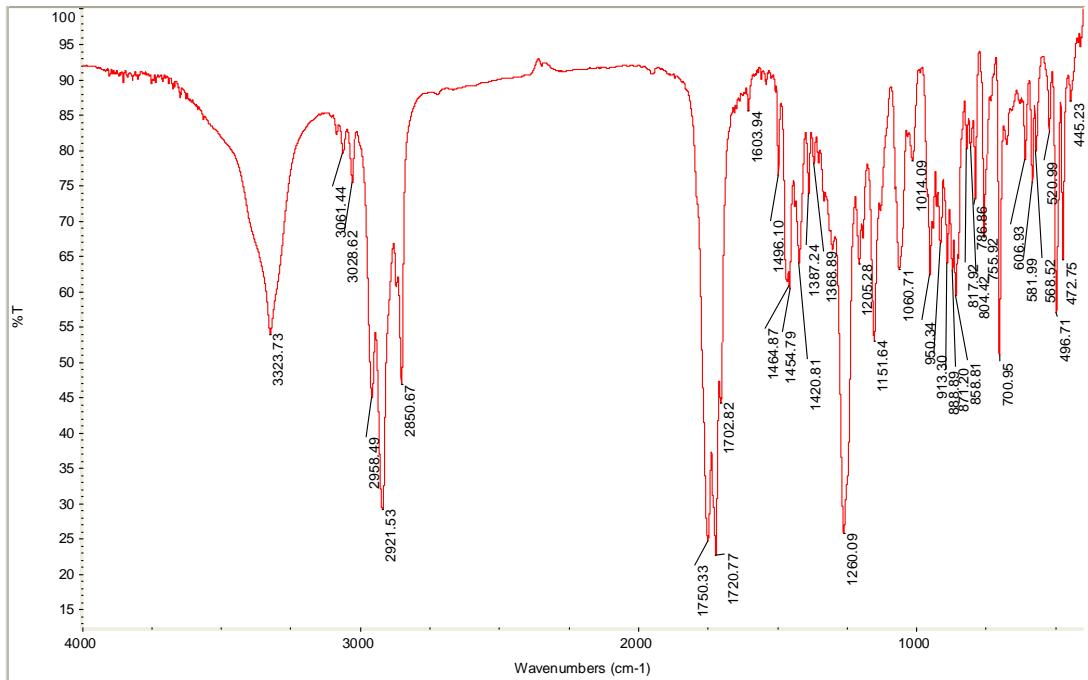
¹³C NMR of 3c'4



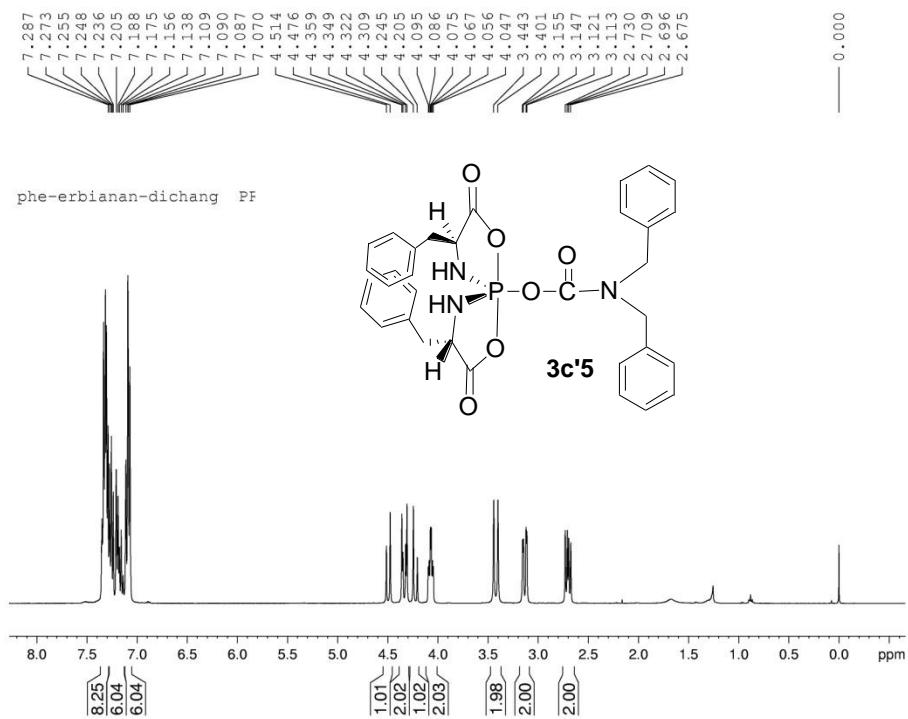
³¹P NMR of 3c'4



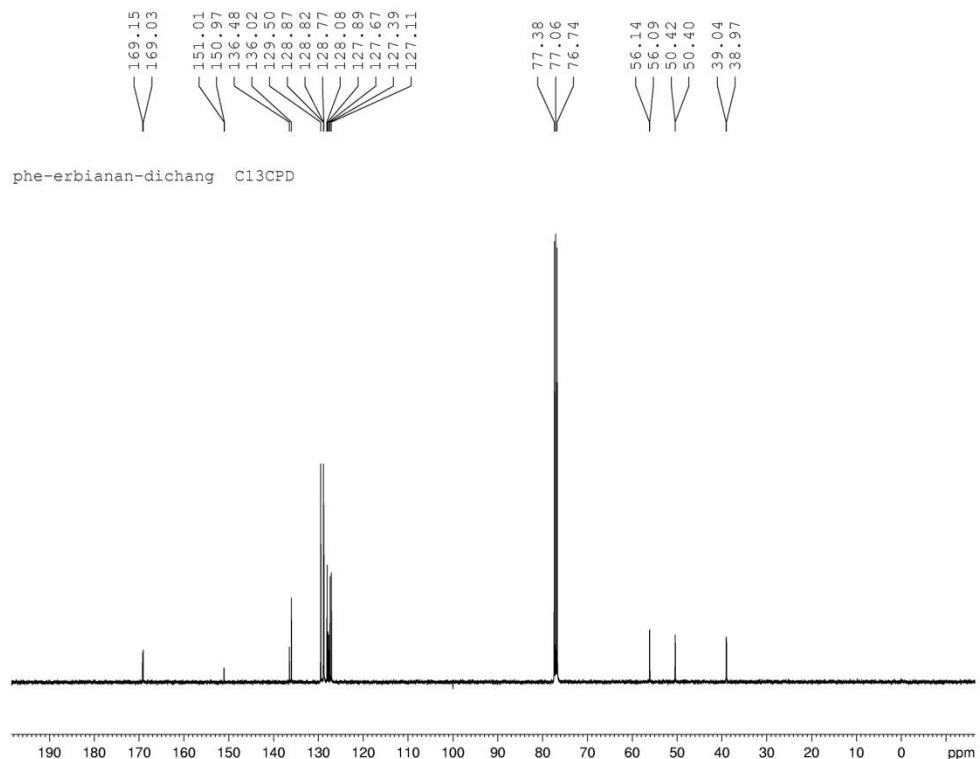
IR of 3c'4



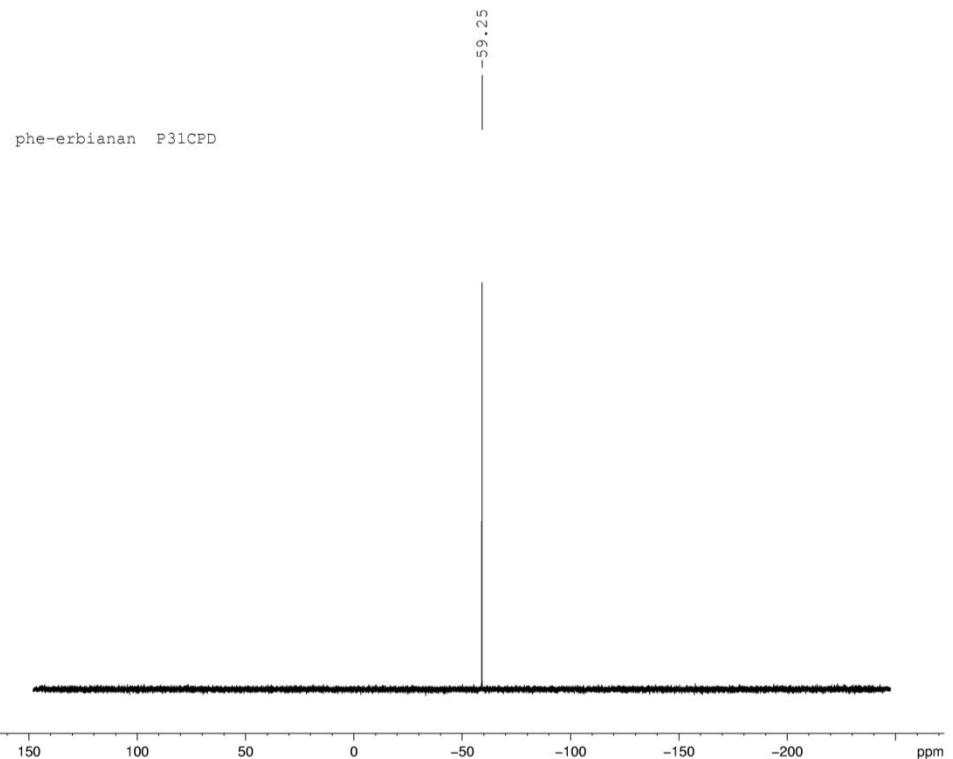
¹ H NMR of 3c'5



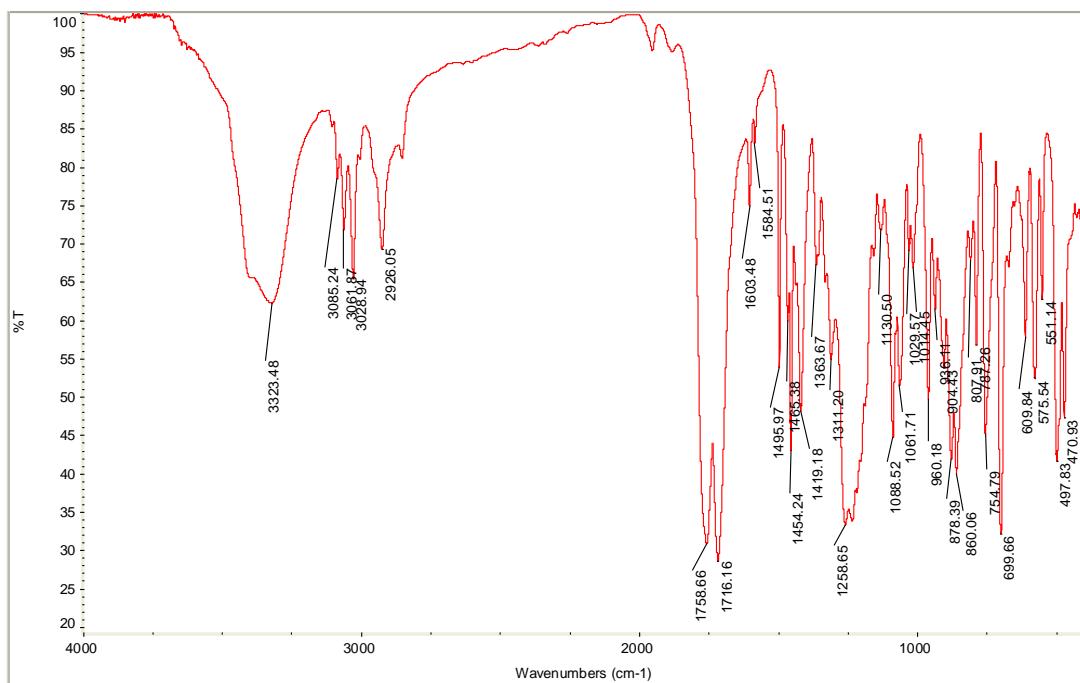
¹³C NMR of 3c'5



³¹P NMR of 3c'35



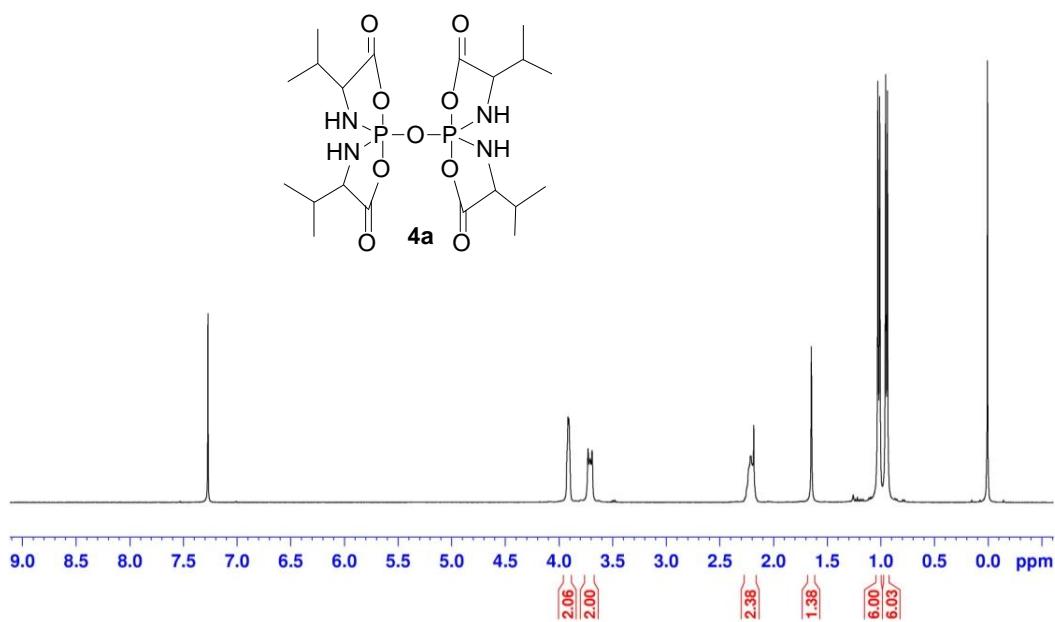
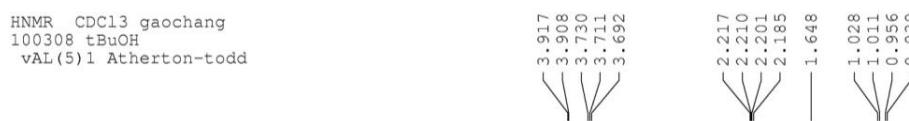
IR of 3c'5



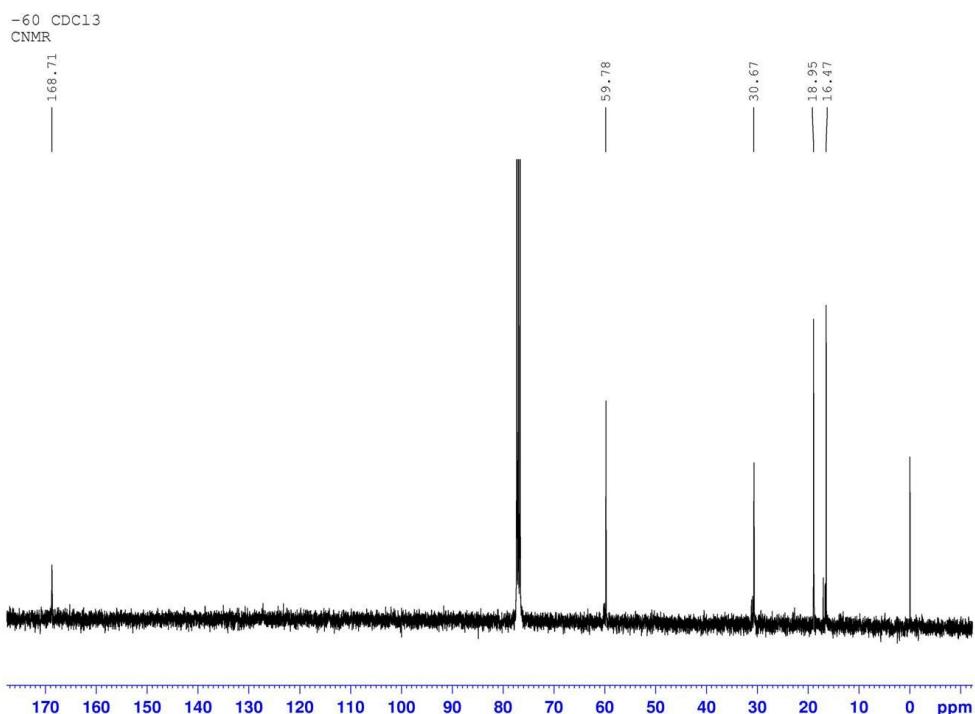
8. NMR and IR Spectra for compounds 4a and 4b

¹H NMR of 4a

HNMR CDCl₃ gaochang
100308 tBuOH
vAL(5)1 Atherton-todd

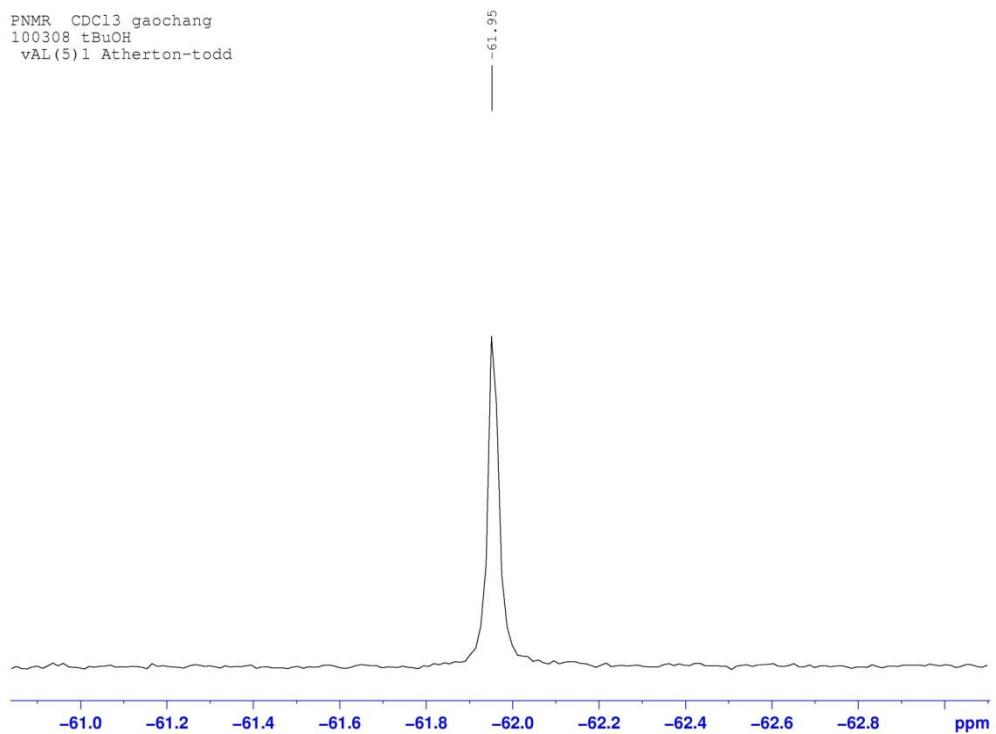


¹³C NMR of 4a

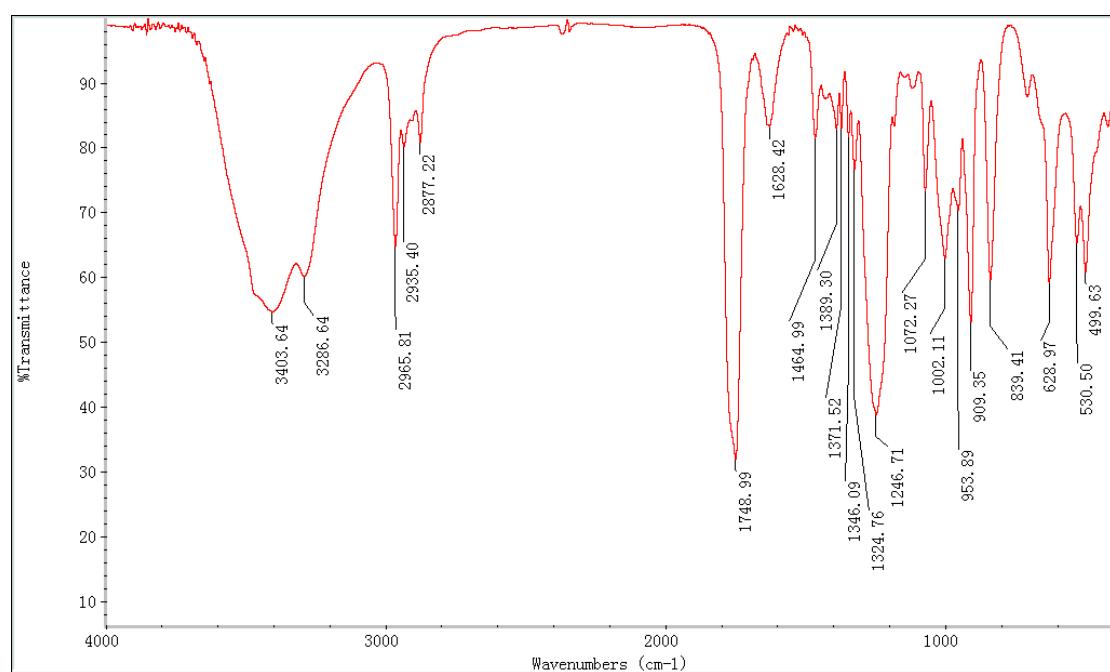


³¹P NMR of 4a

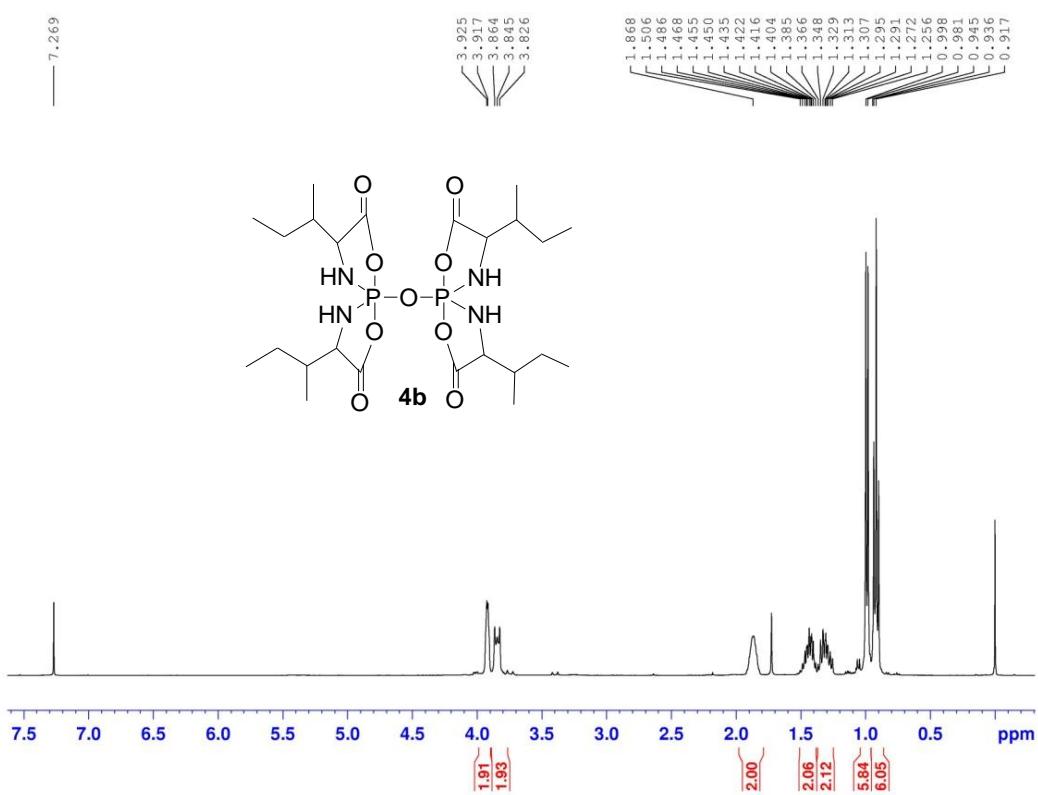
PNMR CDC13 gaochang
100308 tBuOH
vAL(5)1 Atherton-todd



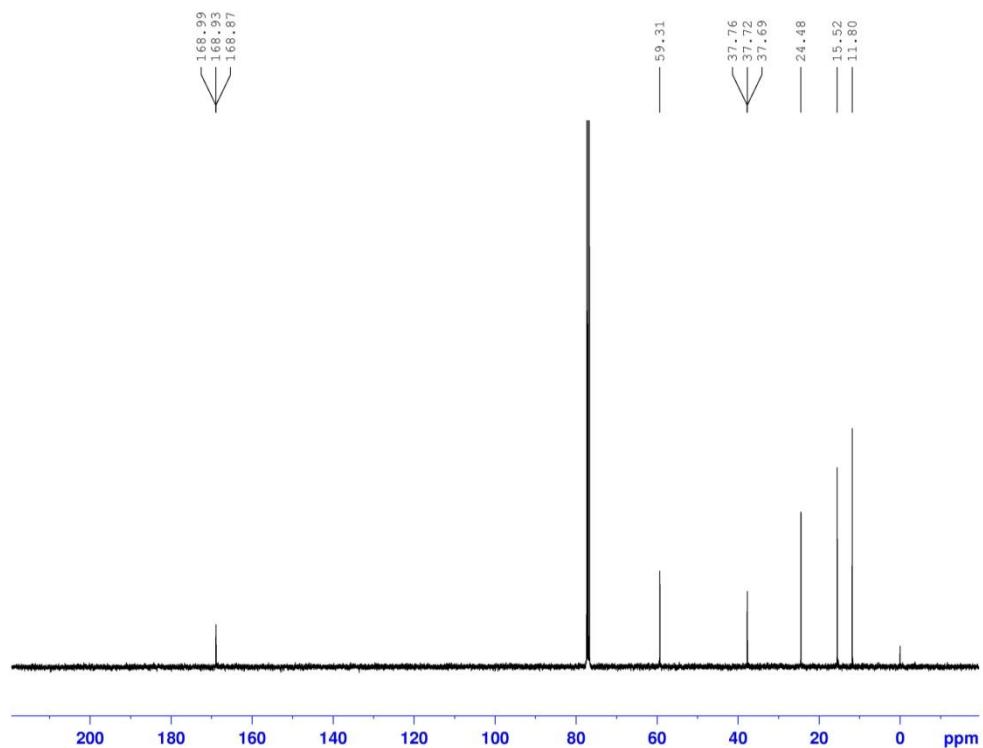
IR of 4a



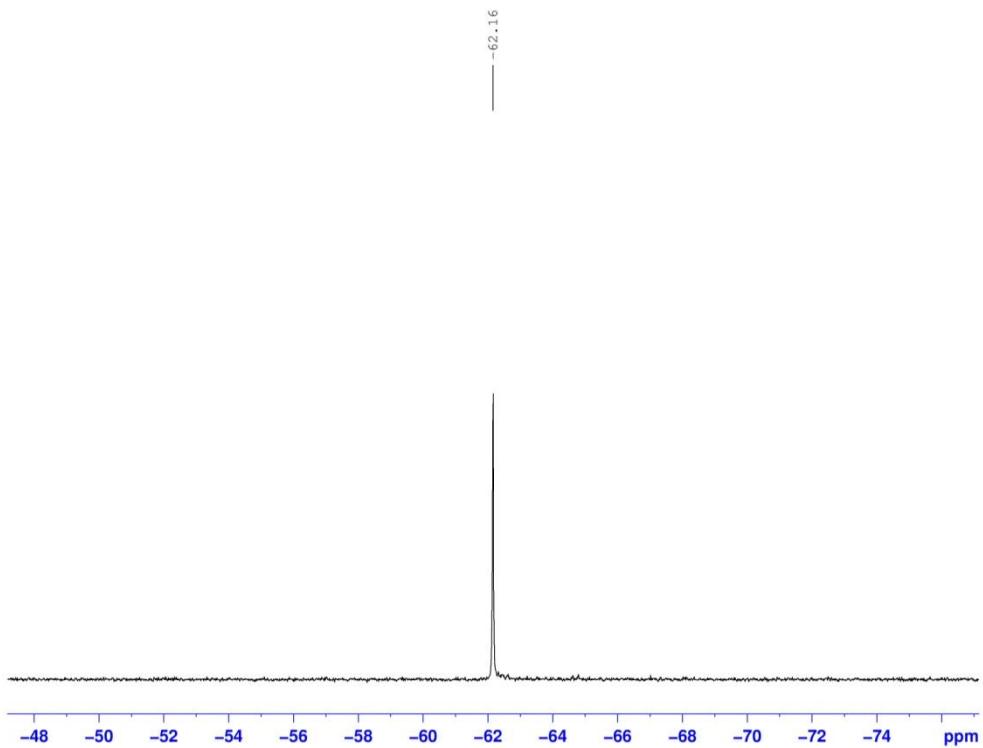
^1H NMR of 4b



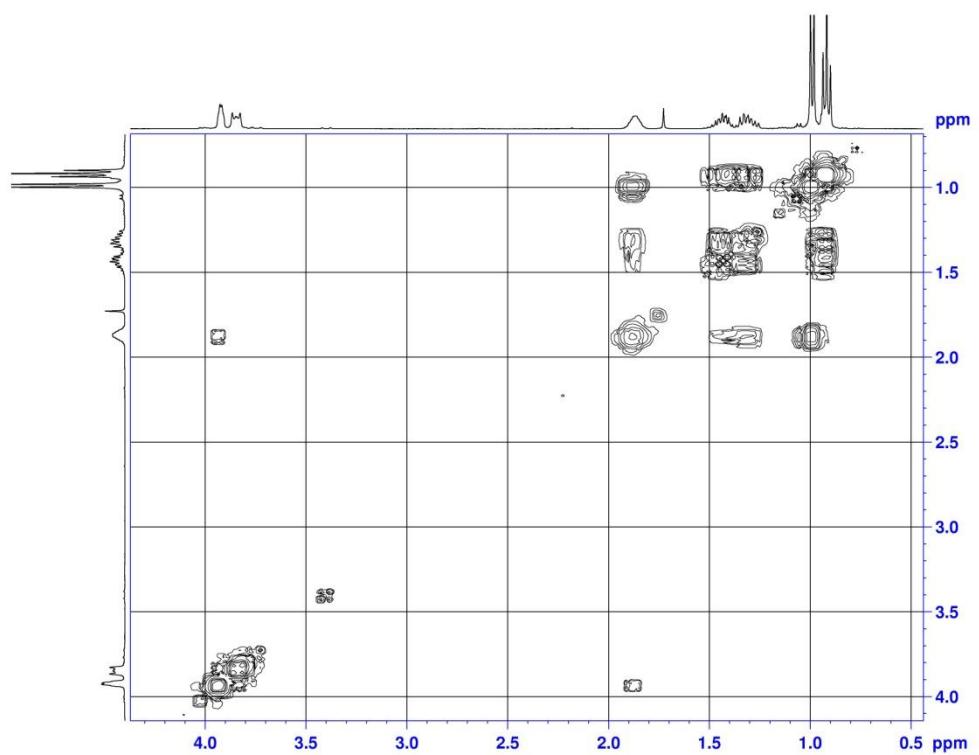
^{13}C NMR of 4b



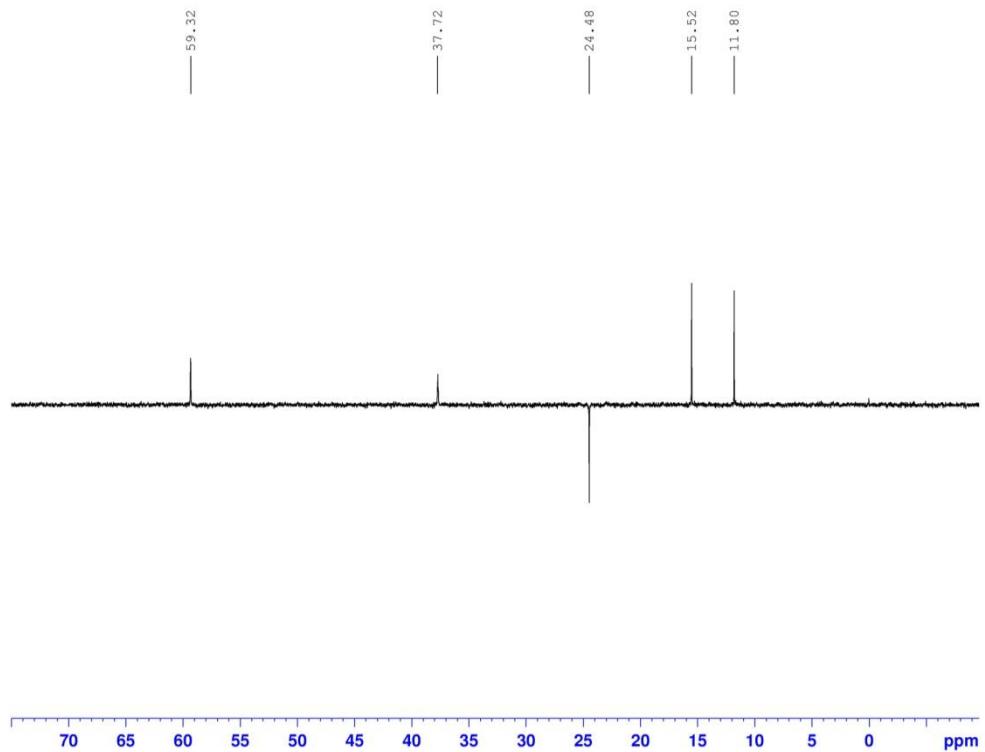
^{31}P NMR of 4b



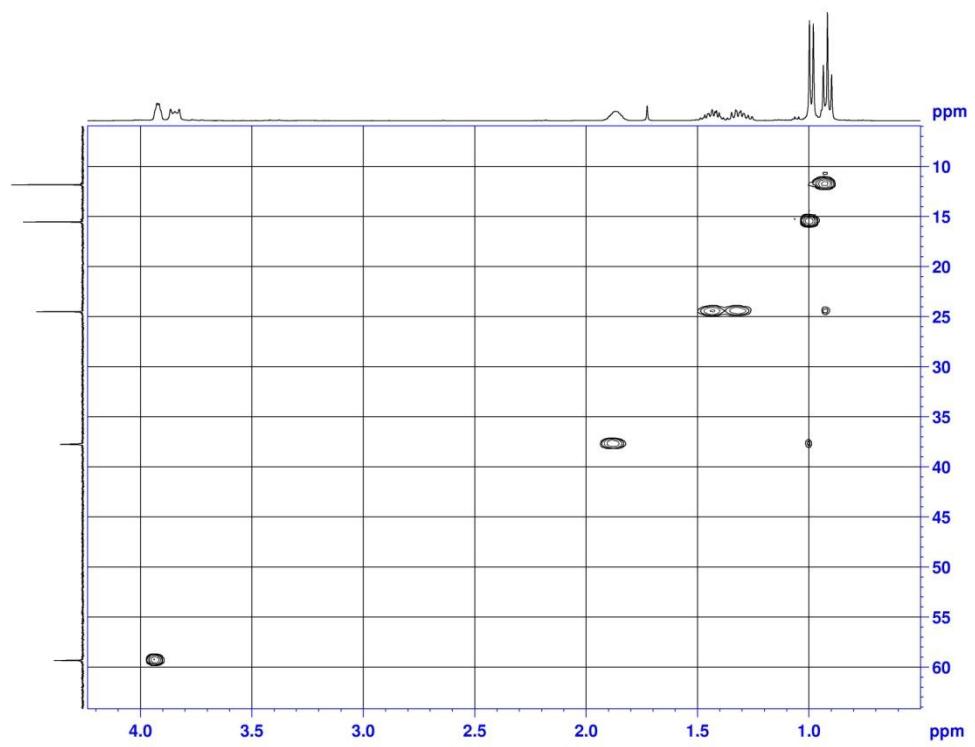
H-H COSY of 4b



DEPT 135 of 4b



HSQC of 4b



IR of 4b

