

Supplementary Information

A crystalline molecular gyrotop with germanium junctions between a phenylene rotor and alkyl spokes

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1. Copies of NMR Spectra for All New Compounds

Fig S1. ¹ H NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl ₃ S2
Fig S2. ¹³ C NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl ₃ S2
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Fig S16. ¹ H- ¹³ C hmbc NMR spectrum of Molecular Gyrotop (2) in CDCl ₃ S9
Fig S17. ¹ H NMR spectrum of Molecular Gyrotop Isomer (2i) in CDCl ₃ S10
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1. Copies of NMR Spectra for All New Compounds

a. Spectra of Ethoxytris(7-octenyl)germane (3)

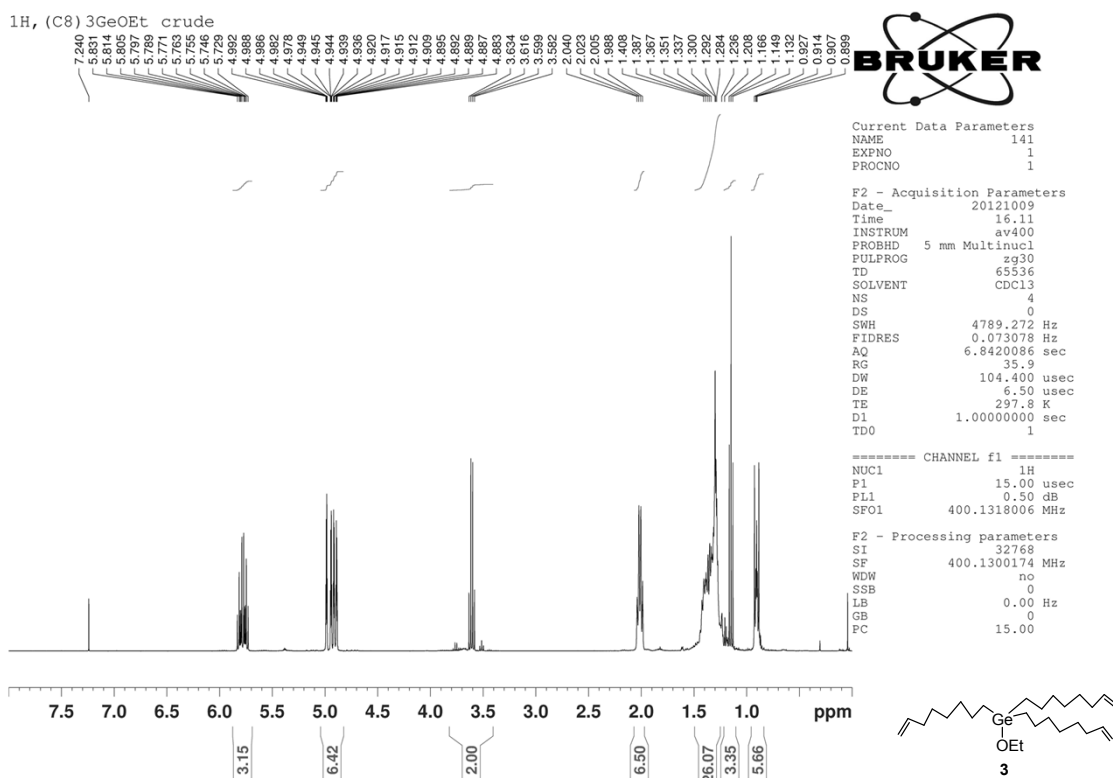


Fig S1. ¹H NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl₃.

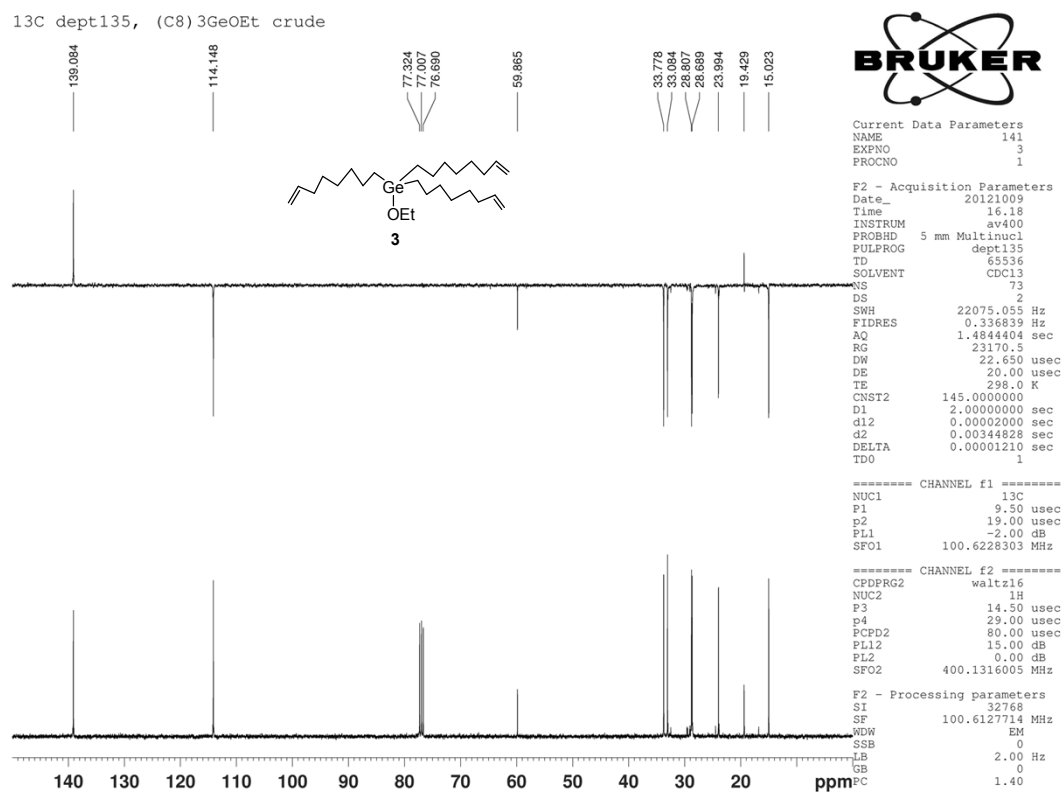
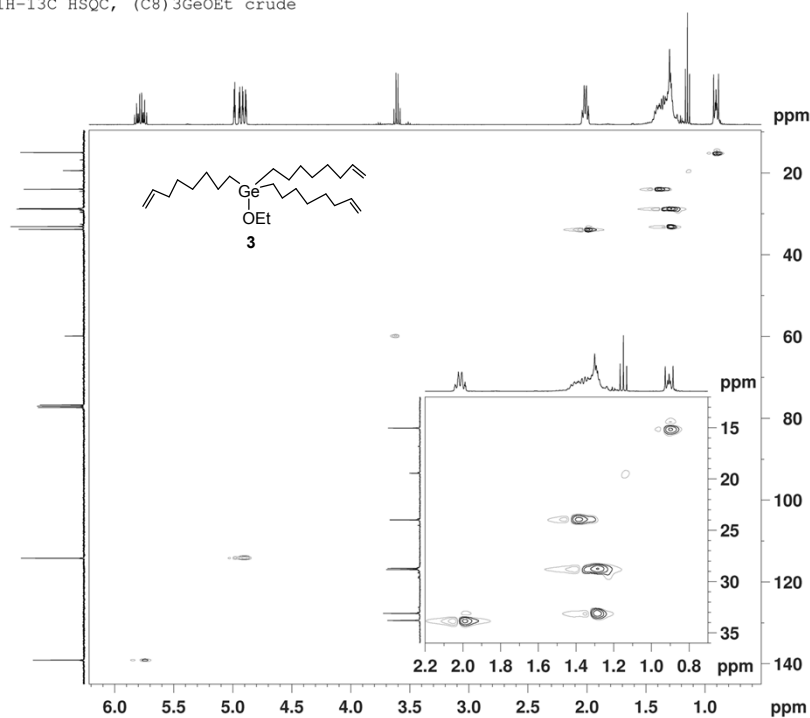


Fig S2. ¹³C NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl₃.

¹H-¹³C HSQC, (C8) 3GeOEt crude



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PROCNO   1

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PULPROG  hsqcdeq
TD        65536
SOLVENT  CDCl3
NS        4
DS        1
SWH       2997.602 Hz
FIDRES   0.854501 Hz
AQ        0.0854516 sec
RG        502
DR        166.800 usec
DE        6.50 usec
TE        297.7 K
CST2     145.000000 sec
d0       0.0000000 sec
d1       1.12837200 sec
d16      0.00010000 sec
d2       0.08009400 sec
d3       0.00100000 sec
d4       0.00345000 sec
d5       0.00172144 sec
DELTA    0.00231400 sec
DELTA1   0.00070144 sec
INTENT   0.00003105 sec
RG2      128

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P1       15.00 usec
PC       30.00 usec
PF1     0.50 dB
PFL1    400.131805 MHz

===== CHANNEL f2 =====
CPDPRG2  9ap
NUC2     13C
P2       8.70 usec
PC       17.40 usec
PF2     70.00 usec
PFL2    100.621629 MHz
PFL2    100.621629 MHz

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GPNAM3   SINE.100
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GP2      20.10 %
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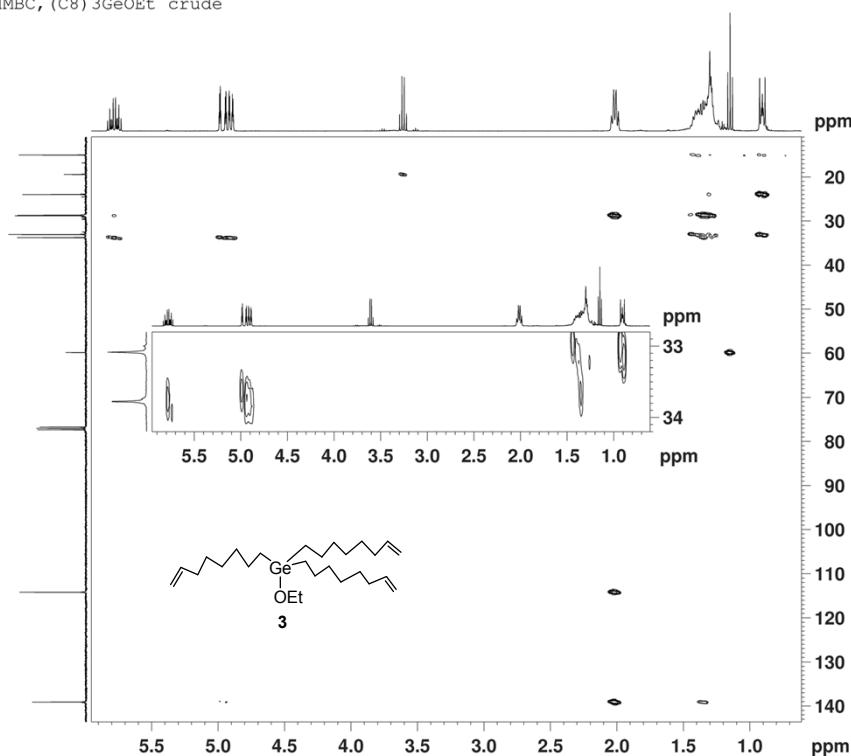
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TD        256
SF01     100.6216 MHz
FIDRES   62.902576 Hz
SW       140.036 ppm
F2MODE   Echo-antischo

F2 - Processing parameters
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SF        400.130150 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
MC2      GF
SF        100.612714 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```

Fig S3. ¹H-¹³C hsqc NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl₃.

HMBC, (C8) 3GeOEt crude



```

Current Data Parameters
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EXPNO    6
PROCNO   1

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Time     16.48
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TD        1024
SOLVENT  CDCl3
NS        8
DS        1
SWH       3289.474 Hz
FIDRES   3.212377 Hz
AQ        0.1558980 sec
RG        11285.2
DR        152.000 usec
DE        6.50 usec
TE        297.7 K
CST13    8.0000000
CST2     145.0000000
d0       0.0000000 sec
d1       1.12050903 sec
d16      0.00010000 sec
d2       0.00344828 sec
d3       0.00100000 sec
d4       0.06250000 sec
d5       0.00003105 sec

===== CHANNEL f1 =====
NUC1     1H
P1       15.00 usec
P2       30.00 usec
PF1     0.50 dB
SF01    400.1318530 MHz

===== CHANNEL f2 =====
NUC2     13C
P2       8.70 usec
PFL2    100.621629 MHz
PFL2    100.621629 MHz

===== GRADIENT CHANNEL =====
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GPNAM2   SINE.100
GPNAM3   SINE.100
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GP22     30.00 %
GP23     40.10 %
P16      1000.00 usec

F1 - Acquisition parameters
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TD        256
SF01     100.6216 MHz
FIDRES   62.902576 Hz
SW       140.036 ppm
F2MODE   QF

F2 - Processing parameters
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SF        400.130150 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
MC2      GF
SF        100.612760 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
  
```

Fig S4. ¹H-¹³C hmbc NMR spectrum of Ethoxytris(7-octenyl)germane (3) in CDCl₃.

b. Spectra of Chlorotris(7-octenyl)germane (4)

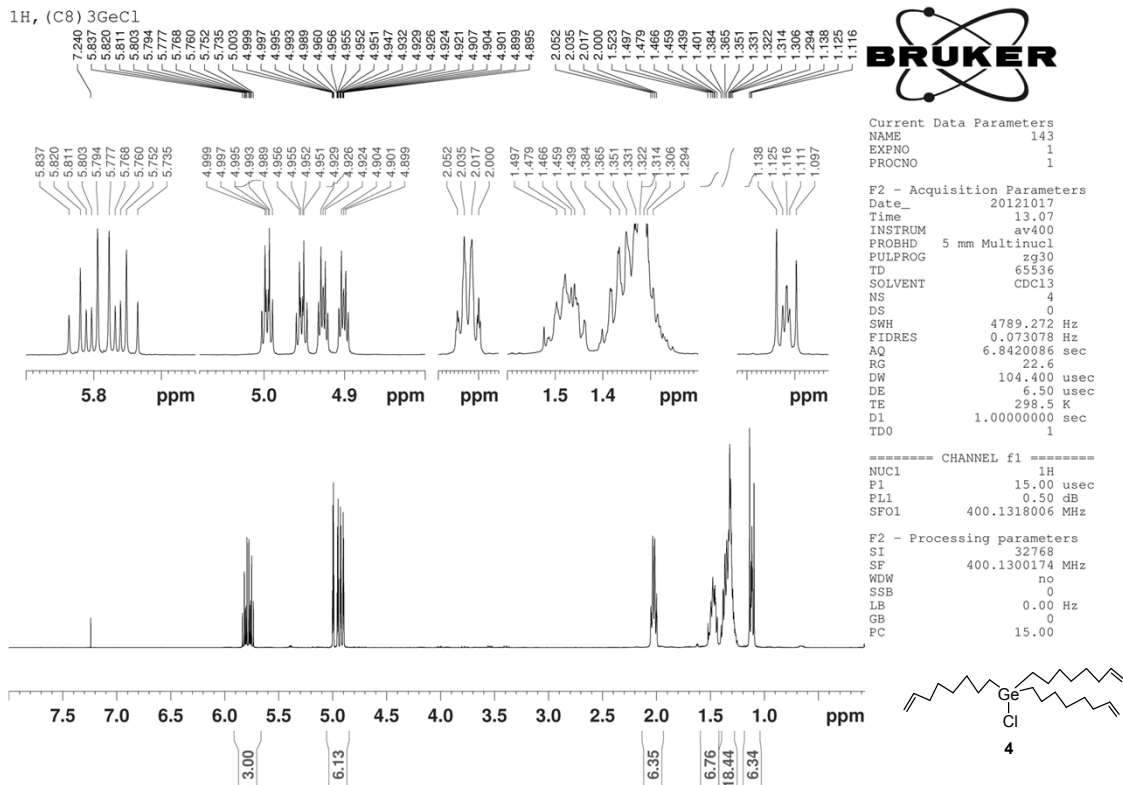


Fig S5. ¹H NMR spectrum of Chlorotris(7-octenyl)germane (4) in CDCl₃.

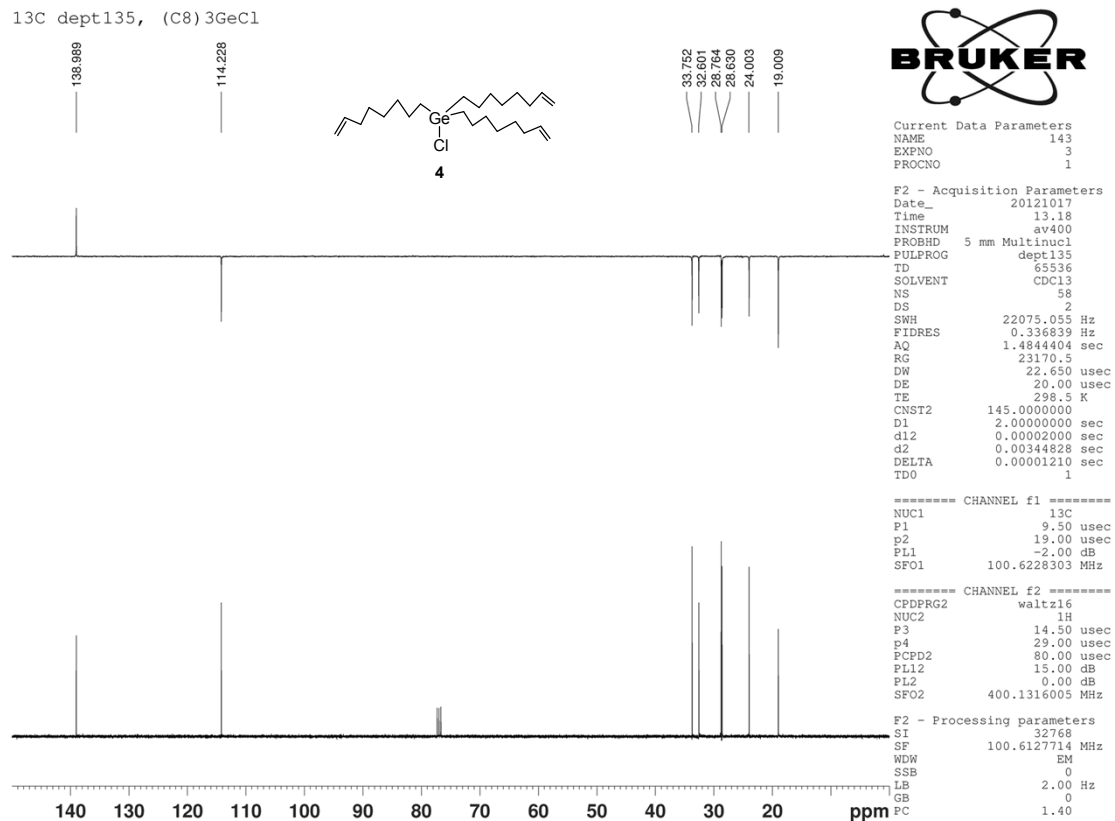
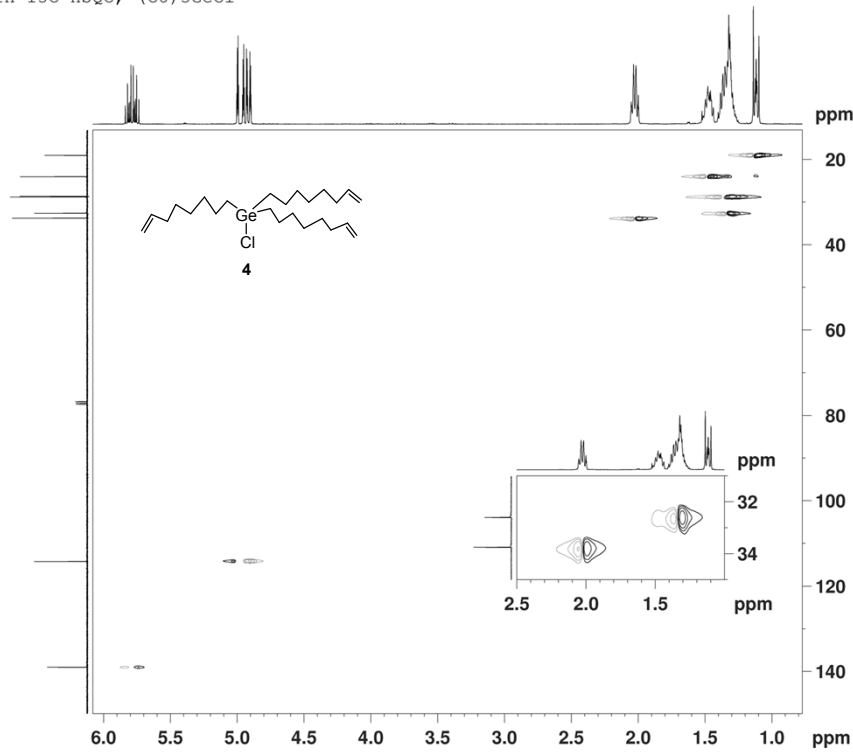


Fig S6. ¹³C NMR spectrum of Chlorotris(7-octenyl)germane (4) in CDCl₃.

^1H - ^{13}C HSQC, (C8) 3GeCl



```

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EXPNO    5
PROCNO   1

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PROBHD   5 mm Multinuc
PULPROG  hsgqetm9
TD       512
SOLVENT  CDCl3
NS       4
DS       1
SWH      2997.602 Hz
FIDRES   5.85165 Hz
AQ       0.0854516 sec
RG       620
DM       164.850 usec
DE       6.50 usec
TE       298.5 K
CNST1    145.000000 sec
d0       0.0000300 sec
D1       1.3287200 sec
d11      0.0300000 sec
d13      0.0000040 sec
D16      0.0001000 sec
D21      0.0030000 sec
d6       0.0017244 sec
DELTA    0.0023160 sec
DELTA1   0.0007164 sec
IN0      0.0000310 sec
STCNT    128
ZGFTRM

===== CHANNEL f1 =====
NUC1     1H
P1       15.00 usec
P2       30.00 usec
P3       0.00 usec
PL1      0.50 dB
PL2      400.1314853 MHz

===== CHANNEL f2 =====
CPDPRG2  gddp
NUC2     13C
P1       8.70 usec
P2       31.40 usec
P3       70.00 usec
PL1      0.00 dB
PL2      -2.00 dB
PL3      100.6216229 MHz

===== GRADIENT CHANNEL =====
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GPMAX2   SINE.100
GPMAX3   SINE.100
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GP22     30.00 %
GP33     40.10 %
P16     1000.00 usec

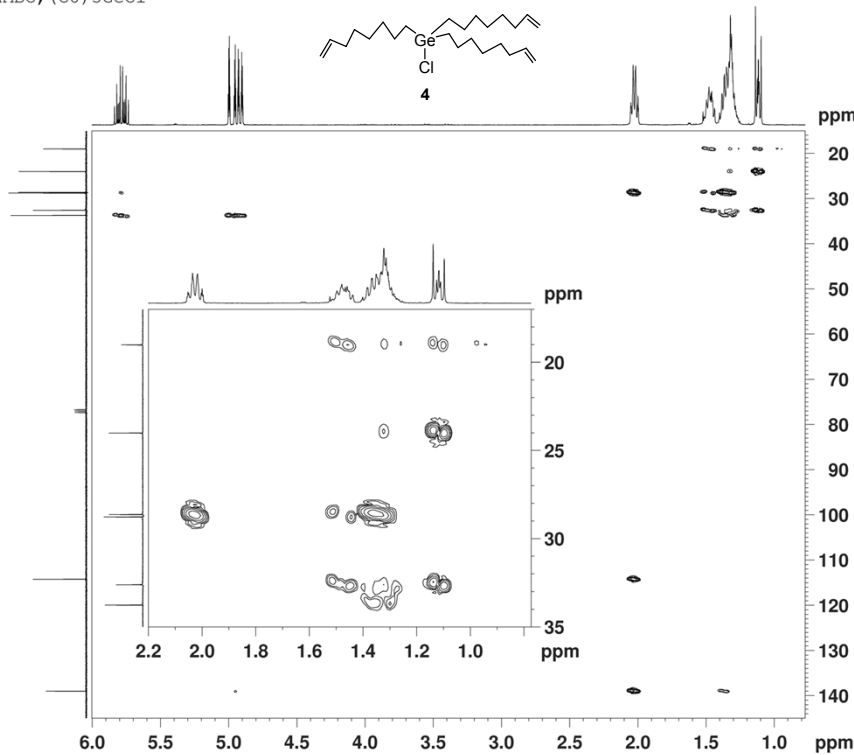
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TD       256
SF01     100.6216 MHz
FIDRES   62.902576 Hz
SW       160.036 ppm
FRMODE   Echo-Antiecho

F2 - Processing parameters
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SF       400.1300167 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
PC       1.40

F1 - Processing parameters
SI       2048
MC2     echo-antiecho
SF       100.6127714 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
    
```

Fig S7. ^1H - ^{13}C hsqc NMR spectrum of Chlorotris(7-octenyl)germane (**4**) in CDCl_3 .

HMBC, (C8) 3GeCl



```

Current Data Parameters
NAME      143
EXPNO    6
PROCNO   1

F2 - Acquisition Parameters
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Time     13.46
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PULPROG  hmbcgp1prp3d7
TD       1024
SOLVENT  CDCl3
NS       12
DS       1
SWH      3289.4 Hz
FIDRES   3.212377 Hz
AQ       0.1153680 sec
RG       1195.2
DM       152.000 usec
DE       6.50 usec
TE       298.4 K
CNST13   8.0000000 sec
CNST2    145.000000 sec
d0       0.0000300 sec
D1       1.1205090 sec
D16      0.0001000 sec
d2       0.0034482 sec
d6       0.0025000 sec
IN0      0.0000310 sec

===== CHANNEL f1 =====
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P2       30.00 usec
PL1      0.50 dB
PL2      400.1318530 MHz

===== CHANNEL f2 =====
NUC2     13C
P1       8.70 usec
P2       -2.00 dB
PL2      100.6216229 MHz

===== GRADIENT CHANNEL =====
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GPMAX2   SINE.100
GPMAX3   SINE.100
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GP22     30.00 %
GP33     40.10 %
P16     1000.00 usec

F1 - Acquisition parameters
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SF01     100.6216 MHz
FIDRES   62.902576 Hz
SW       160.036 ppm
FRMODE   QF

F2 - Processing parameters
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SF       400.1300150 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
PC       1.40

F1 - Processing parameters
SI       1024
MC2     QF
SF       100.6127690 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
    
```

Fig S8. ^1H - ^{13}C hmbc NMR spectrum of Chlorotris(7-octenyl)germane (**4**) in CDCl_3 .

c. Spectra of 1,4-bis(tri-7-octenylgermyl)benzene (5)

¹H, (C8) ³GePhGe (C8) 3

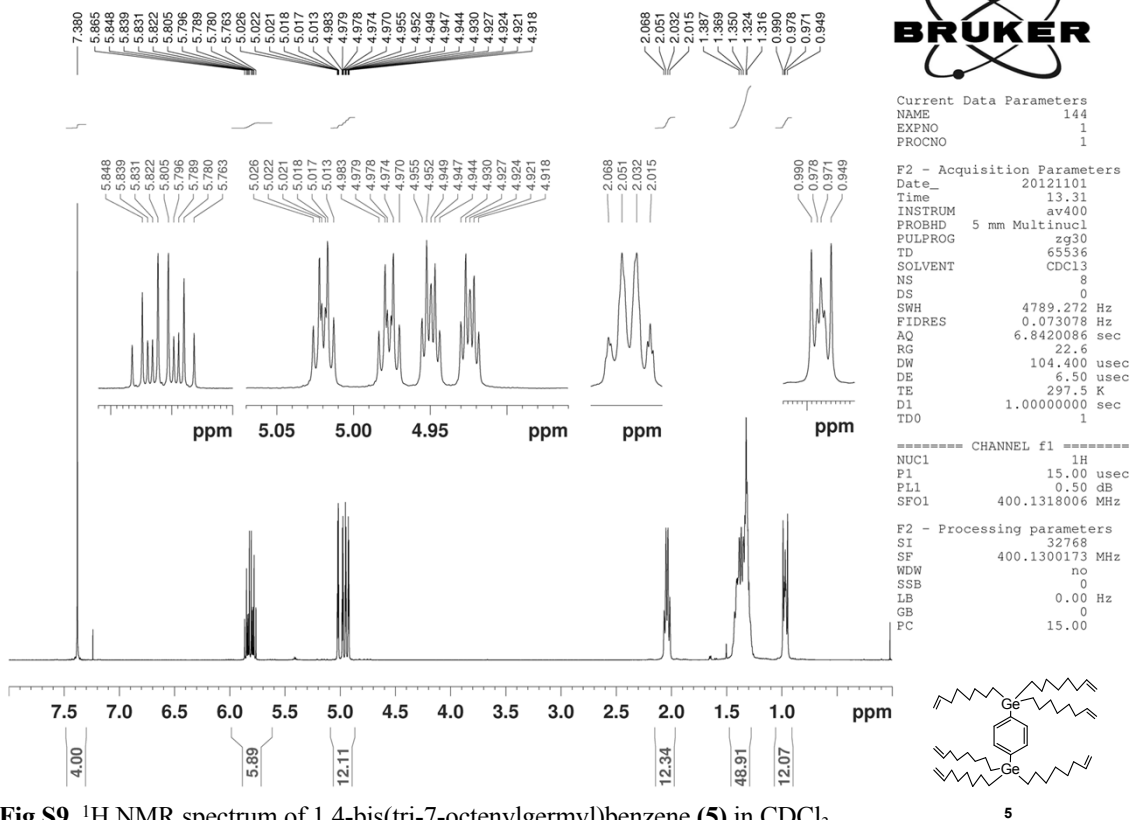


Fig S9. ¹H NMR spectrum of 1,4-bis(tri-7-octenylgermyl)benzene (5) in CDCl₃.

¹³C dept135, (C8) ³GePhGe (C8) 3



Fig S10. ¹³C NMR spectrum of 1,4-bis(tri-7-octenylgermyl)benzene (5) in CDCl₃.

¹H-¹³C HSQC, (C8) 3GePhGe (C8) 3

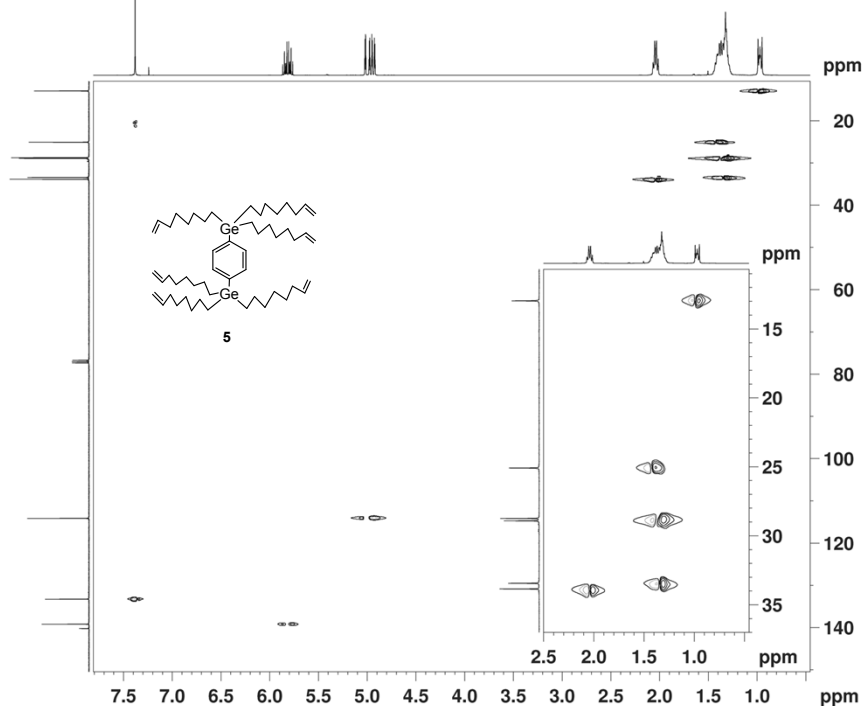


Fig S11. ¹H-¹³C hmbc NMR spectrum of 1,4-bis(tri-7-octenylgermyl)benzene (5) in CDCl₃.

HMBC, (C8) 3GePhGe (C8) 3

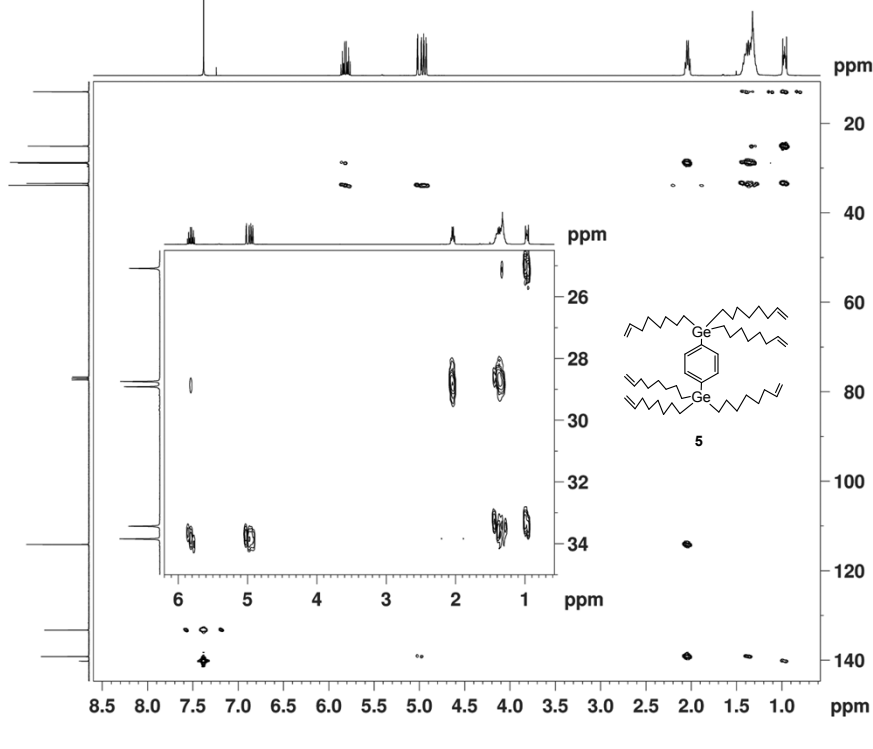


Fig S12. ¹H-¹³C hsqc NMR spectrum of 1,4-bis(tri-7-octenylgermyl)benzene (5) in CDCl₃.

d. Spectra of Molecular Gyrotop (2)

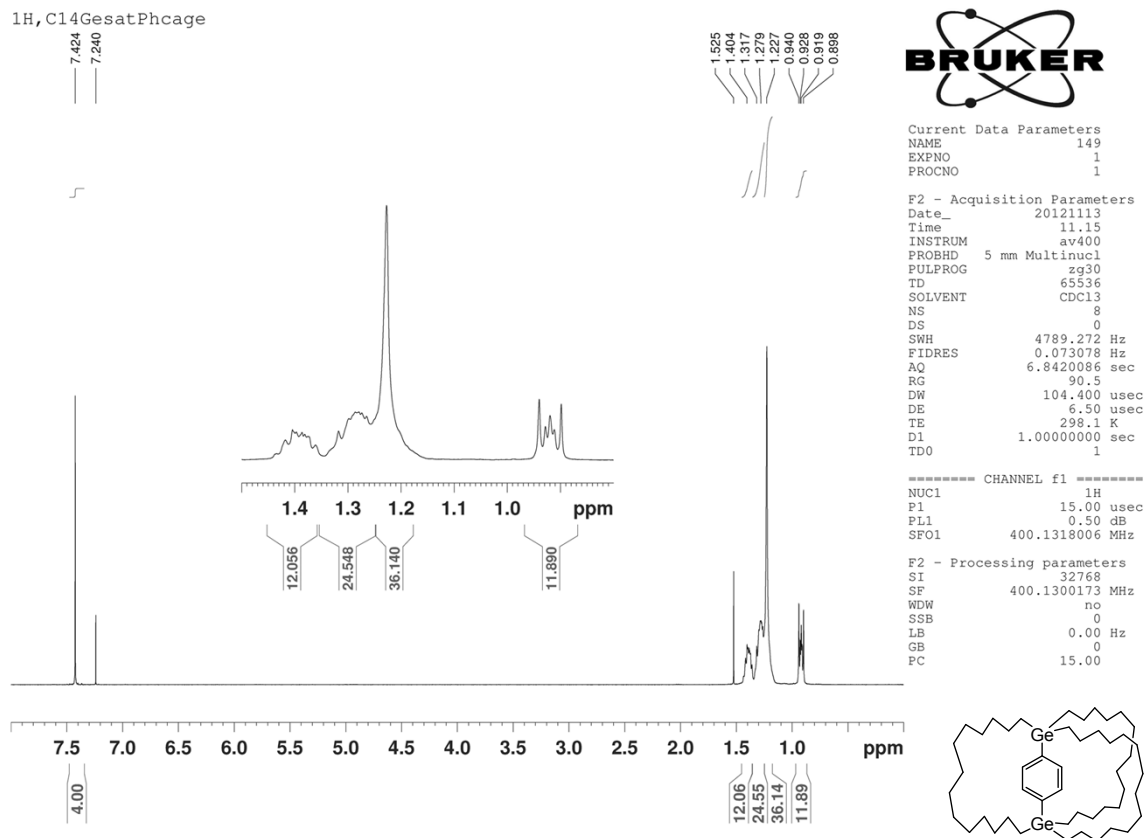


Fig S13. ¹H NMR spectrum of Molecular Gyrotop (2) in CDCl₃.

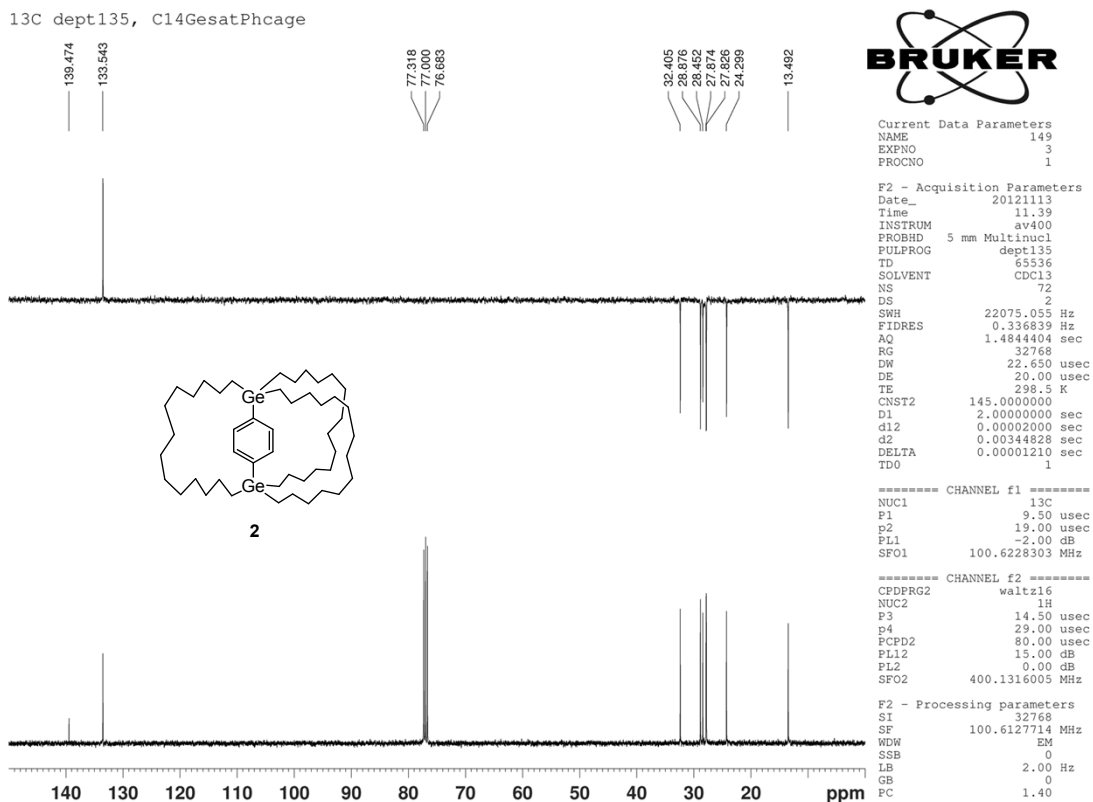
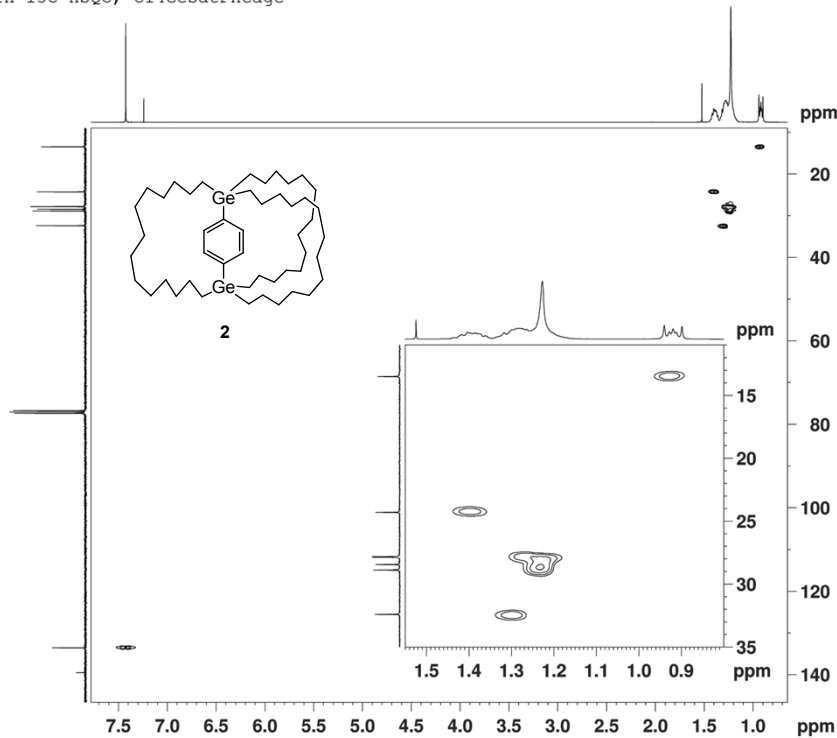


Fig S14. ¹³C NMR spectrum of Molecular Gyrotop (2) in CDCl₃.

1H-13C HSQC, C14GesatPhcage



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PROCNO    1

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SOLVENT   CDCl3
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DS         1
SWH        2997.602 Hz
FIDRES     9.85491 Hz
AQ         0.0854516 sec
RG         14596.5
DW         166.800 usec
DE         6.50 usec
TE         298.3 K
CMT2      145.000000 sec
d0         0.0000000 sec
d1         1.3283700 sec
d11        0.0300000 sec
d13        0.0000000 sec
d16        0.0001000 sec
d2         0.0010000 sec
d4         0.0017244 sec
DELTA      0.00231600 sec
DELTA1     0.00071614 sec
ZD0        0.0000105 sec
STCNT      128
ZDGFINE

===== CHANNEL f1 =====
NUC1       1H
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P2         30.00 usec
P3         0.00 usec
PL1        0.50 dB
PL2        400.1316800 MHz

===== CHANNEL f2 =====
CPDPRG2    gddp
NUC2       13C
P3         8.70 usec
P4         17.40 usec
P5         70.00 usec
PL1        16.00 dB
PL2        -2.00 dB
PL3        100.6216229 MHz

===== GRADIENT CHANNEL =====
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GPF2       30.00 %
GPF3       40.10 %
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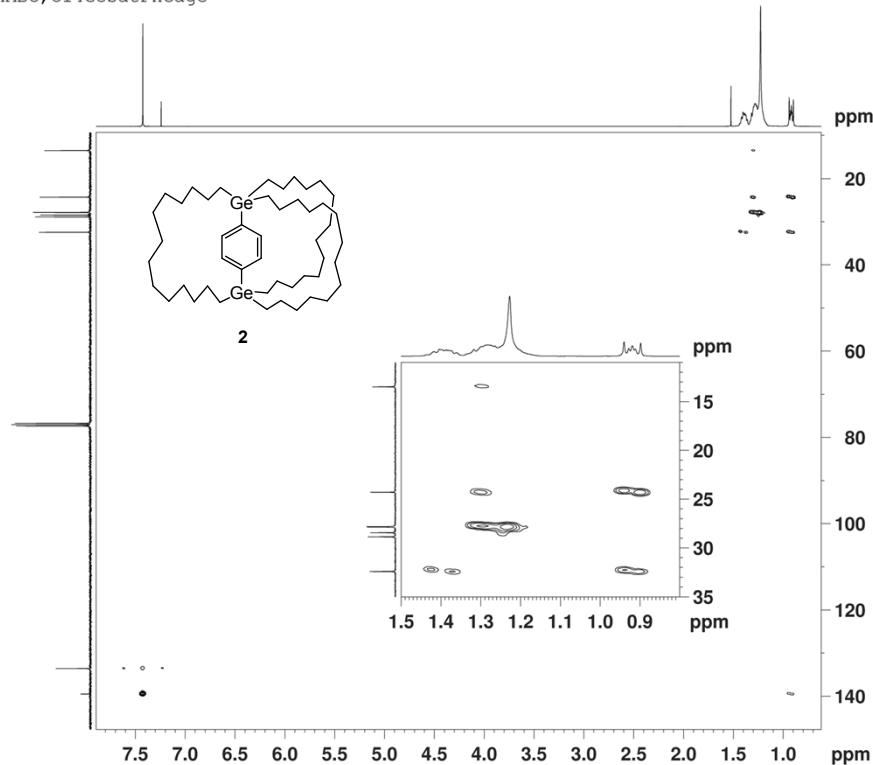
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FIDRES     9.85491 Hz
SW         160.036 ppm
F2MODE     Echo-AntiEcho

F2 - Processing parameters
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SF         400.1301100 MHz
WDW        SINE
SSB        2
LB         0.00 Hz
GB         0
PC         1.40

F1 - Processing parameters
SI         2048
SF         100.6216900 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         0
    
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Fig S15. ¹H-¹³C hsqc NMR spectrum of Molecular Gyrotop (2) in CDCl₃.

HMBC, C14GesatPhcage



```

Current Data Parameters
NAME      149
EXPNO     6
PROCNO    1

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Date_     20121113
Time      12.14
INSTRUM   av400
PROBHD    5 mm Multinucl
PULPROG   hmbcgp1prg
TD         1024
SOLVENT   CDCl3
NS         16
DS         1
SWH        3289.474 Hz
FIDRES     3.212377 Hz
AQ         0.1556980 sec
RG         20642.5
DW         152.000 usec
DE         6.50 usec
TE         298.1 K
CMT13     8.0000000 sec
CMT2      145.000000 sec
d0         0.0000000 sec
d1         1.12050903 sec
d15        0.00010000 sec
d2         0.00344828 sec
d6         0.06250000 sec
LNO       0.00003105 sec

===== CHANNEL f1 =====
NUC1       1H
P1         15.00 usec
P2         30.00 usec
PL1        0.50 dB
PL2        400.1318530 MHz

===== CHANNEL f2 =====
NUC2       13C
P3         8.70 usec
P4         17.40 usec
P5         70.00 usec
PL1        16.00 dB
PL2        -2.00 dB
PL3        100.6216229 MHz

===== GRADIENT CHANNEL =====
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GPNAM2     SINE:100
GPNAM3     SINE:100
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GPF2       30.00 %
GPF3       40.10 %
P16        1000.00 usec

F1 - Acquisition parameters
NUC1       1H
TD         1024
SF01       400.1301100 MHz
FIDRES     3.212377 Hz
SW         160.036 ppm
F2MODE     QF

F2 - Processing parameters
SI         1024
SF         400.1301100 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         1.40

F1 - Processing parameters
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SF         100.6216900 MHz
WDW        SINE
SSB        0
LB         0.00 Hz
GB         0
PC         0
    
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Fig S16. ¹H-¹³C hmbc NMR spectrum of Molecular Gyrotop (2) in CDCl₃.

e. Spectra of Molecular Gyrotop Isomer (2i)

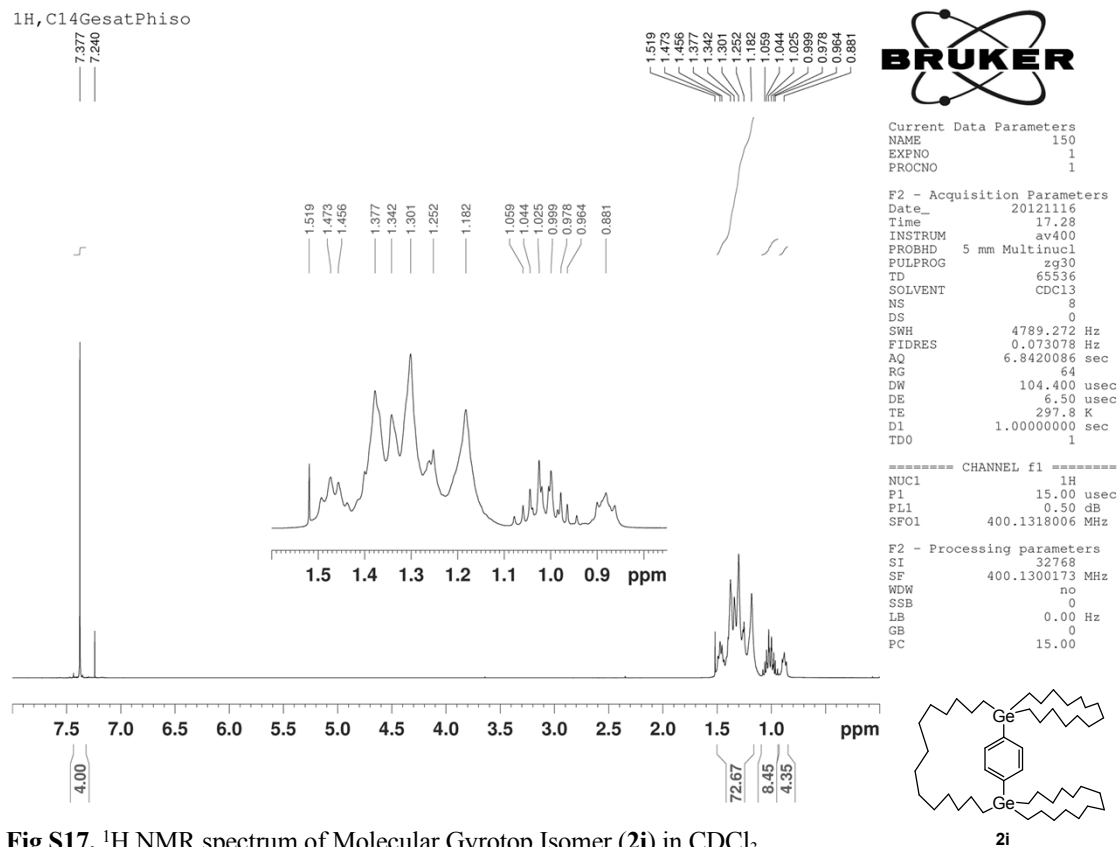


Fig S17. ¹H NMR spectrum of Molecular Gyrotop Isomer (**2i**) in CDCl₃.

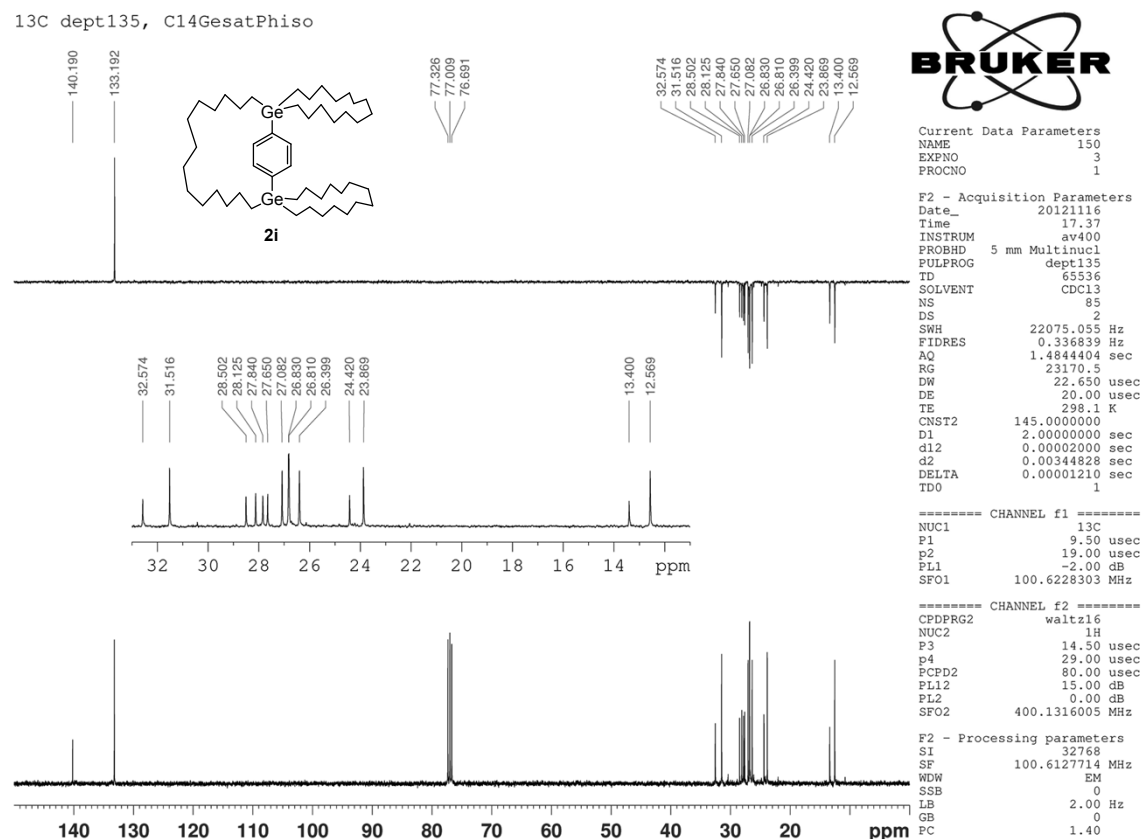
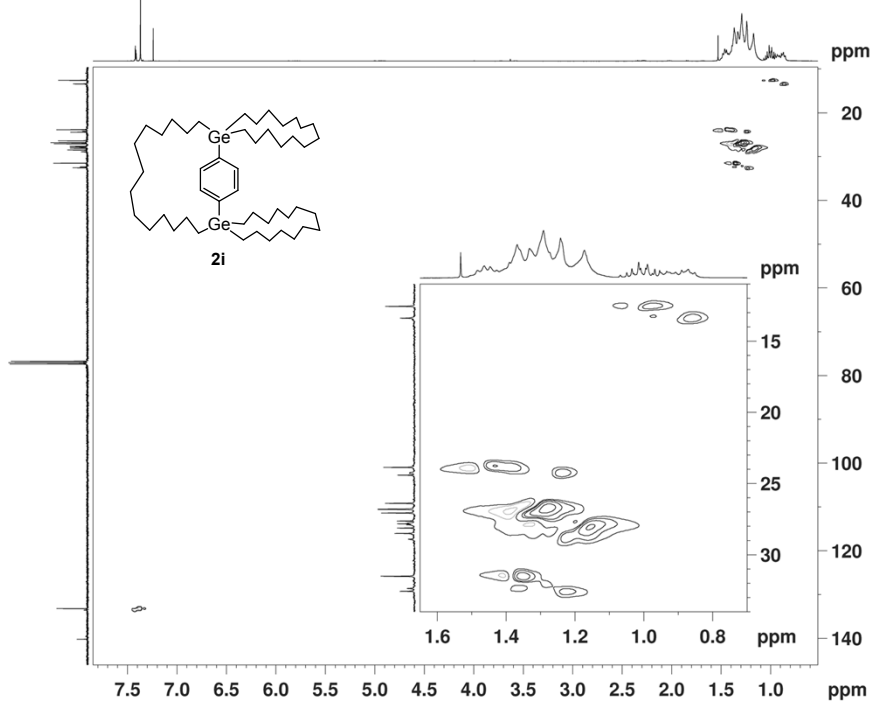


Fig S18. ¹³C NMR spectrum of Molecular Gyrotop Isomer (**2i**) in CDCl₃.

1H-13C HSQC, C14GesatPhiso



```
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EXPNO    5
PROCNO   1

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PULPROG  hsqcetqp
TD        312
SOLVENT  CDCl3
NS        2
DS        1
SWH       2397.602 Hz
FIDRES   0.0546918 Hz
AQ        0.0854518 sec
RG        1585.2
SWH       186.800 usec
DE        4.50 usec
TE        298.2 K
CNS1     145.000000 sec
d0        0.0000000 sec
d1        3.3283720 sec
d11       0.0300000 sec
d13       0.0000000 sec
d16       0.0001000 sec
d21       0.0034500 sec
d4        0.0017244 sec
DELTA    0.0021500 sec
DELTA1   0.0007164 sec
INDO     0.0000000 sec
STCNT    128
SFOFMS

===== CHANNEL f1 =====
NUC1      1H
P1        15.00 usec
P2        30.00 usec
P2R       0.50 usec
PL1       0.50 dB
SFO1     400.1318898 MHz

===== CHANNEL f2 =====
CPDPRG2  gspg
NUC2      13C
P3        8.70 usec
P4        17.40 usec
PCPD2    70.00 usec
PL2       2.00 dB
PL3       -2.00 dB
SFO2     100.6216229 MHz

===== GRADIENT CHANNEL =====
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GPMAN2   SINE.100
GE1       80.00 %
GE2       20.10 %
P16      1000.00 usec

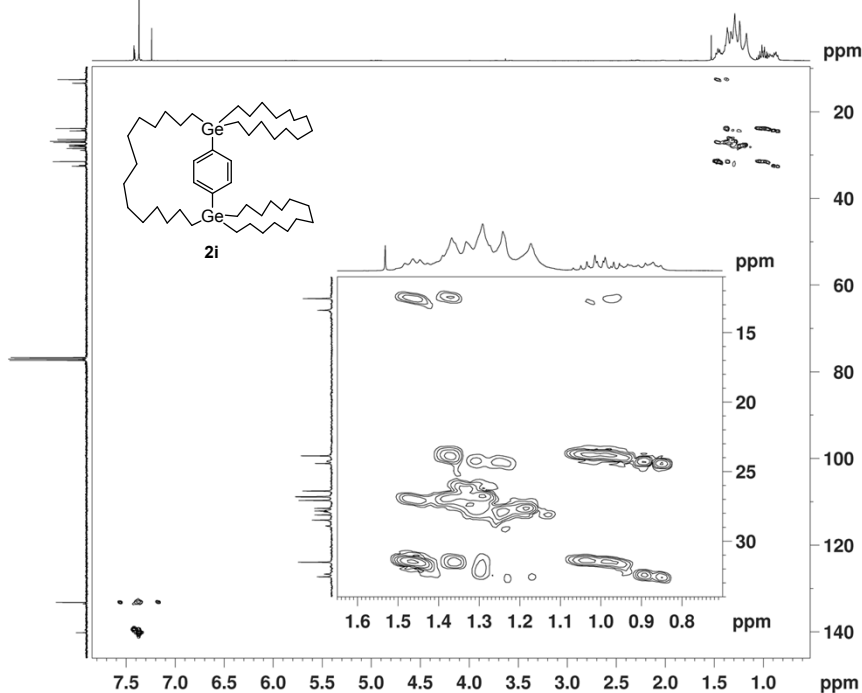
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TD        256
SFO1     100.6216 MHz
FIDRES   62.902576 Hz
SWH       160.316 ppm
F2NODE   Echo-Antiecho

F2 - Processing parameters
S1        1324
SF        400.1300167 MHz
WDW       QLINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40

F1 - Processing parameters
S1        1024
XC2       QP
SF        100.6127690 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
```

Fig S19. ¹H-¹³C hsqc NMR spectrum of Molecular Gyrotop Isomer (2i) in CDCl₃.

HMBC, C14GesatPhiso



```
Current Data Parameters
NAME      150
EXPNO    6
PROCNO   1

F2 - Acquisition Parameters
Date_    20121113
Time     14.57
INSTRUM  av400
PROBHD   5 mm Multinuc1
PULPROG  hmbcgp1pddg
TD        424
SOLVENT  CDCl3
NS        16
DS        1
SWH       3289.474 Hz
FIDRES   3.212377 Hz
AQ        0.1354980 sec
RG        20642.5
SWH       152.000 usec
DE        4.50 usec
TE        298.2 K
CNS1     145.000000 sec
d0        0.0000000 sec
d1        1.1205903 sec
d16       0.0001000 sec
d2        0.0034828 sec
d4        0.0025000 sec
INDO     0.0000105 sec

===== CHANNEL f1 =====
NUC1      1H
P1        15.00 usec
P2        30.00 usec
PL1       0.50 dB
SFO1     400.1318530 MHz

===== CHANNEL f2 =====
NUC2      13C
P3        8.70 usec
P4        17.40 usec
PL2       2.00 dB
PL3       -2.00 dB
SFO2     100.6216229 MHz

===== GRADIENT CHANNEL =====
GPMAN1   SINE.100
GPMAN2   SINE.100
GPMAN3   SINE.100
GE1       50.00 %
GE2       30.10 %
GE3       40.10 %
P16      1000.00 usec

F1 - Acquisition parameters
ND0       2
TD        256
SFO1     100.6216 MHz
FIDRES   62.902576 Hz
SWH       160.316 ppm
F2NODE   QP

F2 - Processing parameters
S1        1024
SF        400.1300150 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
PC        1.40

F1 - Processing parameters
S1        1324
XC2       QP
SF        100.6127690 MHz
WDW       SINE
SSB       0
LB        0.00 Hz
GB        0
```

Fig S20. ¹H-¹³C hmbc NMR spectrum of Molecular Gyrotop Isomer (2i) in CDCl₃.

2. ORTEP Drawing of Molecule Gyrotop 2

The structures were refined using a SHELXL program package. Because of remarkably weak diffraction data at high temperature, it was difficult to refine the structure of the crystal adequately. Certain C-C distances and C-C-C angles of the alkyl chains were restrained by means of DFIX and DANG, respectively, because of the unresolved disorder.

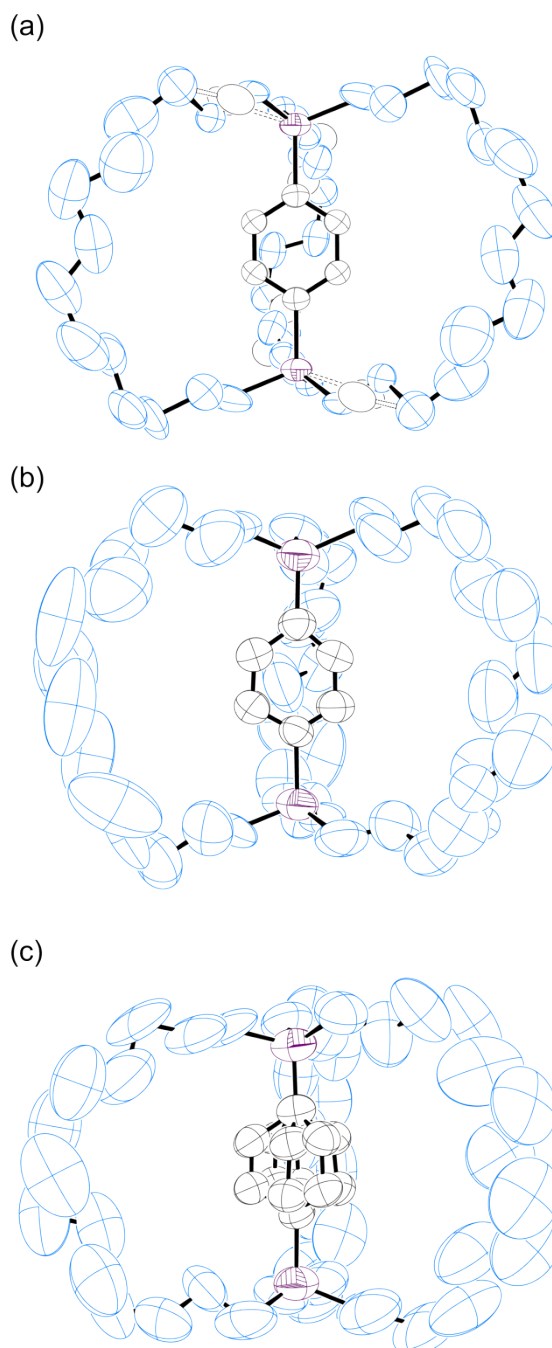


Fig S21. ORTEP drawing of the molecular structure of **2** at (a) 260 K; (b) 300 K; and (c) 340 K (30% thermal probability ellipsoid). Hydrogen atoms are omitted for clarity. Disorders of side chains are indicated.

Table S1. Crystal Data of **2** at 260 K, 300 K, and 340 K

	260 K	300 K	340 K	
CCDC #	1026017	1026018	1026019	
Empirical formula	C ₄₈ H ₈₈ Ge ₂	C ₄₈ H ₈₈ Ge ₂	C ₄₈ H ₈₈ Ge ₂	
Cryst shape	prism	plate	prism	
Cryst color	colorless	colorless	colorless	
Cryst size	0.40 x 0.20 x 0.20 mm ³	0.40 x 0.20 x 0.20 mm ³	0.40 x 0.20 x 0.20 mm ³	
Formula weight / g mol ⁻¹	810.36	810.36	810.36	
Crystal system	Monoclinic	Monoclinic	Monoclinic	
Space group	C2/c	Cc	Cc	
Z	4	4	4	
Temperature / K	260(2)	300(2)	340(2)	
Cell parameter	<i>a</i>	25.736(7) Å	26.056(10) Å	26.170(17) Å
	<i>b</i>	11.733(3) Å	11.558(4) Å	11.561(8) Å
	<i>c</i>	18.790(5) Å	19.190(7) Å	19.398(13) Å
	α	90.00°	90.00°	90.00°
	β	120.046(3)°	118.979(4)°	118.837(7)°
	γ	90.00°	90.00°	90.00°
	<i>V</i>	4911(2) Å ³	5056(3) Å ³	5141(6) Å ³
Calculated density	1.096 Mg/m ³	1.065 Mg/m ³	1.047 Mg/m ³	
F(000)	1760	1760	1760	
Absorption coefficient	1.252 mm ⁻¹	1.216 mm ⁻¹	1.196 mm ⁻¹	
θ range for collec n (deg)	1.83 to 27.10°	2.43 to 16.30°	2.40 to 15.39°	
Index ranges	-24 ≤ <i>h</i> ≤ 31, -8 ≤ <i>k</i> ≤ 14, -23 ≤ <i>l</i> ≤ 23	-24 ≤ <i>h</i> ≤ 30, -13 ≤ <i>k</i> ≤ 11, -22 ≤ <i>l</i> ≤ 22	-25 ≤ <i>h</i> ≤ 32, -14 ≤ <i>k</i> ≤ 11, -23 ≤ <i>l</i> ≤ 24	
Reflections collected	11694	10770	11576	
Independent reflections	4954 [R(int) = 0.0299]	6828 [R(int) = 0.0429]	7471 [R(int) = 0.0445]	
Completeness	99.6 %	99.4 %	99.5 %	
Goodness-of-fit on F ²	1.015	0.895	0.859	
Final R indices [I > 2σ(I)]	R1 = 0.0640, wR2 = 0.1884	R1 = 0.0712, wR2 = 0.1778	R1 = 0.0585, wR2 = 0.1405	
R indices (all data)	R1 = 0.1390, wR2 = 0.2352	R1 = 0.1889, wR2 = 0.2648	R1 = 0.2226, wR2 = 0.2312	
Largest diff. peak and hole	0.439 and -0.311 e.Å ⁻³	0.358 and -0.176 e.Å ⁻³	0.177 and -0.094 e.Å ⁻³	

3. Details of Solid-state ^2H NMR Study of $2-d_4$

The temperature-dependent, solid-state ^2H NMR spectra of $2-d_4$ were obtained through the same procedure as reported previously for $1-d_4$.^{4e} The details are as follows: the data were recorded using a quadrupolar echo pulse sequence (d1-90° pulse- τ 1-90° pulse- τ 2-FID; 90° pulse = 4.2 μs , τ 1 = 30 μs , τ 2 = 20 μs , d1 = 20 s). Simulations of the ^2H NMR spectra were carried out using NMR-WEBLAB. The following parameters were used for the simulations: quadrupolar coupling constant q_{cc} = 122 kHz, asymmetry parameter η = 0, line broadening = 3 kHz.

The temperature dependence of the spin-lattice relaxation time (T_1) in the ^2H NMR spectra was recorded using an inversion-recovery quadrupolar echo pulse sequence (d1-180° pulse-d2-90° pulse- τ 1-90° pulse- τ 2-FID; 90° pulse = 4.2 μs , τ 1 = 30 μs , τ 2 = 20 μs , d1 = 5–3 s, d2 varied) and standard T_1 analysis software. The spin-lattice relaxation time (T_1) was analyzed using the general relaxation model (eq. 1). T_1 is known to depend on the motional model for the exchange process; several special motions have been discussed so far.

a. VT-Solid state ^2H NMR spectra of $2-d_4$.

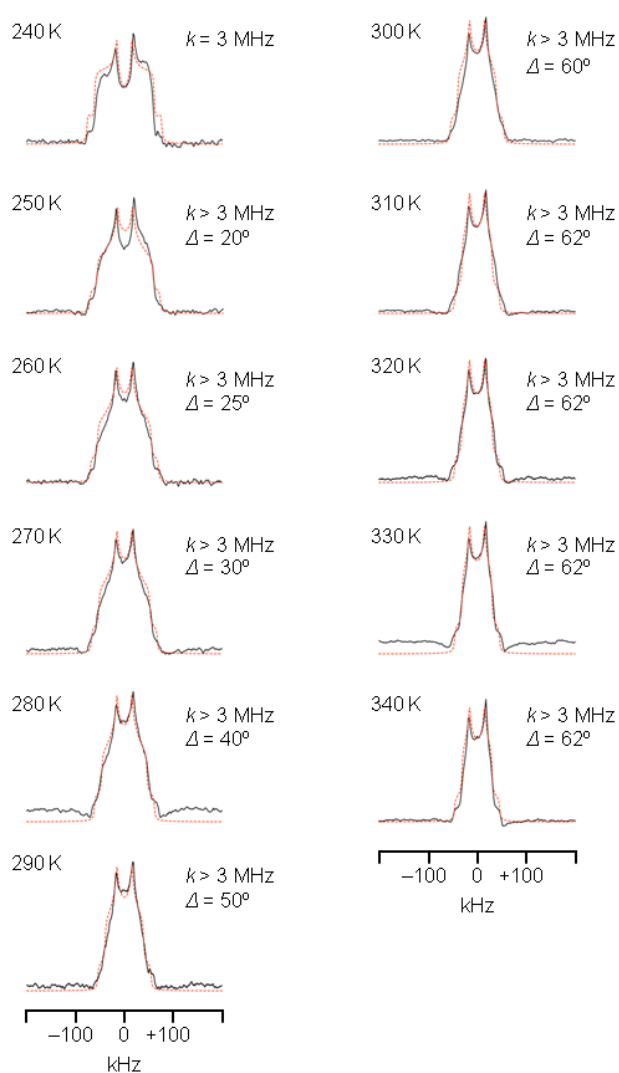


Fig S22. Temperature dependence of solid-state ^2H NMR spectra of $2-d_2$ [solid black line: observed spectra; dotted red line: spectra simulated with designated exchange rate constants, k , and degree of angular displacement, Δ . The simulation model is mentioned in main text].

b. Analysis of temperature dependence of the ^2H NMR spin-lattice relaxation (T_1) measurements of 2- d_2

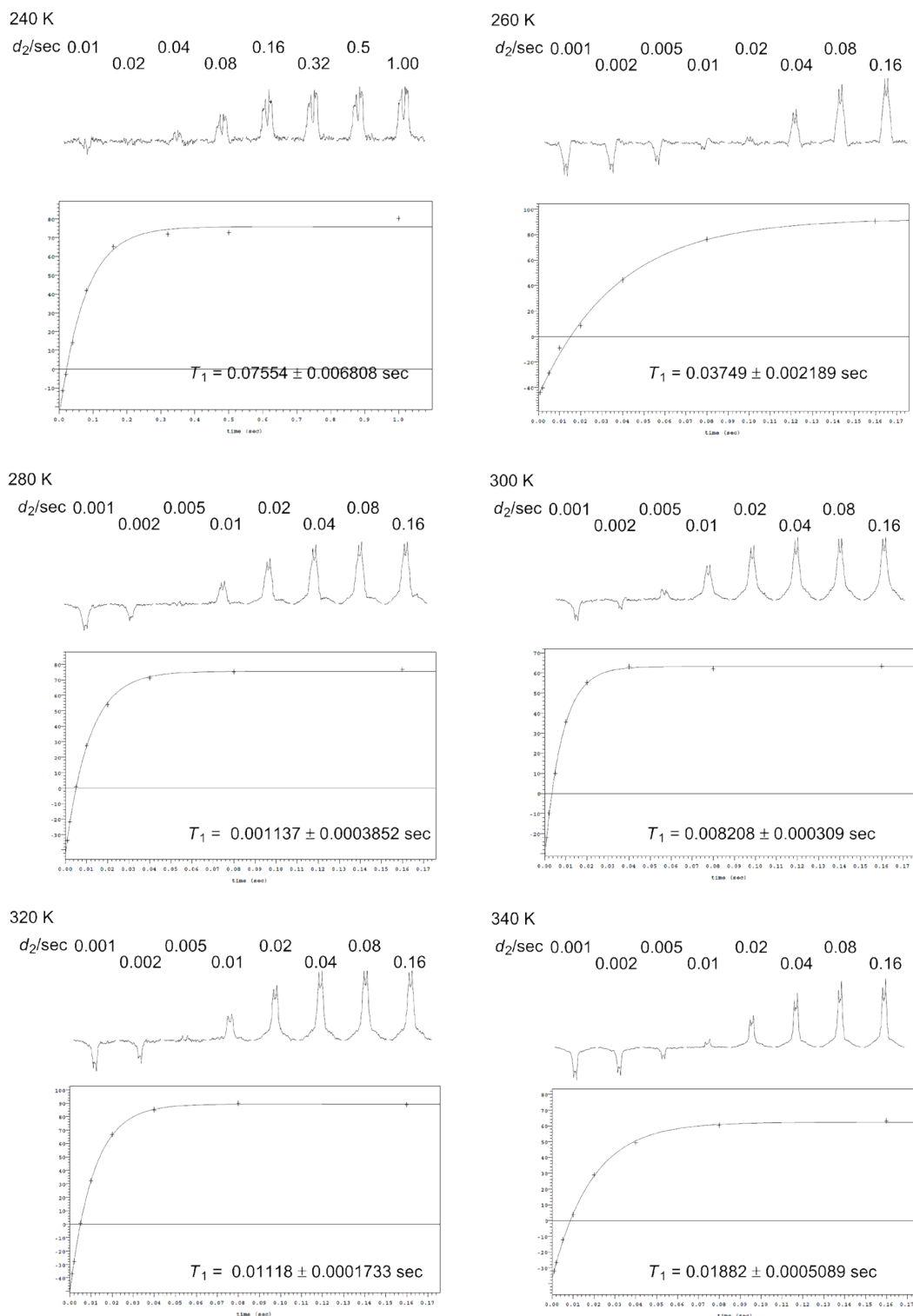


Fig S23. Representative inversion-recovery ^2H NMR spectroscopy data and single exponential fit from solid sample of molecular gyrotop 2- d_4 (240 K – 340 K).

4. Details of Optical properties of a single crystal of 2

The fast and slow optical axes were confirmed by a polarized-light microscope equipped with a sensitive color plate. Retardations were observed by the polarized-light microscope equipped with a Berek compensator and monochromatic light at 546 nm generated by a color filter. The thickness of the crystal was measured by a laser displacement sensor at 300 K. The Δn value was calculated from the retardation/thickness of the sample.

a. Crystal orientation mapping of a single crystal of 2

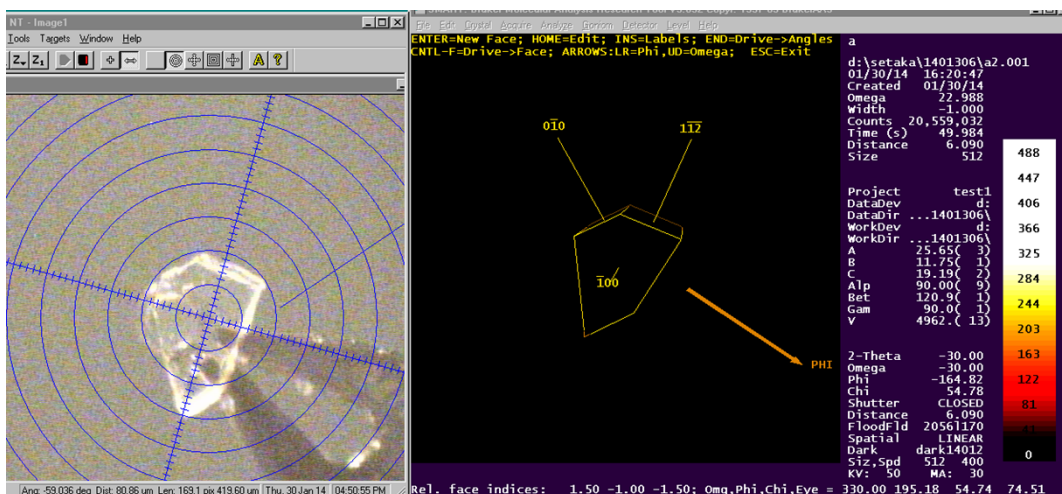


Fig S24. Crystal orientation mapping of a single crystal of 2 as determined by X-ray diffraction study at 300 K.

b. Thickness of the single crystal of 2

The thickness of the crystal was measured at 300 K using a laser displacement sensor (KEYENCE LT-9010M).

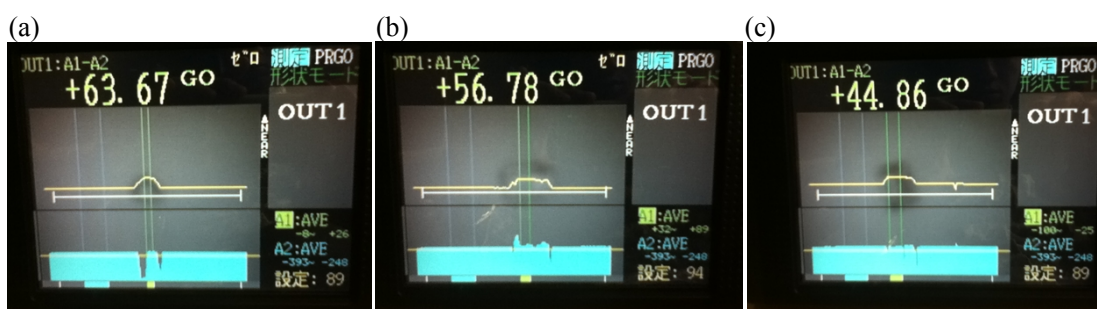


Fig S25. Measurement of the thickness of the single crystal of 2 at 300 K using a laser displacement sensor (KEYENCE LT-9010M); (a) $63.7 \pm 1.0 \mu\text{m}$; (b) $56.8 \pm 1.0 \mu\text{m}$; (c) $44.9 \pm 1.0 \mu\text{m}$.

c. Photograph of single crystals of **2** observed by polarized microscopy

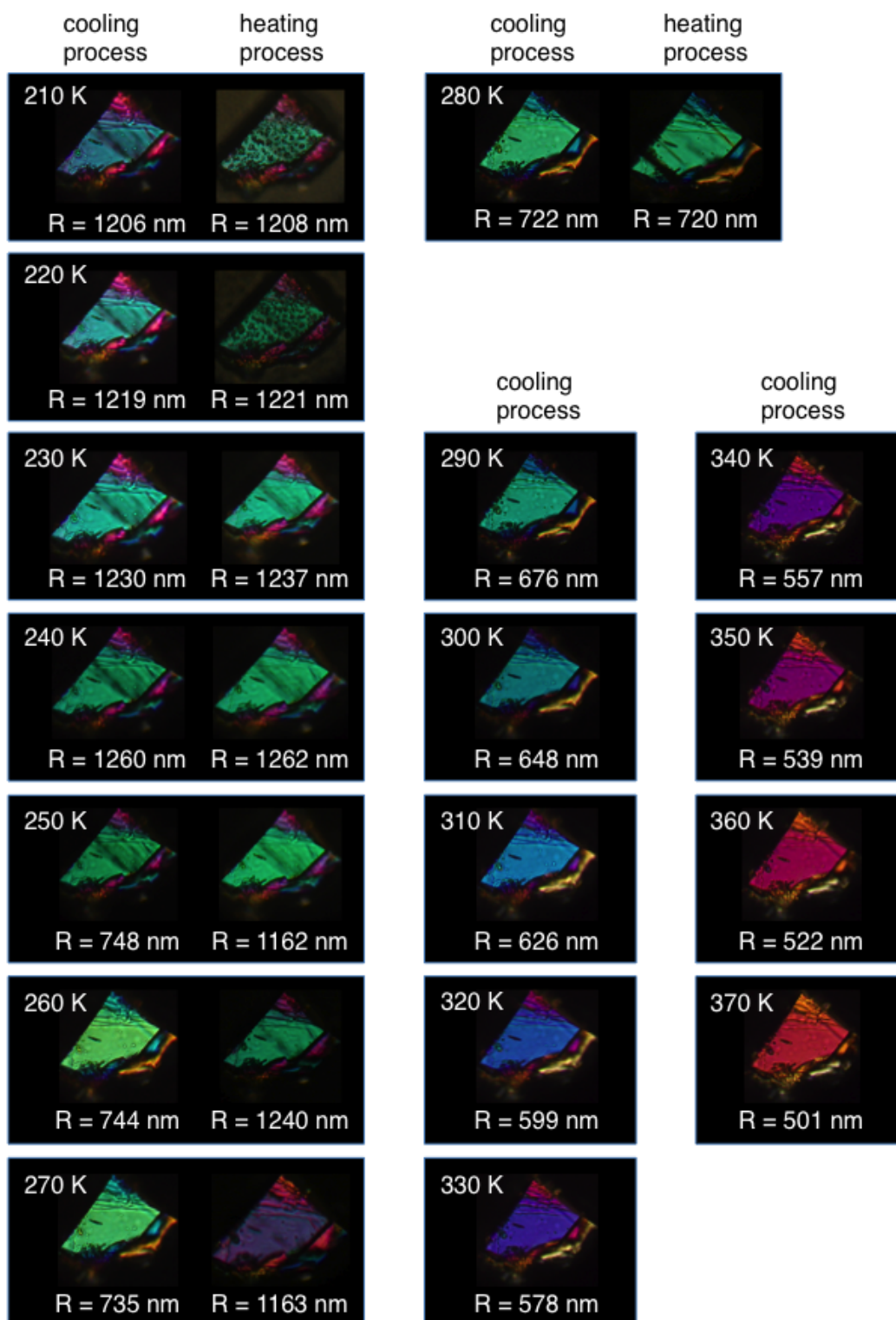


Fig S26a. Photographs of the single crystal of **2** (sample thickness: 64 ± 1 μm) showing the crystal face upon irradiation with polarized white light ($\{100\}$ face at 200 K).

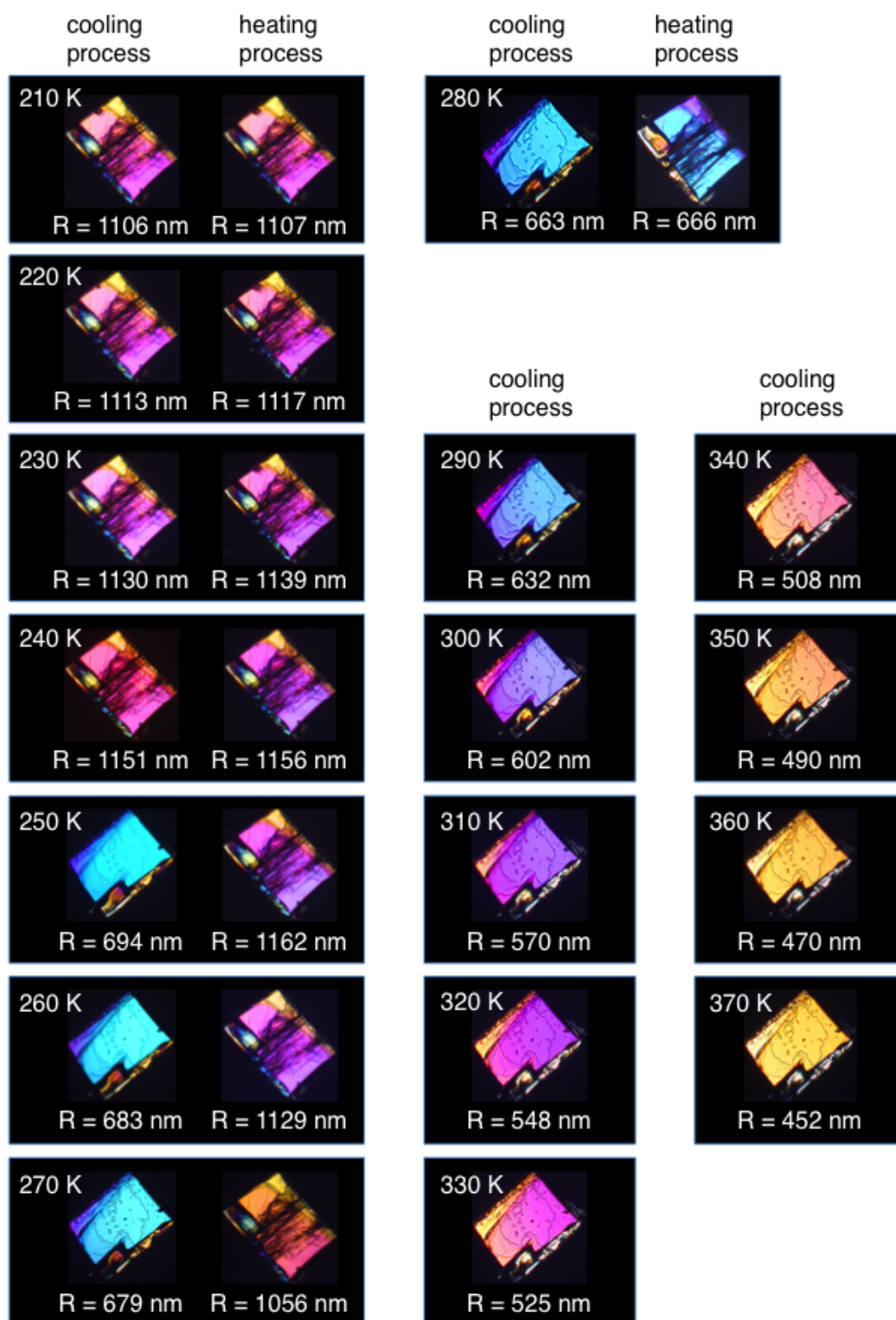


Fig S26b. Photographs of the single crystal of **2** (sample thickness: $57 \pm 1 \mu\text{m}$) showing the crystal face upon irradiation with polarized white light ($\{100\}$ face at 200 K).

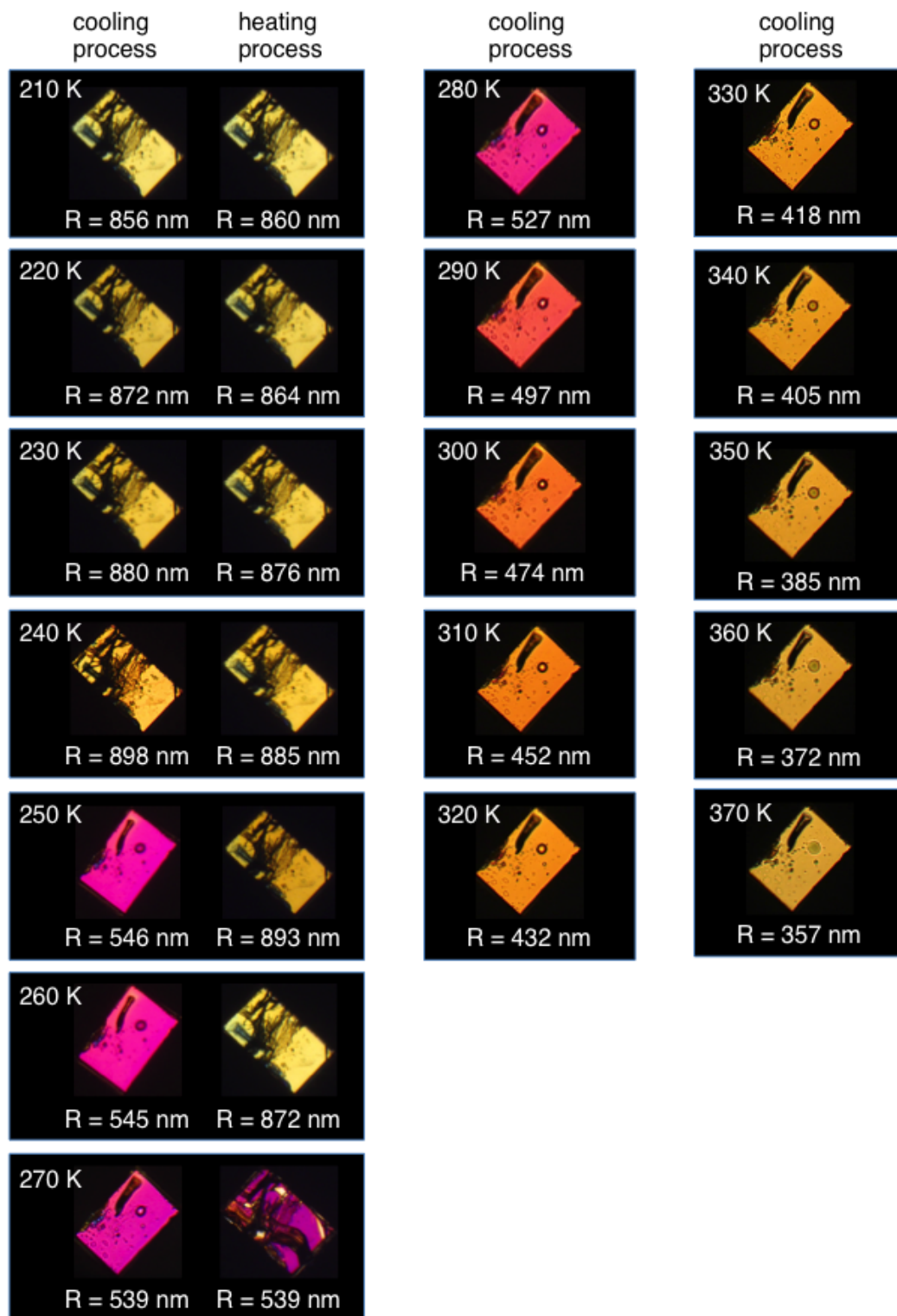


Fig S26c. Photographs of the single crystal of **2** (sample thickness: 45 ± 1 μm) showing the crystal face upon irradiation with polarized white light ($\{100\}$ face at 200 K).

d. Temperature dependence of Δn of **2**

Temperature dependence of birefringence (Δn) of the crystal face of a single crystal of **2**, calculated from Retardation/Thickness as summarized in Table S2.

Table S2-1. Temperature Dependence of Retardation, and Δn of **2**.

(Thickness of the Single Crystal $d = 44.9 \mu\text{m}$)

Temperature / K	Retardation ¹⁾ / nm	Δn ²⁾ / 10^{-3}
	cooling process heating process	cooling process heating process
210	855.7 859.7	19.08 ± 0.60 19.16 ± 0.53
220	871.5 864.1	19.43 ± 0.47 19.26 ± 0.57
230	880.3 876.4	19.63 ± 0.50 19.54 ± 0.47
240	897.8 885.4	20.02 ± 0.53 19.74 ± 0.54
250	546.2 892.5	12.18 ± 0.29 19.90 ± 0.55
260	544.5 872.3	12.14 ± 0.33 19.45 ± 0.49
270	536.4 540.7	11.96 ± 0.29 12.01 ± 0.33
280	526.5 528.0	11.74 ± 0.31 11.79 ± 0.28
290	497.2 499.2	11.08 ± 0.28 11.13 ± 0.28
300	473.6 472.5	10.56 ± 0.28 10.53 ± 0.28
310	451.9 451.4	10.07 ± 0.28 10.07 ± 0.25
320	432.1 435.5	9.63 ± 0.27 9.72 ± 0.23
330	417.7 418.1	9.31 ± 0.24 9.32 ± 0.23
340	405.1 400.5	9.03 ± 0.32 8.93 ± 0.28
350	385.3 387.6	8.59 ± 0.29 8.64 ± 0.26
360	371.6 369.9	8.28 ± 0.26 8.25 ± 0.23
370	357.2 357.3	7.96 ± 0.23 7.97 ± 0.24

1) Mean values of three time measurements.

2) The error for the birefringence Δn includes both a measurement error of retardation and a thickness error (± 1.0).

(Thickness of the Single Crystal $d = 56.8 \mu\text{m}$)

Temperature / K	Retardation ¹⁾ / nm		Δn ²⁾ / 10^{-3}	
	cooling process heating process		cooling process heating process	
210	1105.6	1107.3	19.47 ± 0.43	19.50 ± 0.49
220	1112.5	1117.0	19.59 ± 0.47	19.67 ± 0.37
230	1129.6	1138.9	19.89 ± 0.49	20.06 ± 0.38
240	1151.3	1155.9	20.28 ± 0.42	20.36 ± 0.42
250	693.8	1162.0	12.22 ± 0.25	20.47 ± 0.45
260	683.4	1129.2	12.04 ± 0.24	19.89 ± 0.39
270	673.9	1056.0	11.87 ± 0.23	18.60 ± 0.48
280	663.1	666.0	11.68 ± 0.26	11.73 ± 0.32
290	631.7	628.3	11.13 ± 0.25	11.13 ± 0.25
300	601.1	599.4	10.60 ± 0.20	10.60 ± 0.20
310	570.2	571.0	10.04 ± 0.20	10.04 ± 0.20
320	548.1	548.6	9.65 ± 0.22	9.65 ± 0.22
330	524.7	526.5	9.24 ± 0.20	9.24 ± 0.20
340	508.4	506.5	8.95 ± 0.22	8.95 ± 0.22
350	489.5	489.1	8.62 ± 0.16	8.62 ± 0.16
360	470.2	470.2	8.28 ± 0.17	8.28 ± 0.17
370	452.1	449.5	7.96 ± 0.19	7.96 ± 0.19

1) Mean values of three time measurements.

2) The error for the birefringence Δn includes both a measurement error of retardation and a thickness error (± 1.0).

e. Details of measurement of the optical axes of the single crystal of 2

On the $\{100\}$ -face of the crystal at 300 K, the fast optical axis is observed to be parallel to $\langle 010 \rangle$ axis as ascertained from the decrease in the retardation by 147 nm, observed using a polarized-light microscope equipped with a $1/4\lambda$ plate, which adds 147 nm along the $\langle 010 \rangle$ axis (FigS27(i)b). After rotation of the crystal by 90° , the retardation observed through the $1/4\lambda$ plate increased by 147 nm (Fig S27(i)c), indicating that the slow optical axis is perpendicular to $\langle 010 \rangle$ axis. On the other hand, in the case at 240 K the increment and decrement of the retardation observed through the $1/4\lambda$ plate were opposite to that observed at 300 K (Fig S27(ii)).

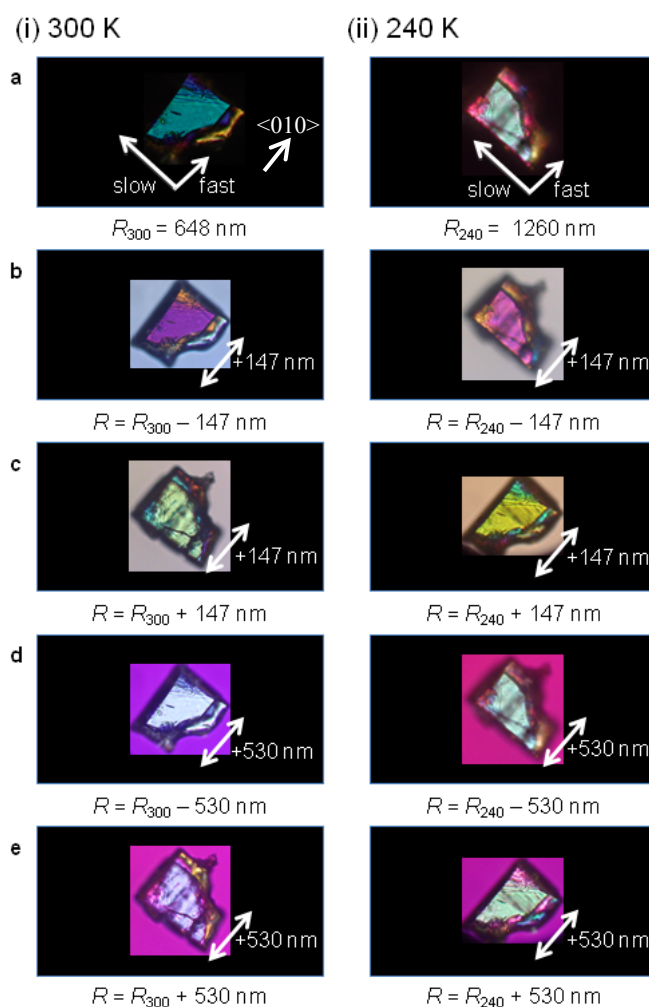


Fig S27. Photographs of the single crystals of **2** (sample thickness: $63.7 \pm 1.0 \mu\text{m}$) on the crystal face upon irradiation with polarized white light and its retardation (R) ($\{100\}$ face at 300 K). **a**, Normal photograph with directions of optical axes. **b**, Photograph through a $1/4\lambda$ plate. **c**, Photograph through a $1/4\lambda$ plate after 90° rotation of the crystal. **d**, Photograph through a sensitive color plate. **e**, Photograph through a sensitive color plate after 90° rotation of the crystal.