

Supporting Information
Bioinspired Indole Prenylation Reaction in Water

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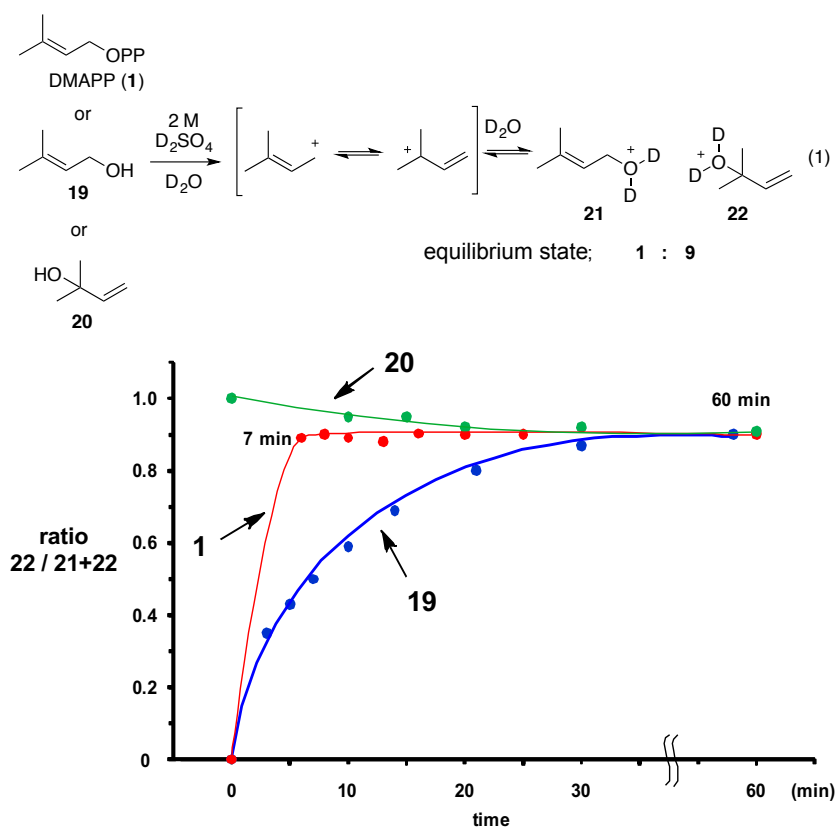
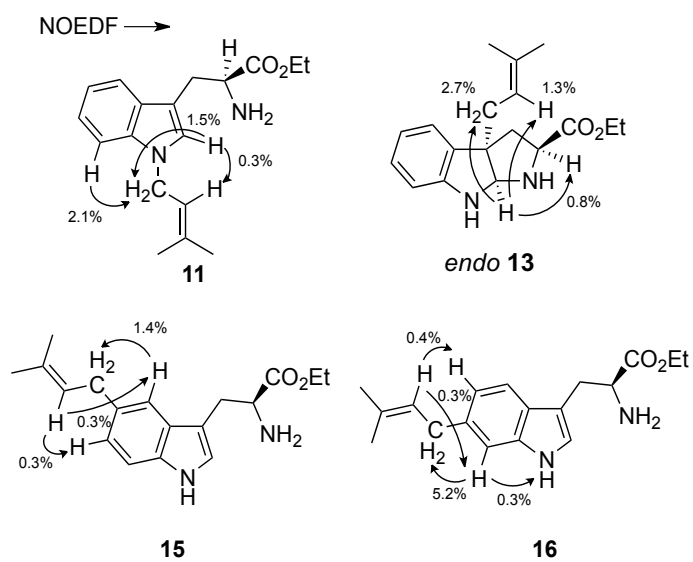


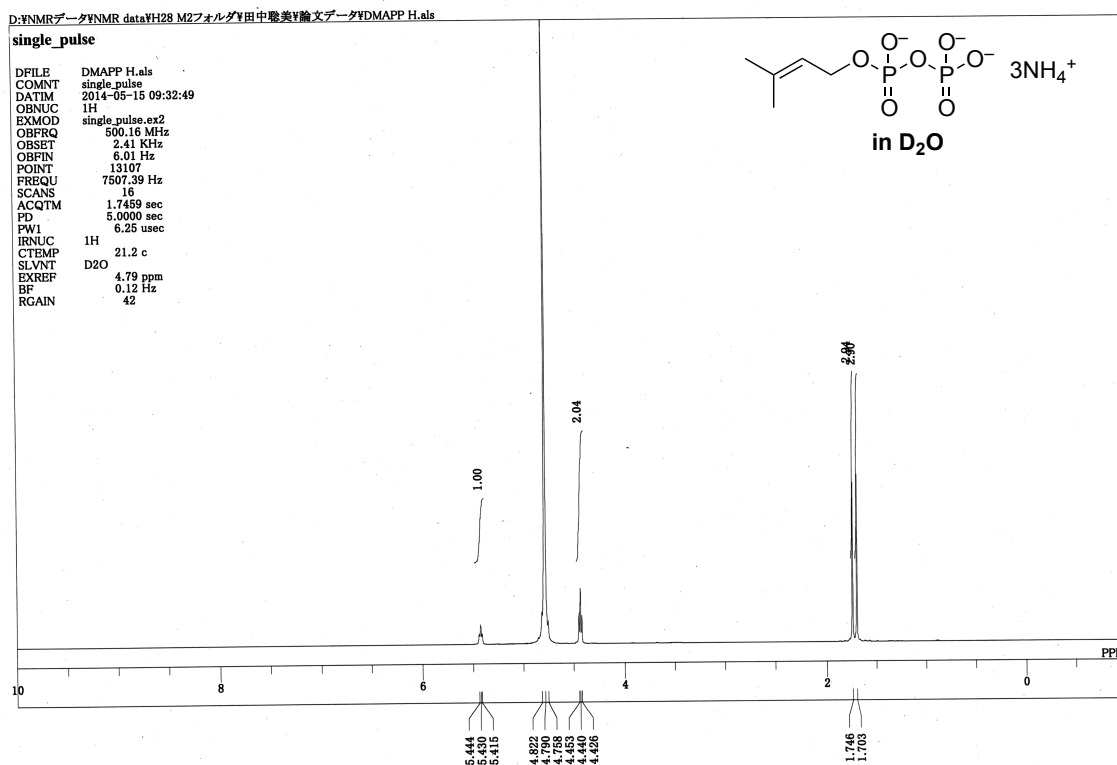
Figure S1. NMR monitoring of oxonium ions generated from **1**, **19**, and **20** in acidic media.

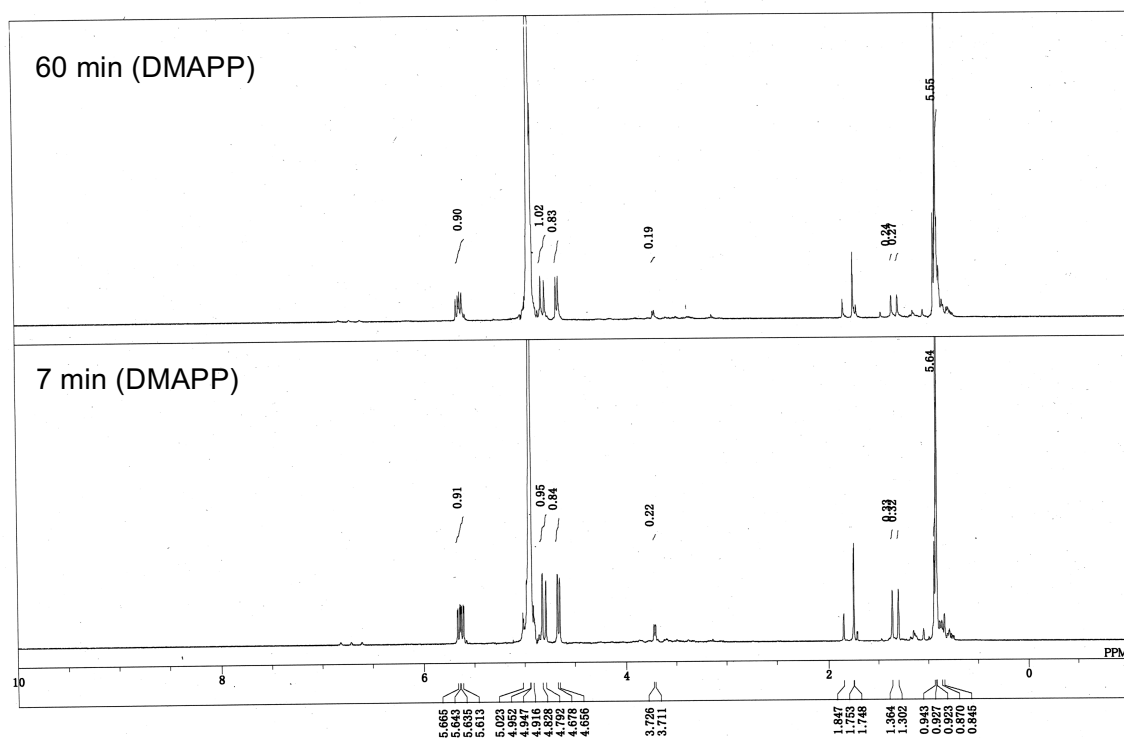
Structure elucidation of **11**, **13**, **15** and **16** using the nuclear Overhauser enhancement difference spectra (NOEDF).



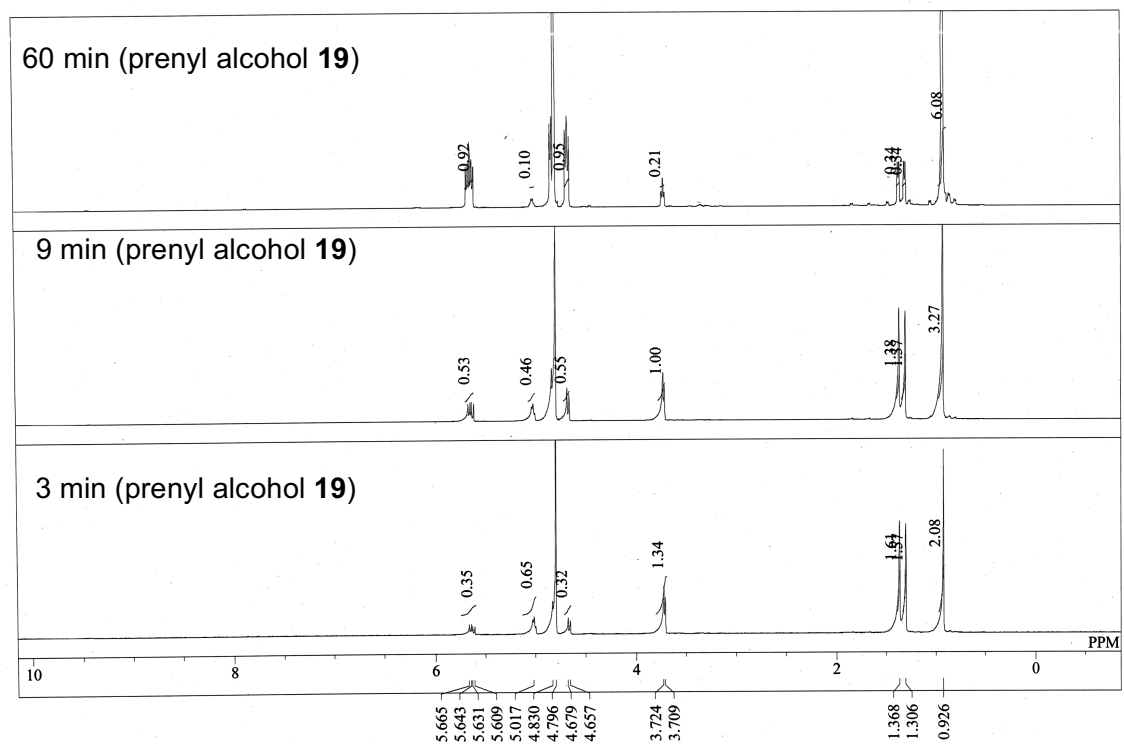
Experiment of NMR monitoring of oxonium ions generated from **1**, **19** and **20**.

DMAPP (**1**, 28.3 mg, 0.095 mmol) was added 2M D₂SO₄ in D₂O (2 mL). ¹H NMR of the resulting mixture was recorded until 60 min. **1** was immediately converted into a 1:9 mixture of oxonium ion **21** and **22** at 7 min.

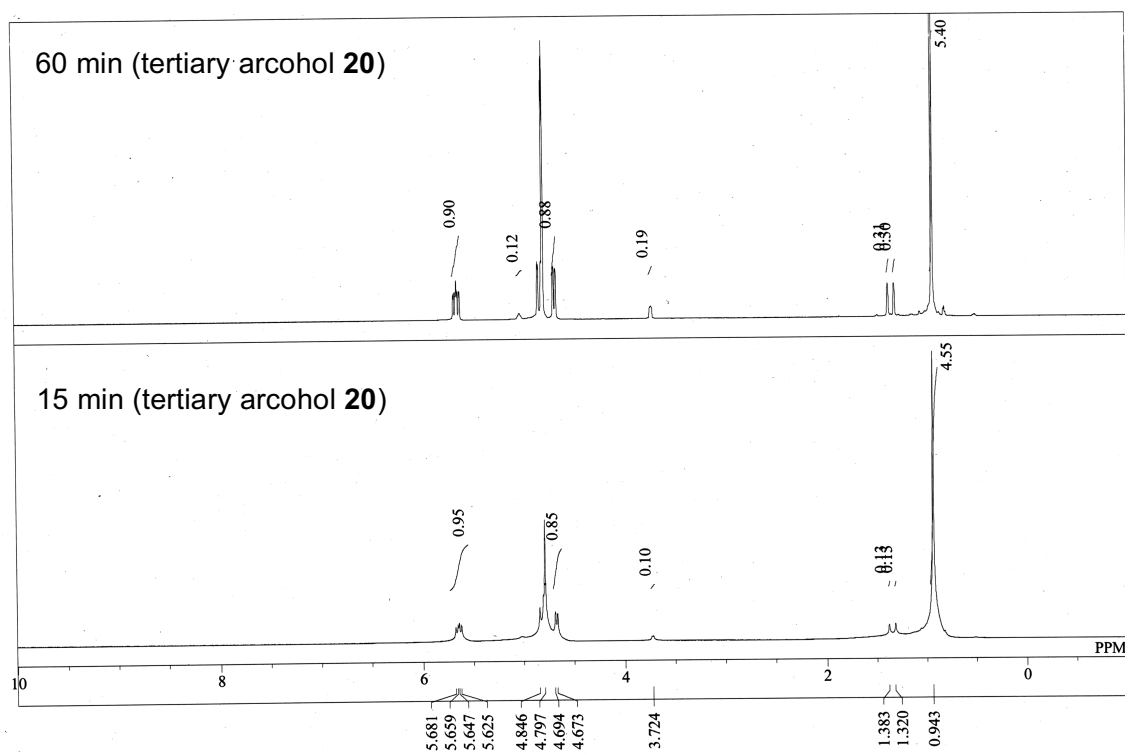




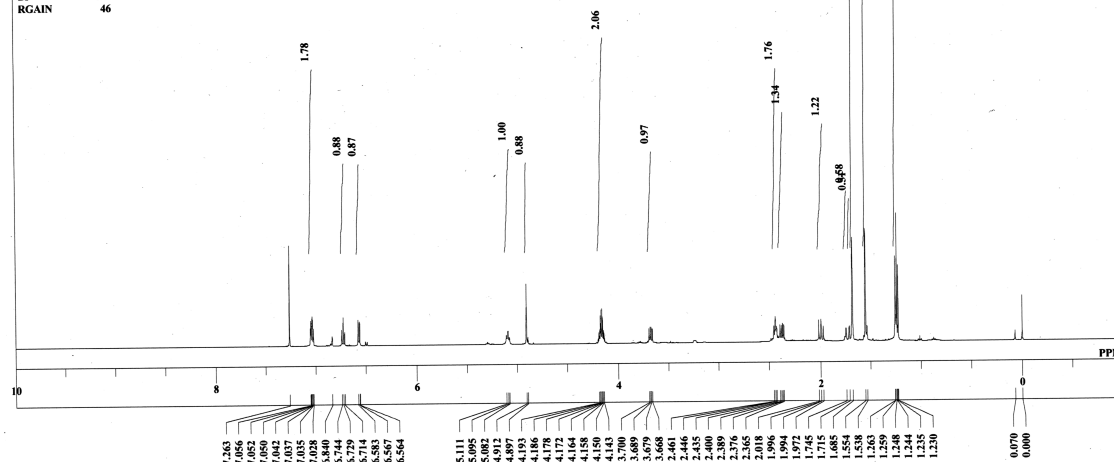
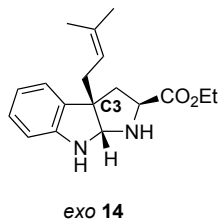
3-Methyl-2-buten-1-ol (prenyl alcohol **19**, 27.4 μL , 0.269 mmol) in D_2O (X mL) was added 2M D_2SO_4 in D_2O (2 mL). ^1H NMR of the resulting mixture was recorded until 60 min. **19** was slowly converted into a 1:9 mixture of oxonium ion **21** and **22** at 60 min.



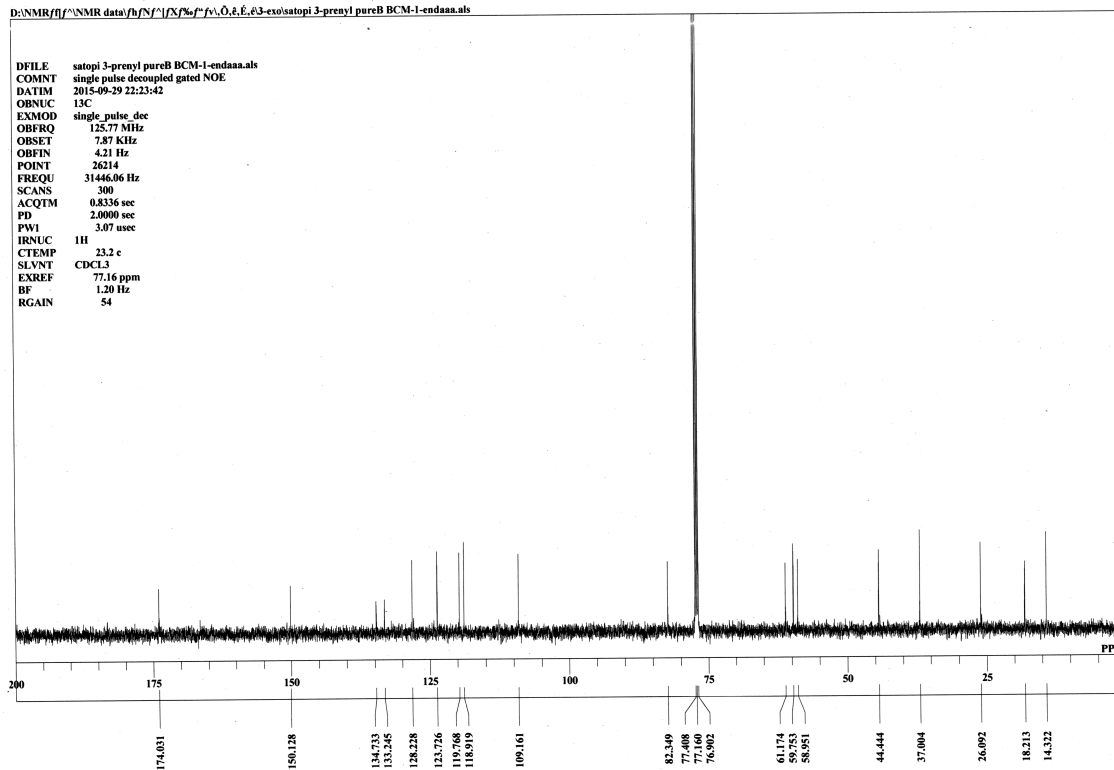
2-Methyl-3-buten-2-ol (tertiary arcohol **20**, 28.1 μL , 0.269 mmol) was added 2M D_2SO_4 in D_2O (2 mL). ^1H NMR of the resulting mixture was recorded until 60 min. **20** was slowly converted into a 1:9 mixture of oxonium ion **21** and **22** at 60 min.



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EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PWI	5.95 usec
IRNUC	1H
CTEMP	23.0 c
SUNVT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46



DFILE	satop1-3-prenyl pureB BCN1-1-endaas.als
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OBNUC	13C
EXMDO	single pulse, 1h
OBFRQ	125.77 MHz
OBSET	7.87 kHz
OBFIN	4.21 Hz
POINT	26214
FREQ	31446.06 Hz
SCANS	300
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.07 usec
IRNUC	1H
CTEMP	23.2 c
SLVNT	CDCl3
EXREF	77.16 ppm
BF	1.20 Hz
RGAIN	54



DFILE TE-5 Hlab
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 DATIM 2015-06-01 18:18:39
 OBNUC 1H
 EXMOD single_pulse.cz2
 OBFREQ 500.16 MHz
 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 16
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PWI 6.25 usec
 IRNUC 1H
 CTEMP 21.5 c
 SLVNT CDCl3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 50

15

0.84, 0.95, 1.05, 1.97, 1.00, 2.06, 1.14, 2.01, 0.98, 0.99, 6.57, 3.58, 0.070, 0.000, -0.007

10, 8, 6, 4, 2, 0

7.394, 7.281, 7.260, 7.023, 7.020, 5.490, 5.480, 5.394, 5.385, 5.382, 5.378, 5.373, 5.371, 5.367, 5.365, 5.358, 5.356, 4.197, 4.188, 4.182, 4.174, 4.171, 4.168, 4.159, 4.154, 4.146, 3.812, 3.812, 3.808, 3.797, 3.773, 3.772, 3.434, 3.434, 3.281, 3.271, 3.271, 3.262, 3.262, 3.052, 3.037, 3.023, 3.008, 1.755, 1.750, 1.748, 1.641, 1.641, 1.268, 1.268, 1.219, 1.216, 0.070, 0.000, -0.007

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OBSET       7.87 KHz
OBFIN       4.21 Hz
POINT       26224
FREQU       31446.06 Hz
SCANS       160
ACQIM       0.8336 sec
PD          2.0000 sec
PWI         3.07 usec
IRNUC       1H
CTEMP       22.4 c
SLVNT       CDCL3
EXREF       225.02 ppm
BF          120 Hz
RGAIN       56
  
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175.086

134.992

133.586

133.750

127.851

124.609

123.408

123.246

117.801

111.251

110.612

77.450

77.193

76.945

61.213

54.777

34.745

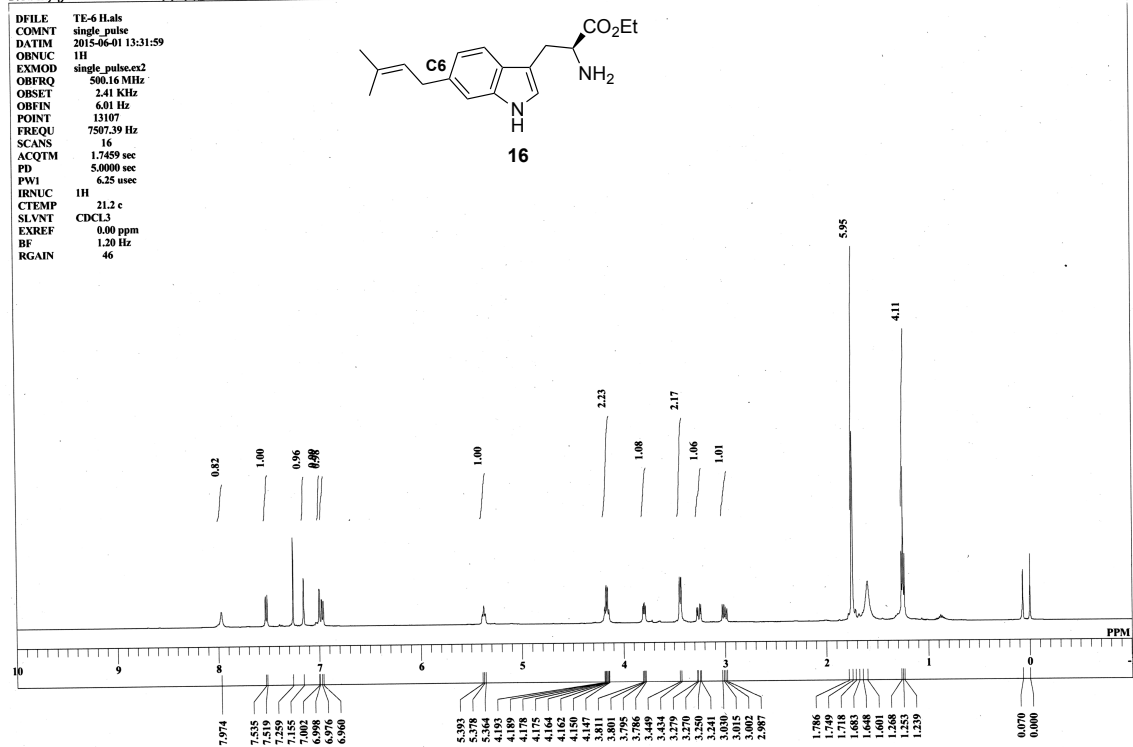
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25.973

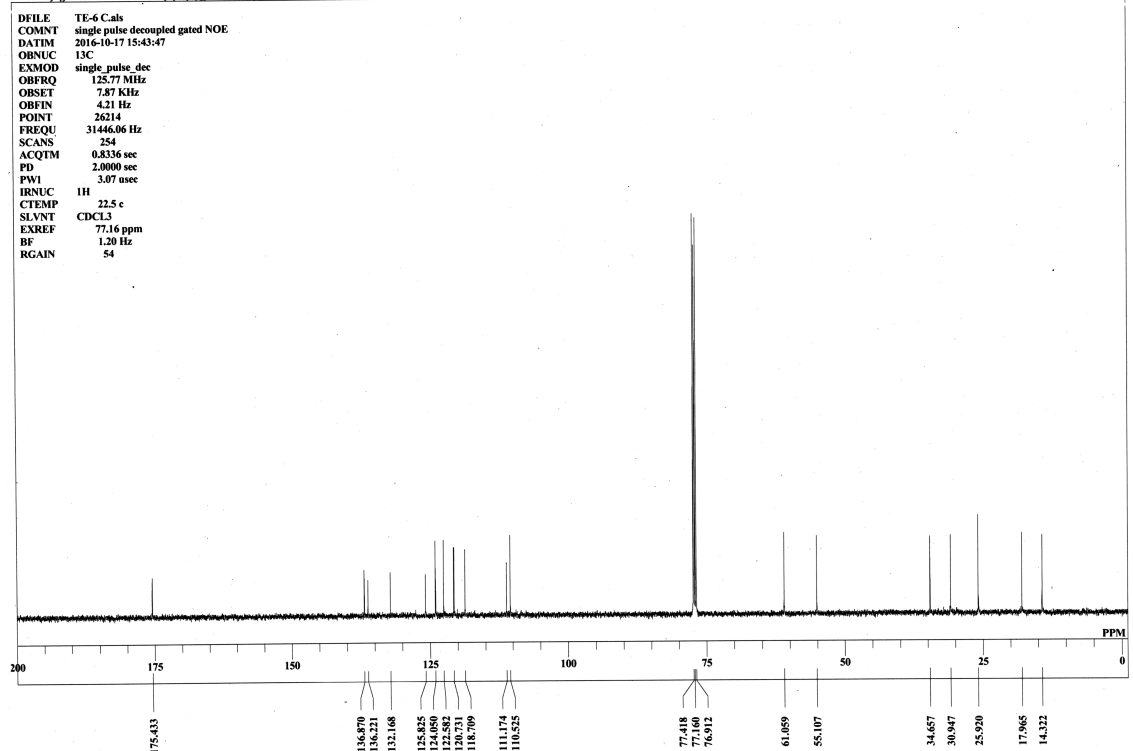
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14.359

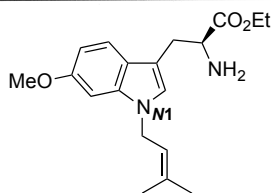
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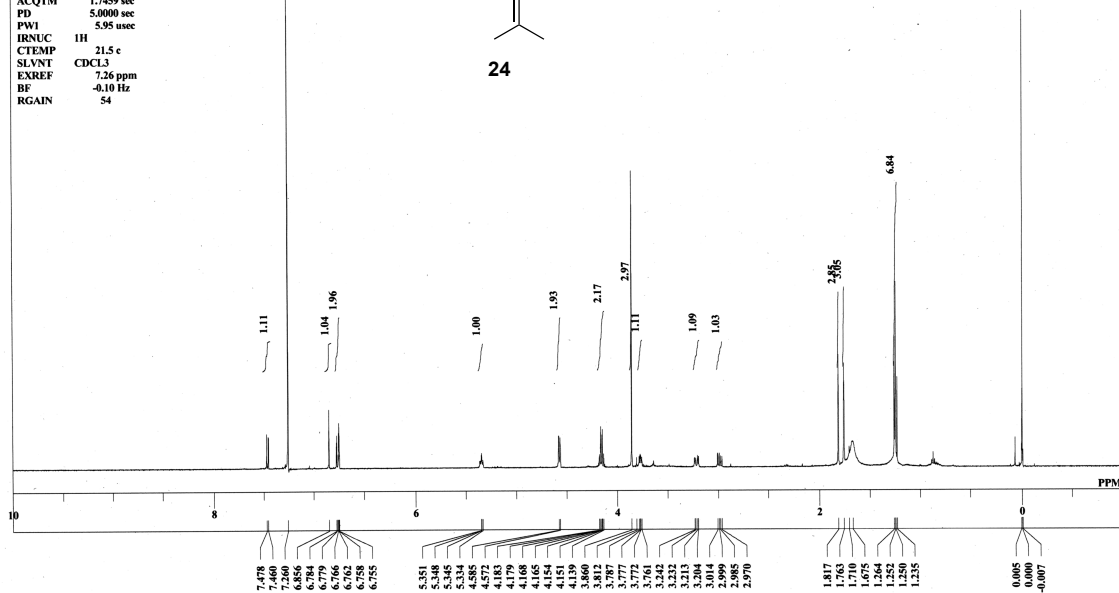
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OFBIN	6.01 Hz
POINT	13107
FREQU	7507.39 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.95 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	-0.10 Hz
RGAIN	54



24

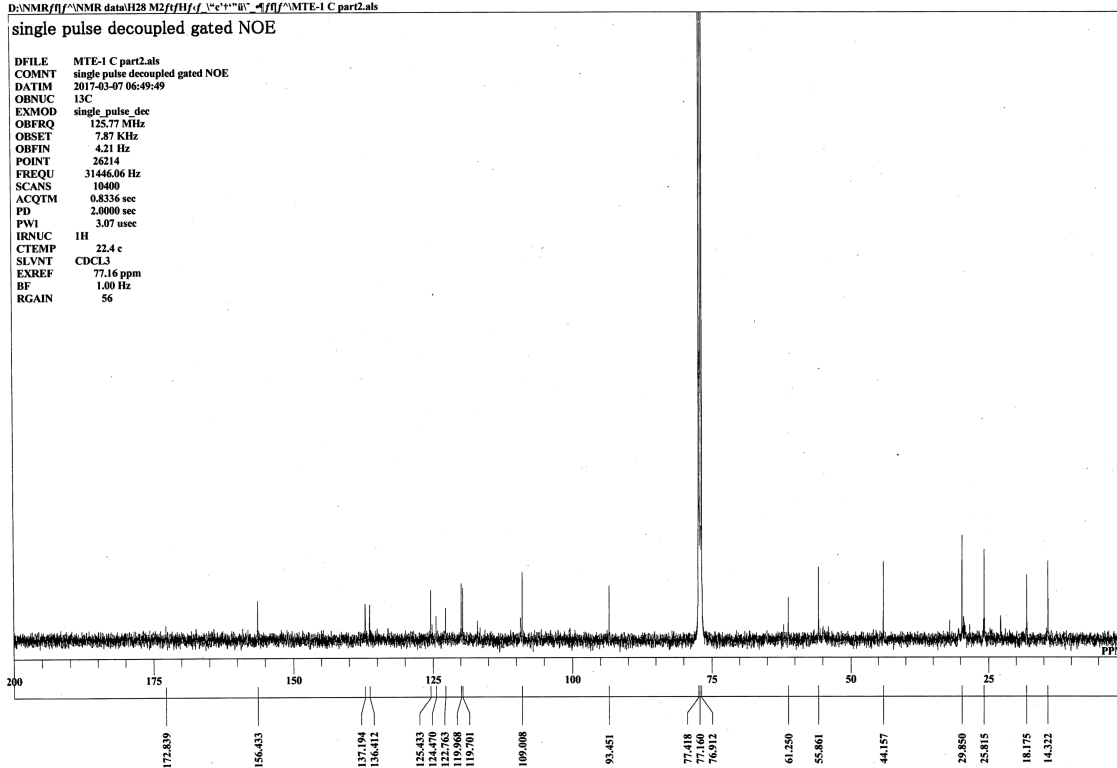


single pulse decoupled gated NOE

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ORBIN 4.21 Hz
POINT 26214
FREQU 131466.8 Hz
SCANS 10400
ACQTM 0.8336 sec
PD 2.0000 sec
PWI 3.07 usec
IRNUC 1H
CTEMP 22.4 c
LVNTP CDCL3
EXRFT 77.15 ppm
BF 1.00 Hz
RGAIN 56

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DFILE MTE-4 Hana.als
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 OBSET 2.41 KHz
 OBFIN 6.01 Hz
 POINT 13107
 FREQU 7507.39 Hz
 SCANS 16
 ACQTM 1.7459 sec
 PD 5.0000 sec
 PW1 5.95 usec
 IRNUC 1H
 CTEMP 22.2 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF -0.10 Hz
 RGAIN 56

27

MeO
 C7
 NH
 CO₂Et
 NH₂

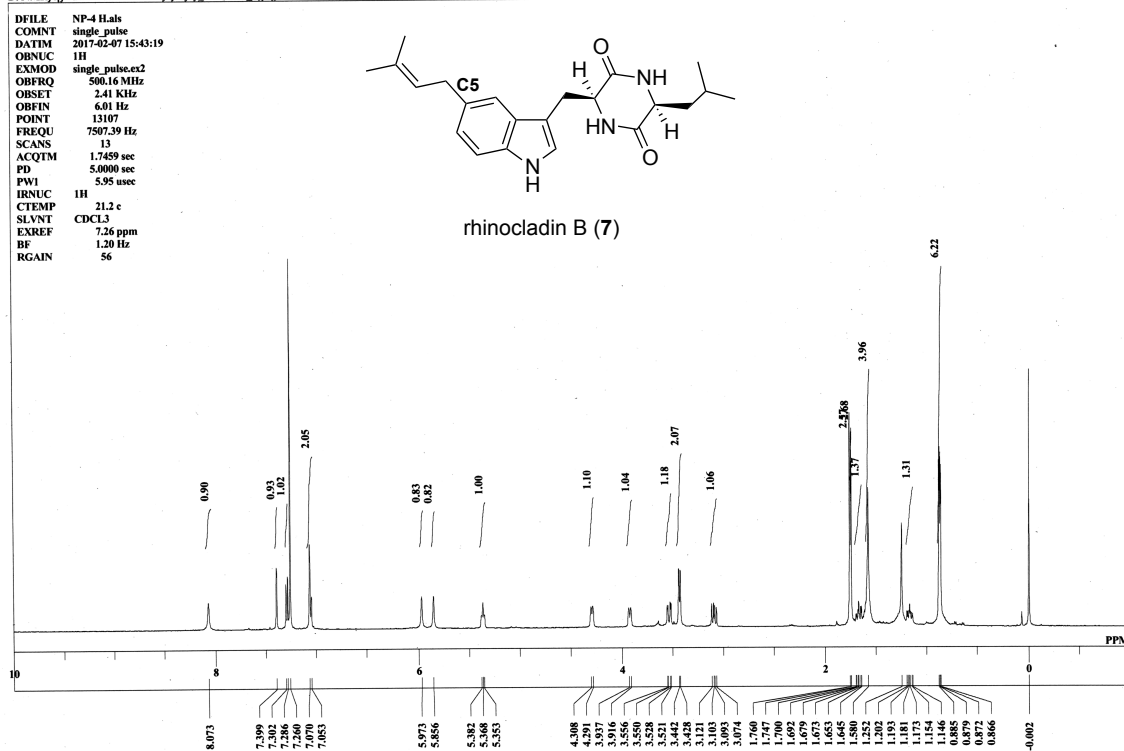
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DFILE MTE-4 Cals
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 OBSET 7.87 KHz
 OBFIN 4.21 Hz
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 FREQU 31446.06 Hz
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 ACQTM 0.8336 sec
 PD 2.0000 sec
 PW1 3.07 usec
 IH 1H
 CTEMP 22.7 c
 SLVNT CDCL3
 EXREF 77.16 ppm
 BF -0.10 Hz
 RGAIN 54

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