Supplementary Information

Synthesis and Rotational Dynamics of Diazamacrocycles Having Bridged 1,4-Naphthylene as Framed Molecular Rotors

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Table of Contents:

1. Copies of NMR and HRMS Spectra for All New Compounds

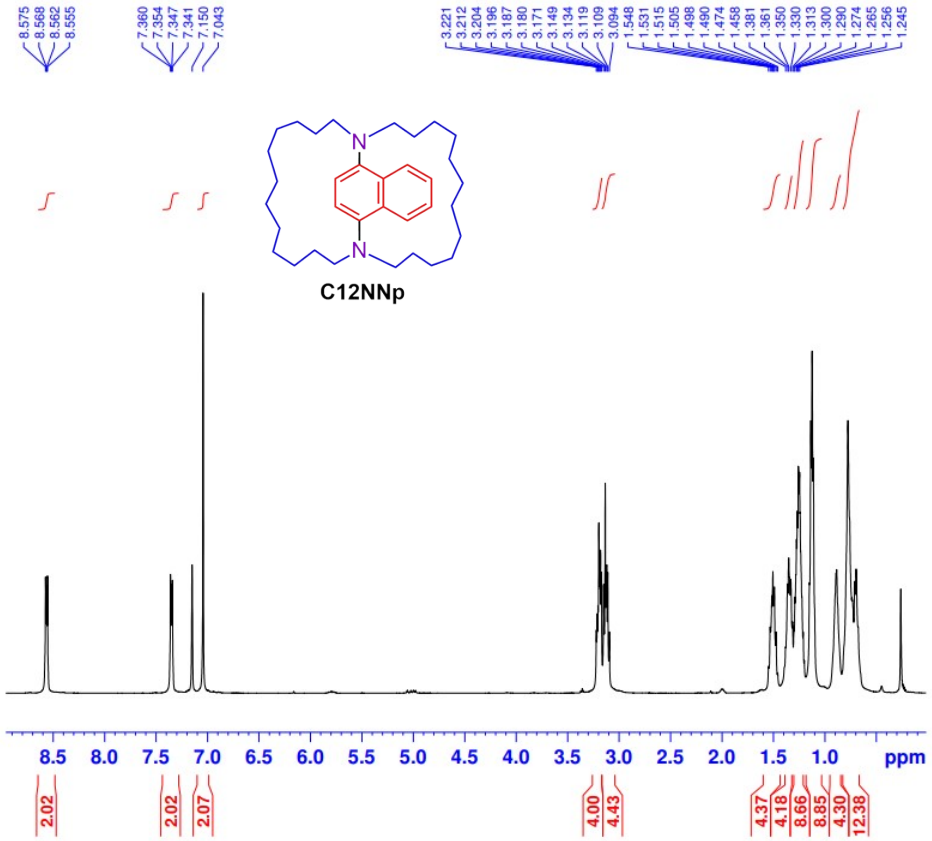


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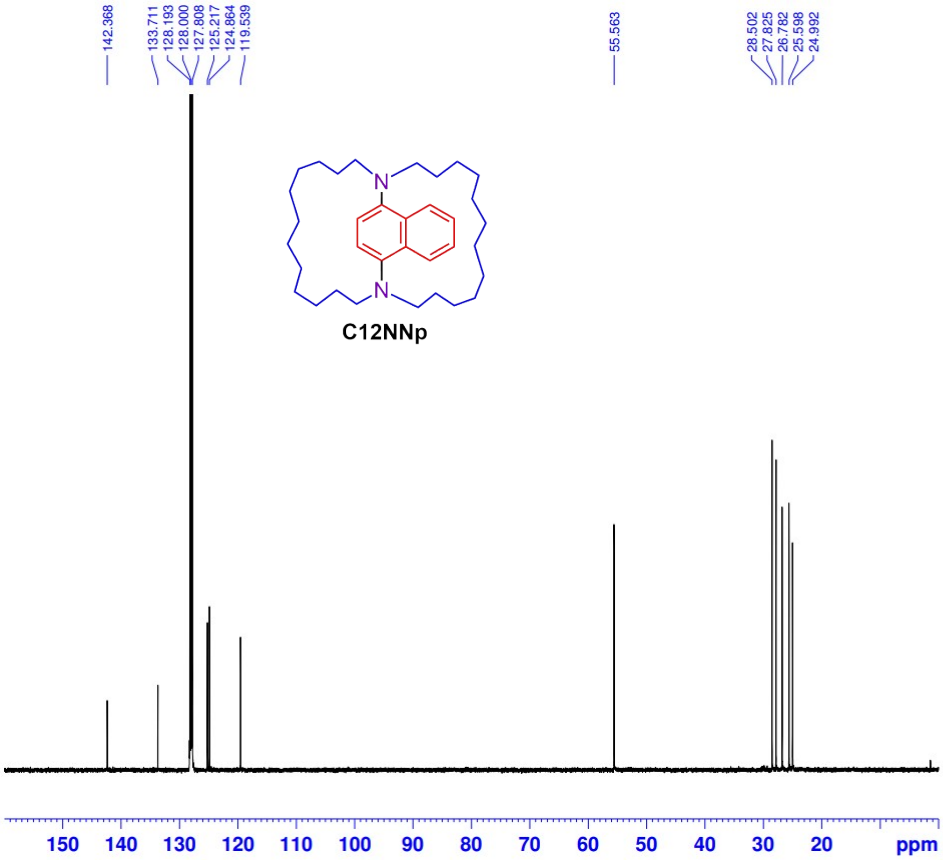
Fig. S1. ^{1}H NMR spectrum of **C12Np** in C_6D_6.

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NUC2                      1H
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Fig. S2. ^{13}C NMR spectrum of **C12Np** in C_6D_6.

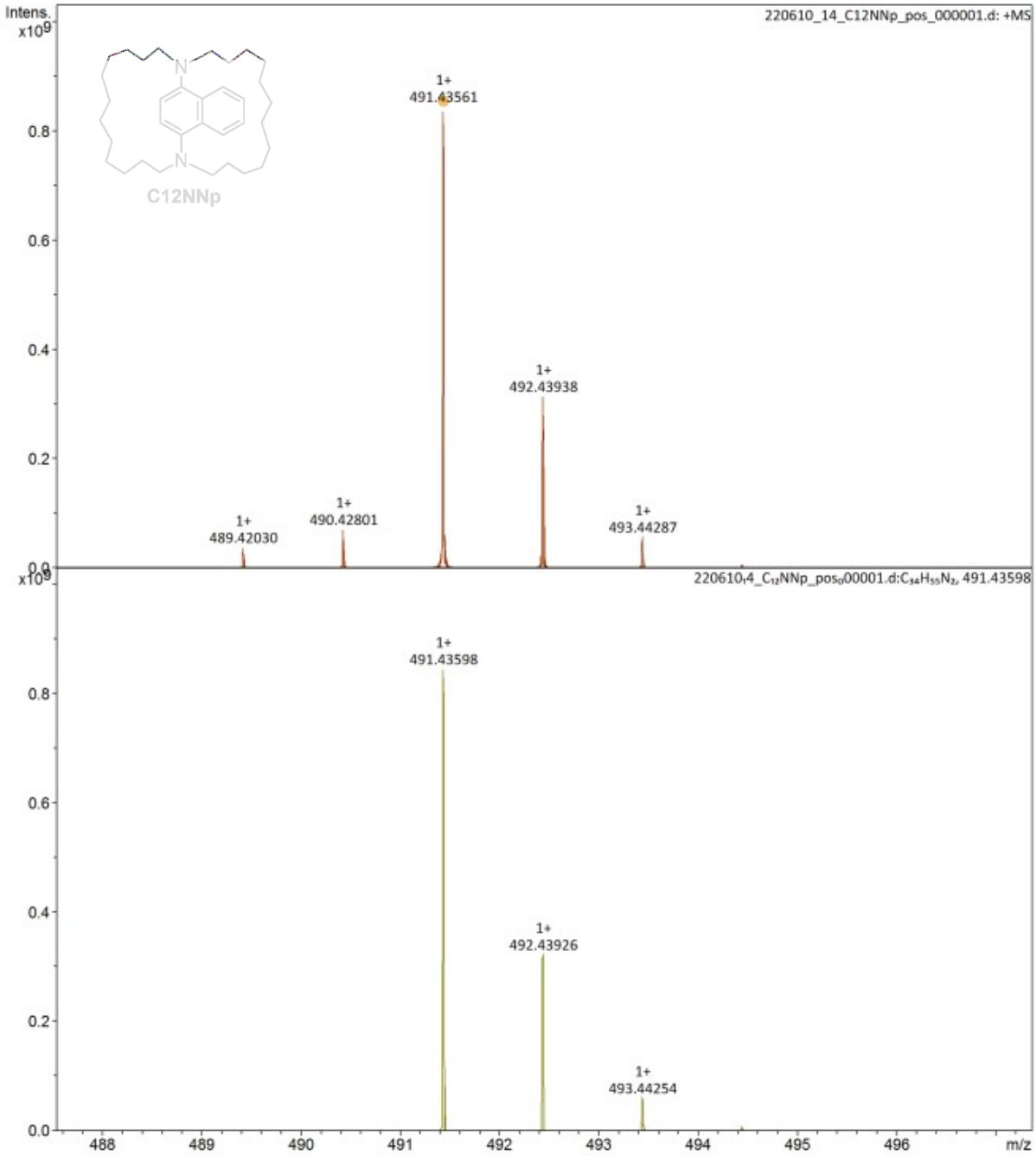
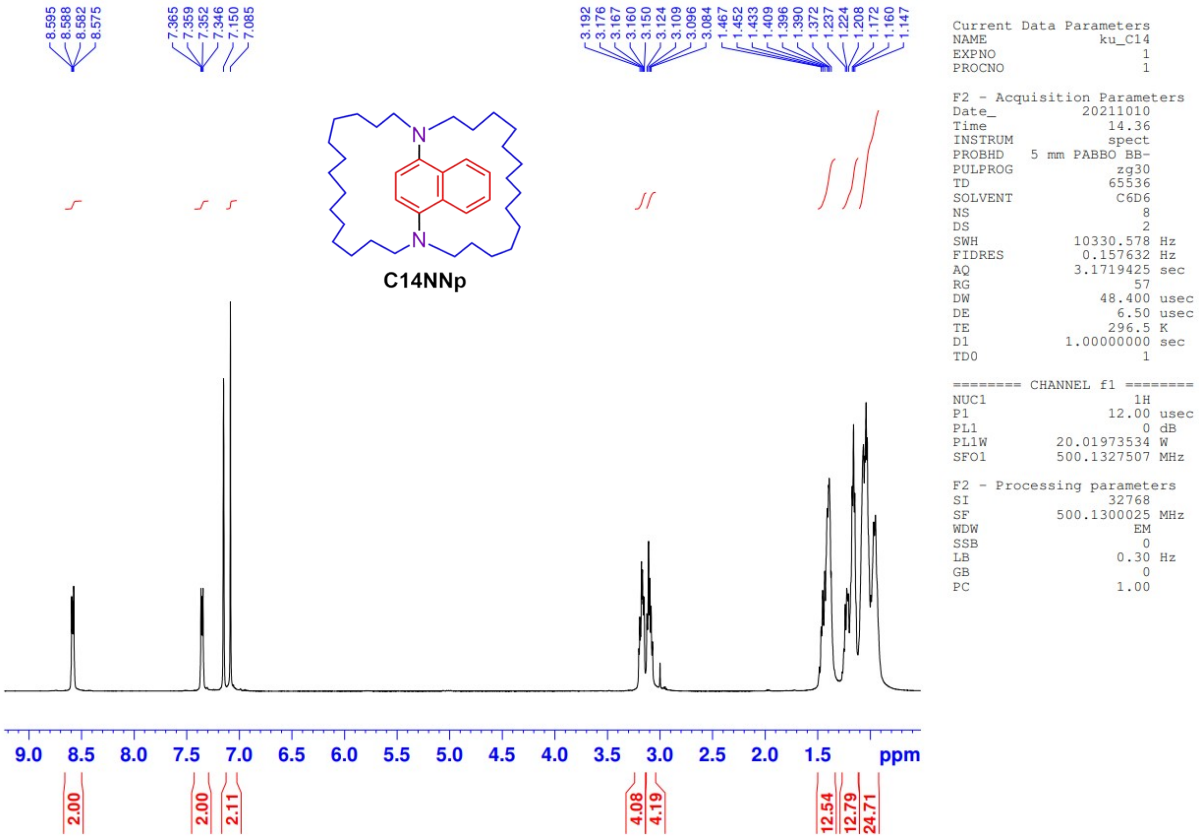


Fig. S3. HRMS spectrum of **C12Np** (APCI, positive). Top: obsd. Bottom: sim.

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NS                        8
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FIDRES            0.157632 Hz
AQ                3.1719425 sec
RG                       57
DW                   48.400 usec
DE                    6.50 usec
TE                   296.5 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
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PL1                        0 dB
PL1W             20.01973534 W
SFO1             500.1327507 MHz

F2 - Processing parameters
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WDW                       EM
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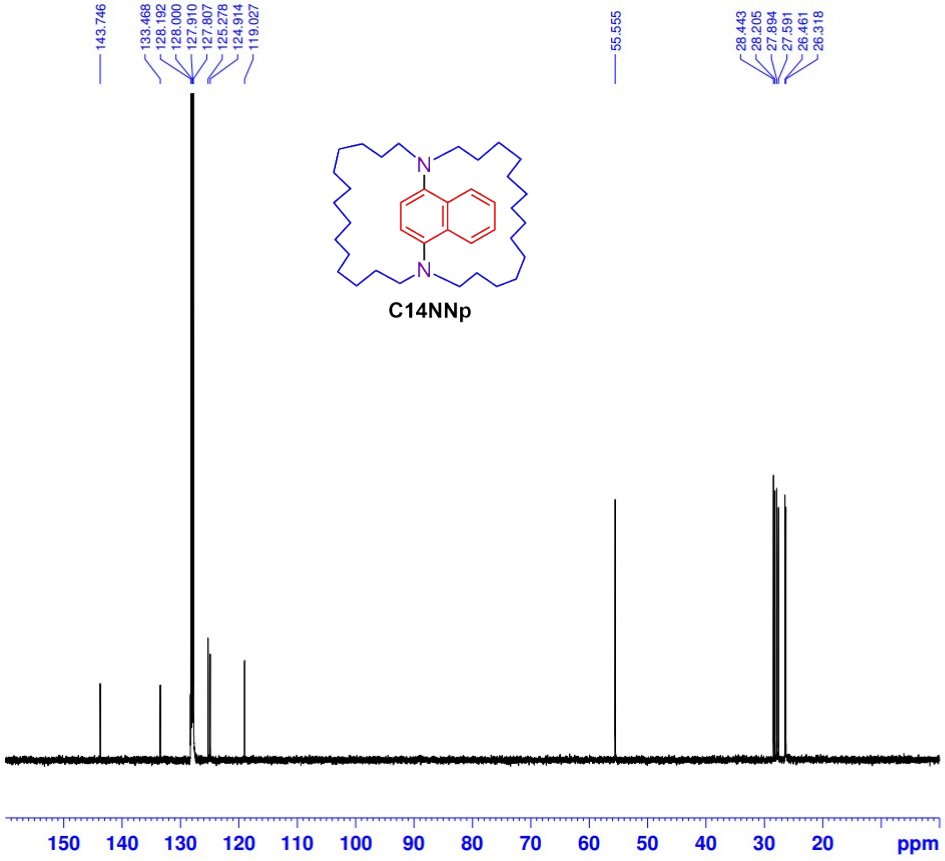
Fig. S4. ^{1}H NMR spectrum of **C14Np** in C_6D_6.

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DS                         4
SWH               29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010048 sec
RG                       203
DW                   16.800 usec
DE                    6.50 usec
TE                   297.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

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PL1                    -0.80 dB
PL1W             96.33646393 W
SFO1             125.7703643 MHz

======== CHANNEL f2 ========
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PCPD2                  80.00 usec
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PL12                   16.50 dB
PL13                   16.50 dB
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PL12W             0.44818604 W
PL13W             0.44818604 W
SFO2             500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF               125.7577490 MHz
WDW                       EM
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PC                      1.40
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Fig. S5. ^{13}C NMR spectrum of **C14Np** in C_6D_6.

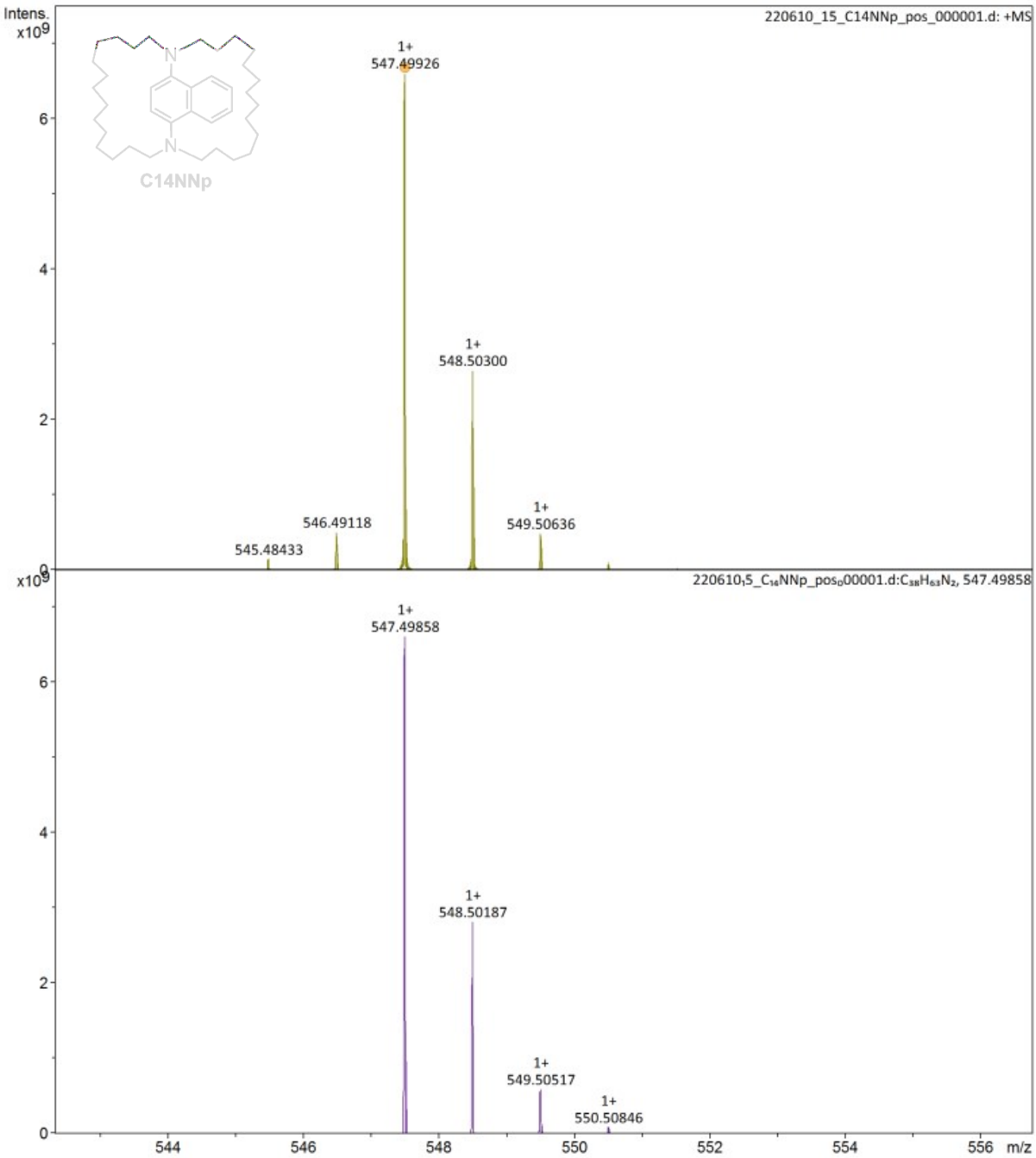
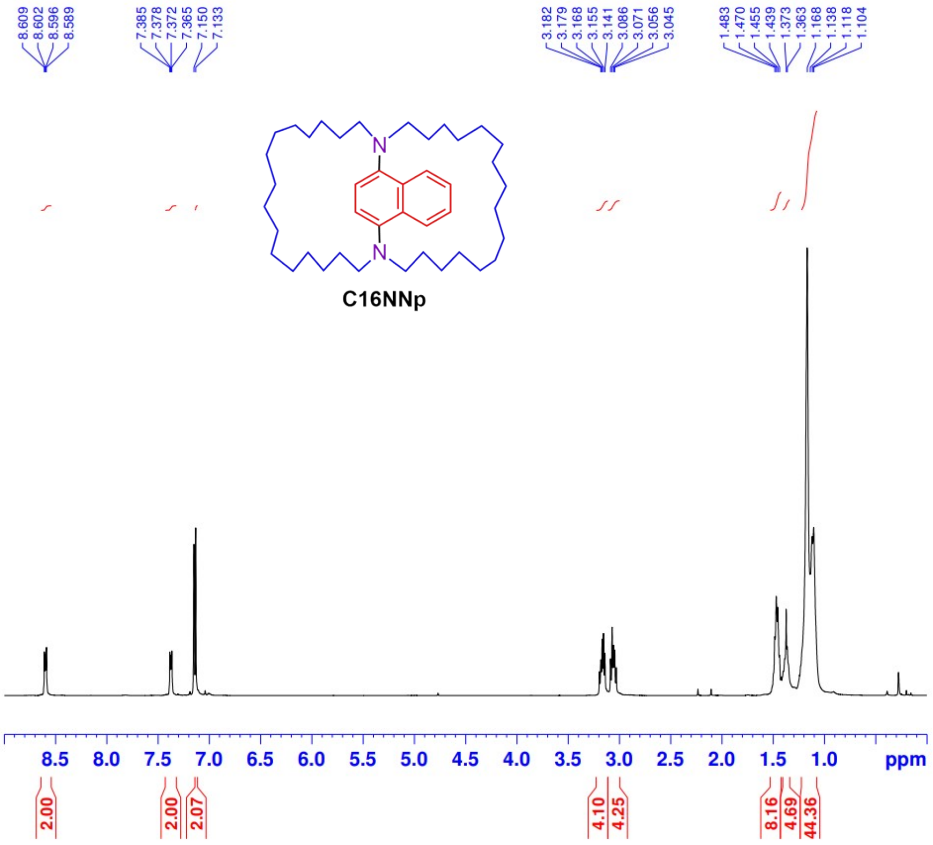


Fig. S6. HRMS spectrum of **C14Np** (APCI, positive). Top: obsd. Bottom: sim.

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FIDRES             0.157632 Hz
AQ                 3.1719425 sec
RG                       57
DW                   48.400 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                     0 dB
PL1W            20.01973534 W
SFO1           500.1327507 MHz

F2 - Processing parameters
SI                     32768
SF              500.1300022 MHz
WDW                       EM
SSB                        0
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GB                         0
PC                      1.00
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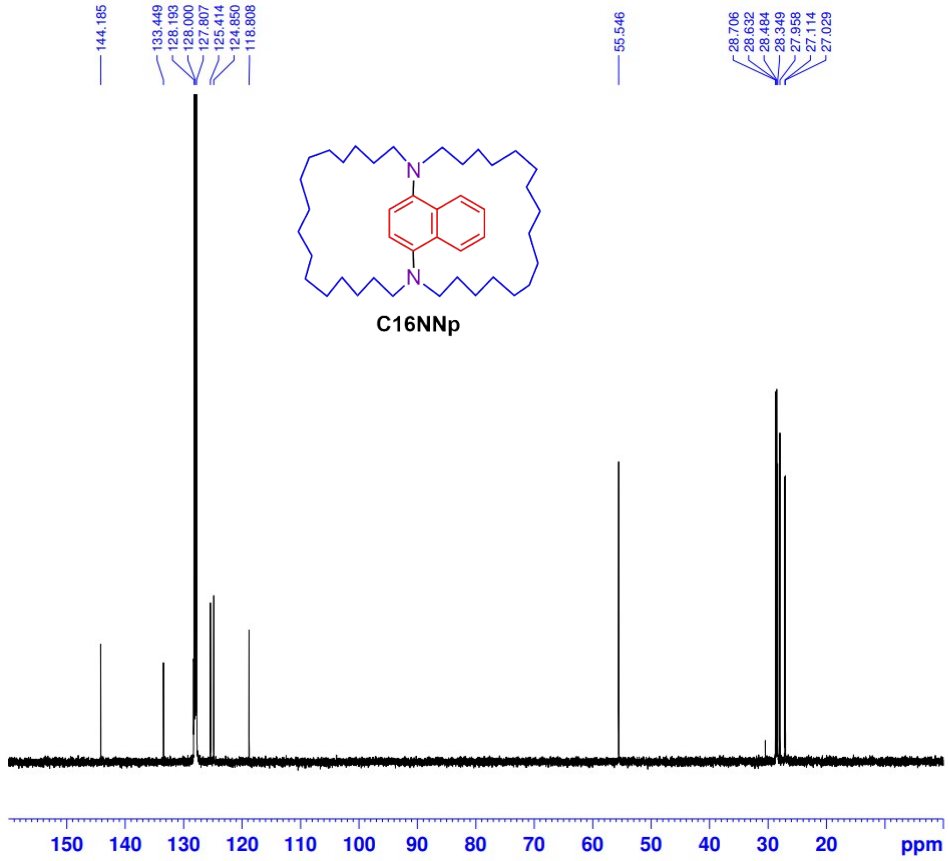
Fig. S7. ^{1}H NMR spectrum of **C16Np** in C_6D_6.

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PROCNO                     1

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SOLVENT                C6D6
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SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                      203
DW                   16.800 usec
DE                    6.50 usec
TE                   298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
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PL1                    -0.80 dB
PL1W            96.33646393 W
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
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NUC2                      1H
PCPD2                  80.00 usec
PL2                     0 dB
PL12                   16.50 dB
PL13                   16.50 dB
PL2W            20.01973534 W
PL12W            0.44818604 W
PL13W            0.44818604 W
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                     32768
SF              125.7577483 MHz
WDW                       EM
SSB                        0
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GB                         0
PC                      1.40
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Fig. S8. ^{13}C NMR spectrum of **C16Np** in C_6D_6.

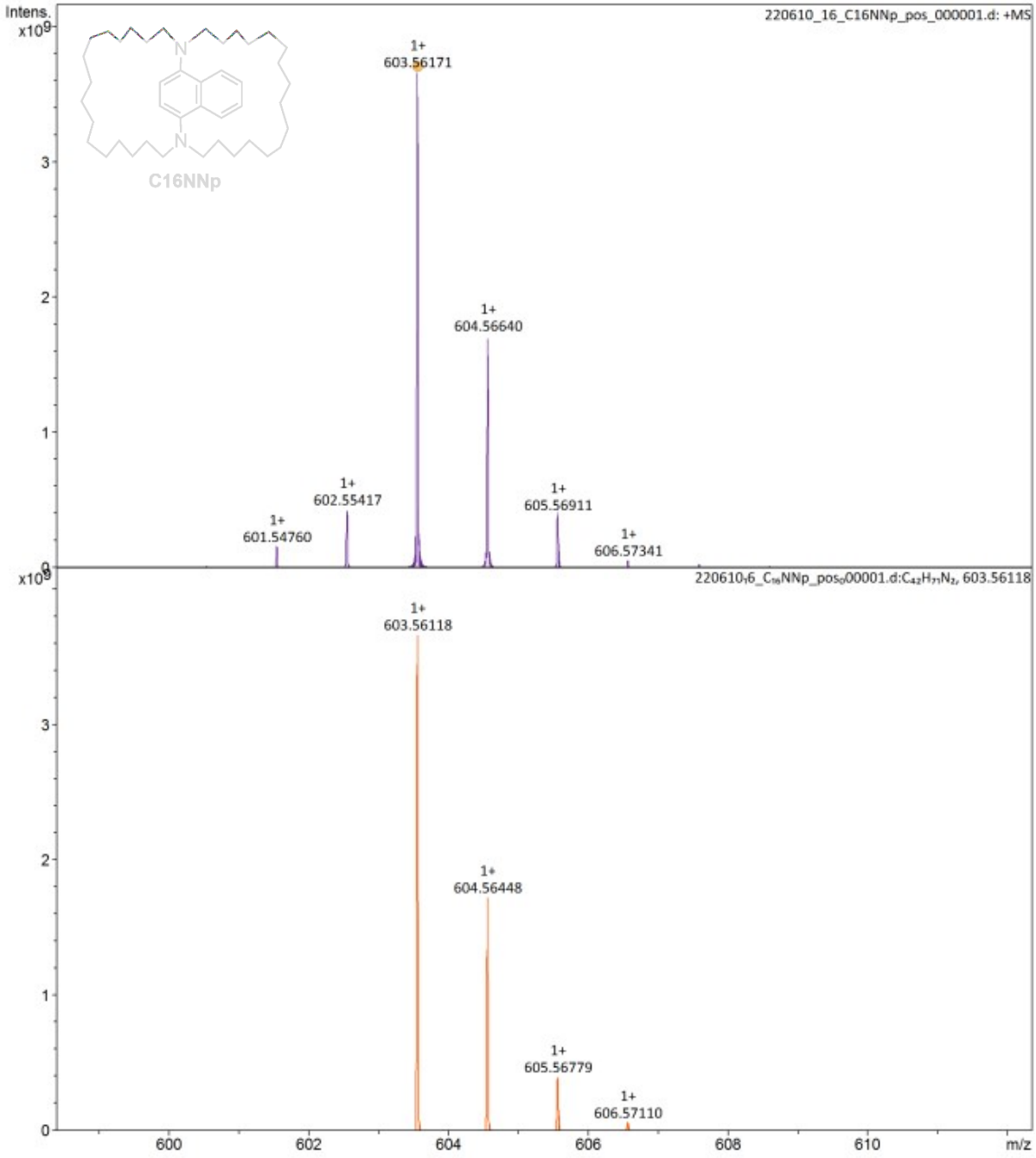
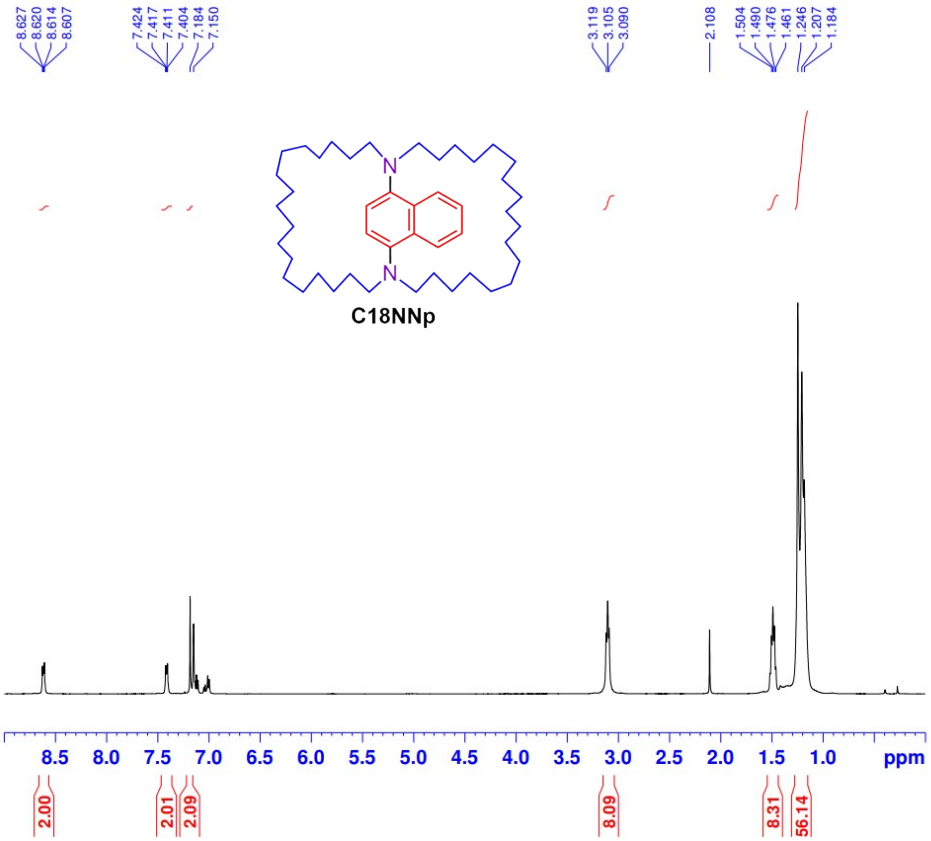


Fig. S9. HRMS spectrum of **C16Np** (APCI, positive). Top: obsd. Bottom: sim.

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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719425 sec
RG                      40.3
DW                    48.400 usec
DE                     6.50 usec
TE                    298.3 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                        0 dB
PL1W              20.01973534 W
SFO1             500.1327507 MHz

F2 - Processing parameters
SI                        32768
SF                500.1300433 MHz
WDW                        EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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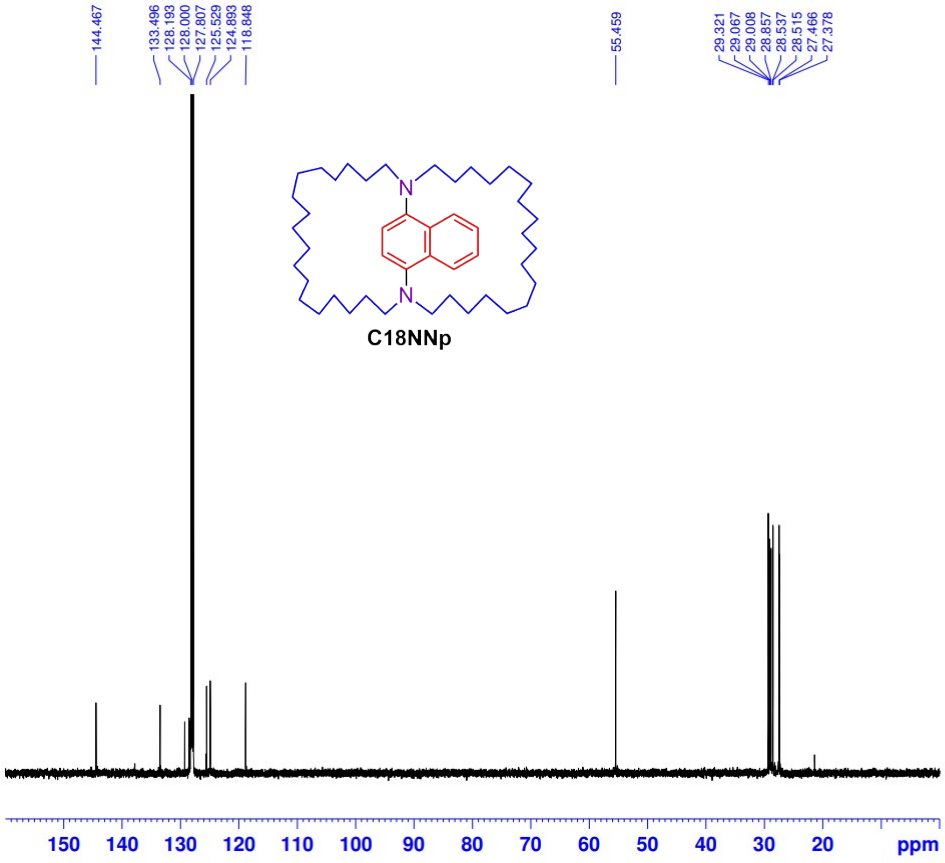
Fig. S10. ^{1}H NMR spectrum of **C18Np** in C_6D_6.

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Current Data Parameters
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EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       50
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010048 sec
RG                       203
DW                    16.800 usec
DE                     6.50 usec
TE                    298.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.00 usec
PL1                    -0.80 dB
PL1W              96.33646393 W
SFO1             125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                        0 dB
PL12                   16.50 dB
PL13                   16.50 dB
PL2W              20.01973534 W
PL12W              0.44818604 W
PL13W              0.44818604 W
SFO2             500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                125.7577582 MHz
WDW                        EM
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LB                      0.50 Hz
GB                         0
PC                      1.40
```

Fig. S11. ^{13}C NMR spectrum of **C18Np** in C_6D_6.

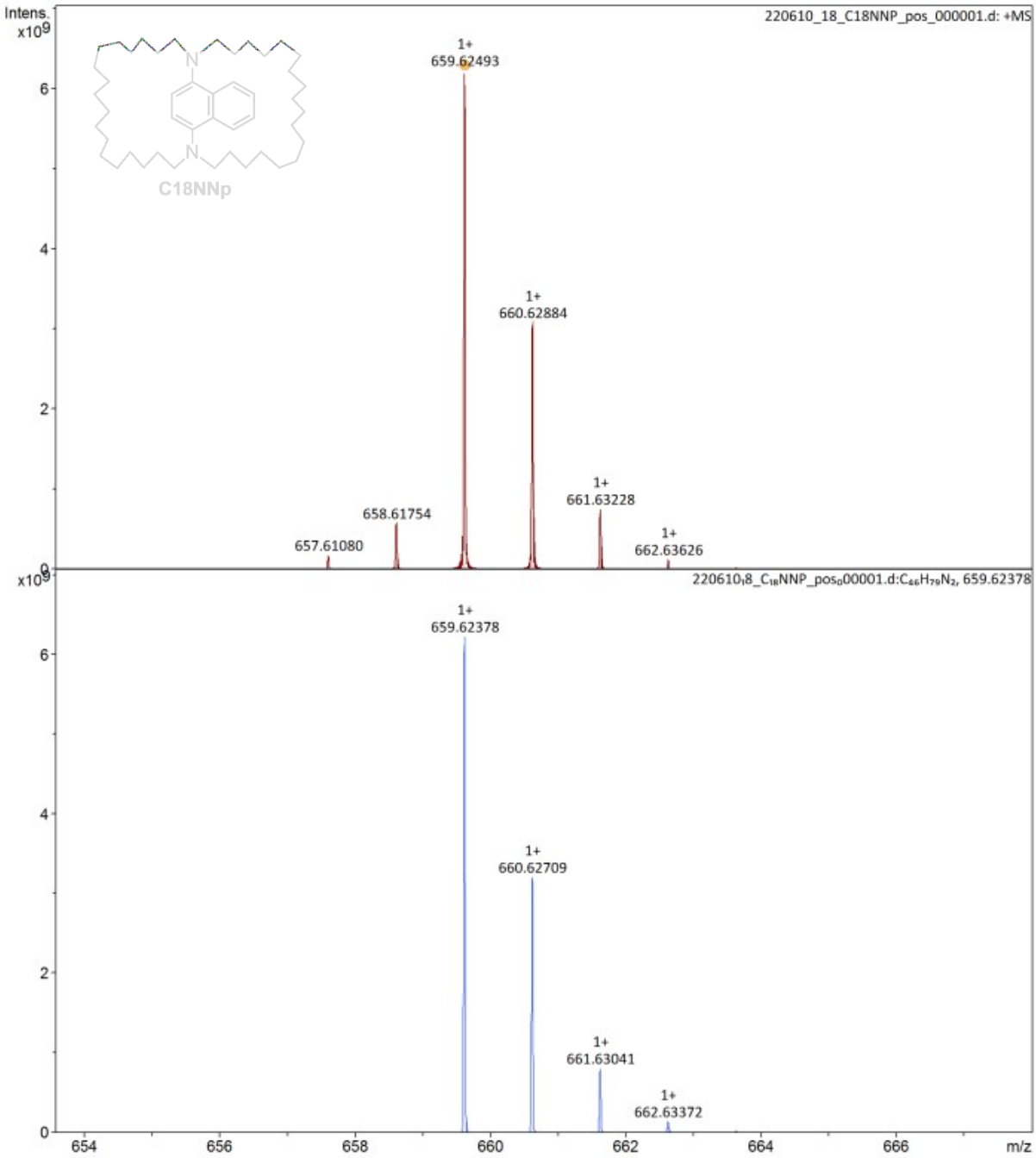

Fig. S12. HRMS spectrum of **C18Np** (APCI, positive). Top: obsd. Bottom: sim.

2. Details of NMR Study

a. NOESY NMR Study

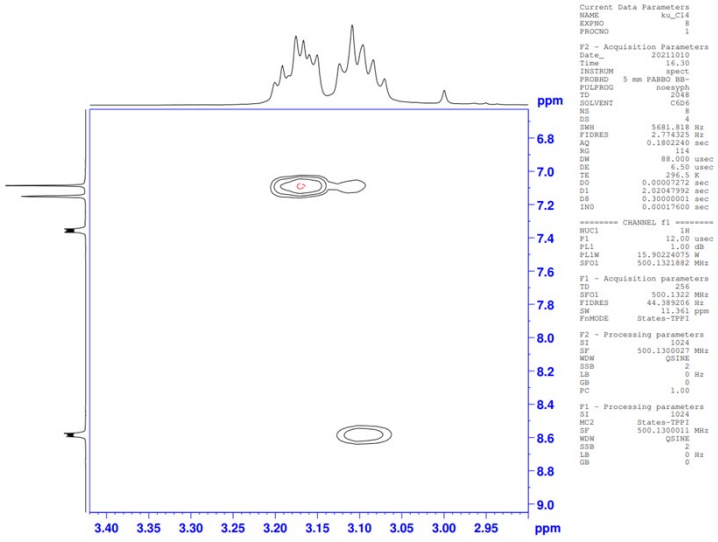

Fig. S13. ^{1}H -^{1}H NOESY spectrum of **C14Np** in C_6D_6.

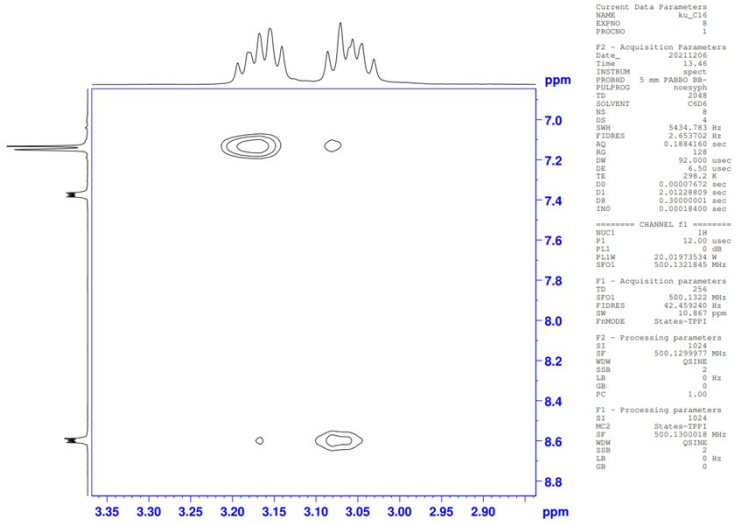

Fig. S14. ^{1}H -^{1}H NOESY spectrum of **C16Np** in C_6D_6.

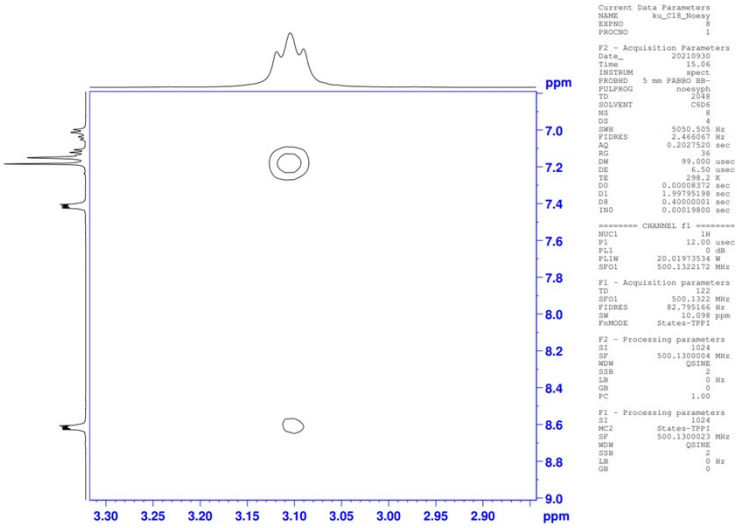

Fig. S15. ^{1}H -^{1}H NOESY spectrum of **C18Np** in C_6D_6.

b. Temperature Dependent NMR of C16Np

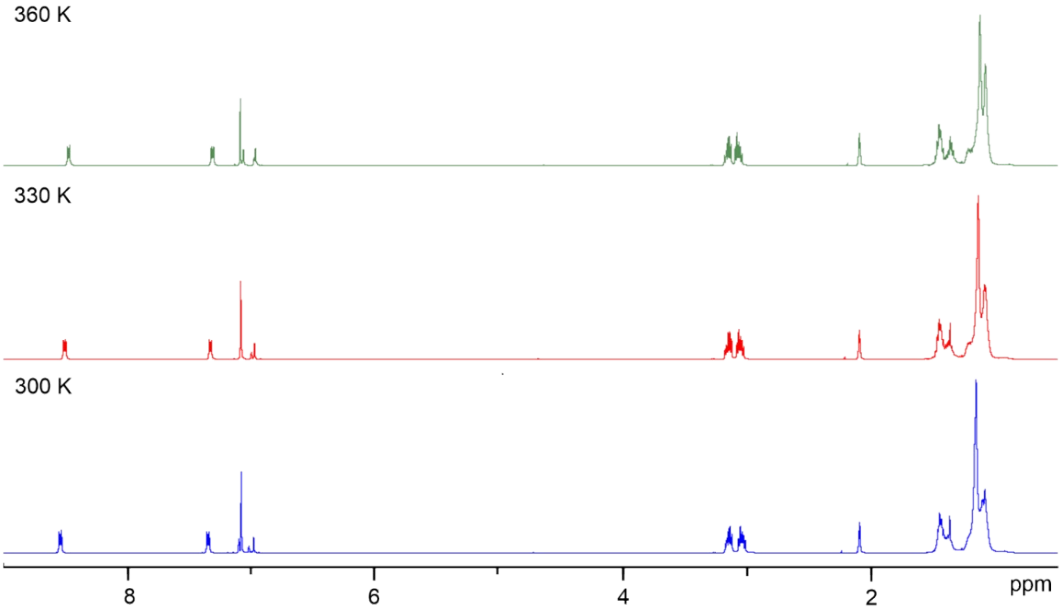

Fig. S16. Temperature dependent ^{1}H NMR spectra of **C16Np** in toluene-d_8.

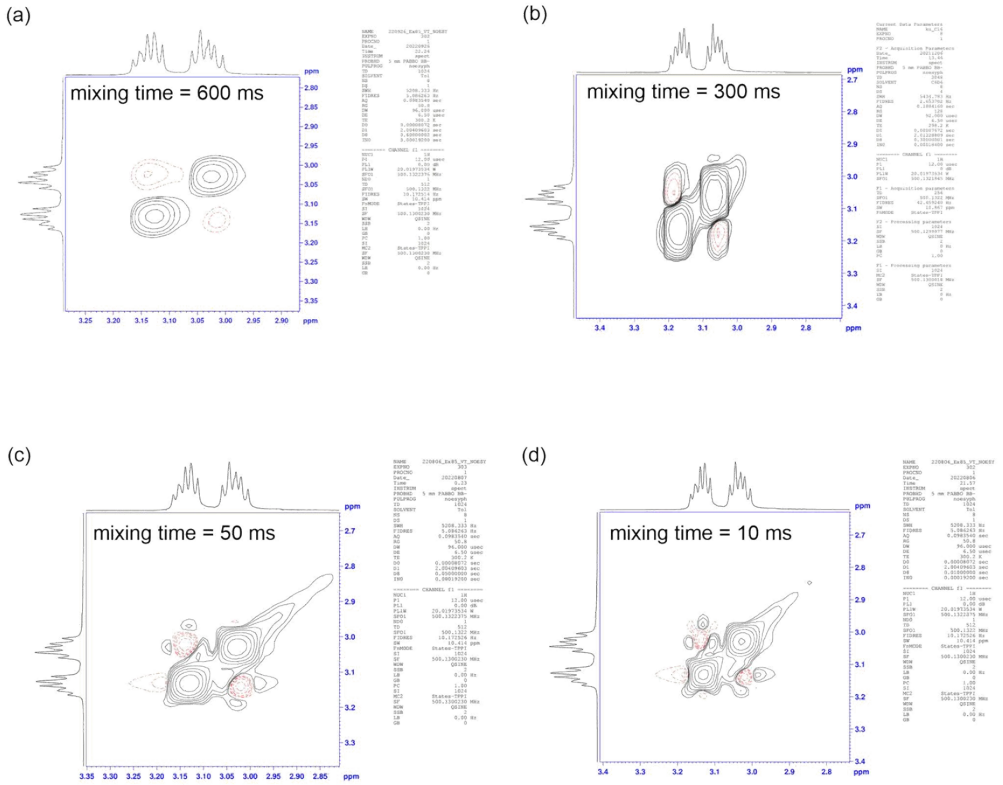

Fig. S17. ^{1}H -^{1}H EXSY(NOESY) spectra of **C16Np** at 300 K in toluene-d_8: (a) mixing time = 600 ms, (b) mixing time = 300 ms, (c) mixing time = 100 ms, (d) mixing time = 50 ms.

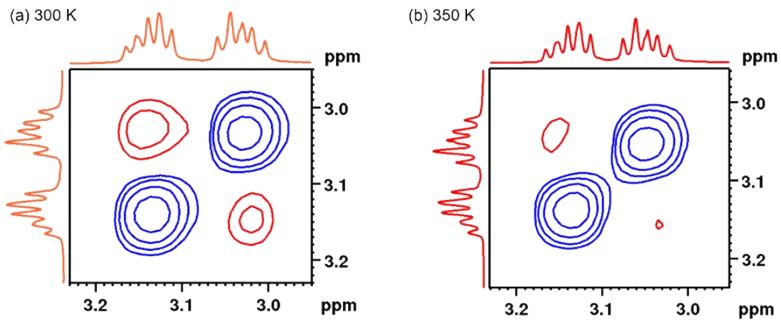

Fig. S18. ^{1}H -^{1}H EXSY(NOESY) spectra of **C16Np** in toluene-d_8 (mixing time = 300 ms): (a) 300 K, (b) 350 K.

c. Temperature Dependent NMR of C18Np

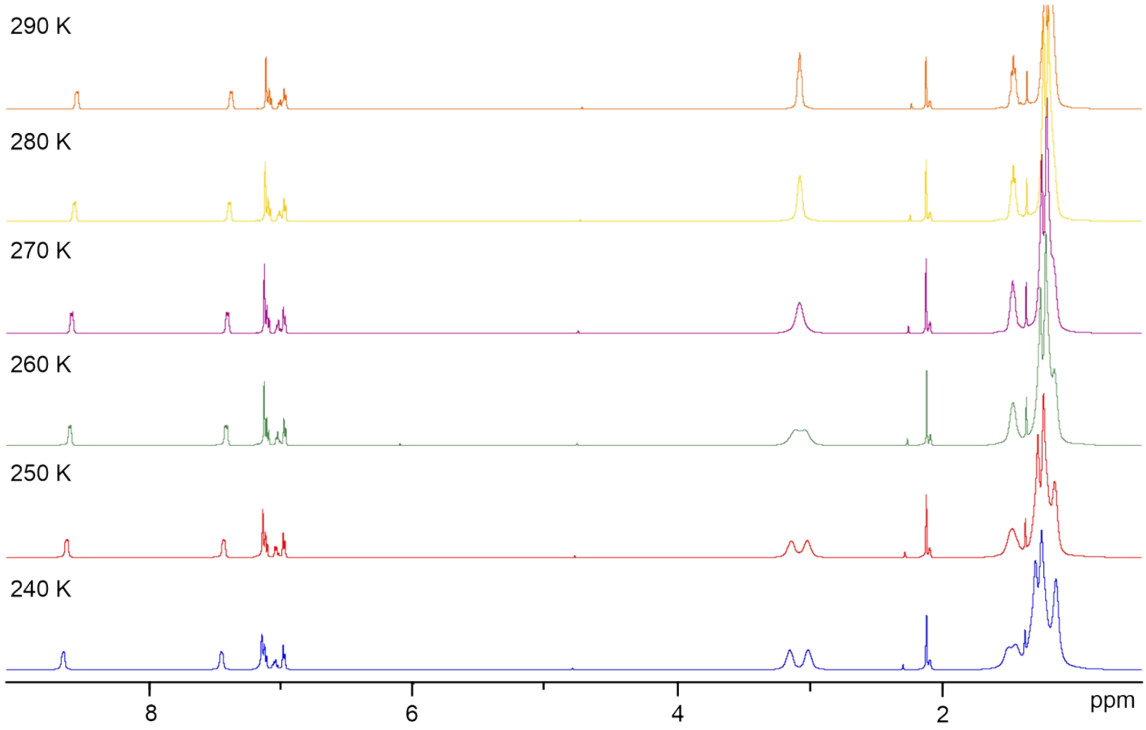

Fig. S19. Temperature dependent ^{1}H NMR spectra of **C18Np** in toluene-d_8.

d. Analysis of Thermodynamic Parameters for Naphtylene Rotation in C18Np

An activation energy for the ring flipping/rotation could be estimated the slope of an Eyring plot for temperature dependent exchange rates. From the plots, the following parameters were determined (errors are shown as standard deviations):

$$\Delta H^{\ddagger} = 13.0 \pm 0.13 \text{ kcal mol}^{-1}, \Delta S^{\ddagger} = 1.48 \pm 0.46 \text{ cal mol}^{-1} \text{ K}^{-1}$$

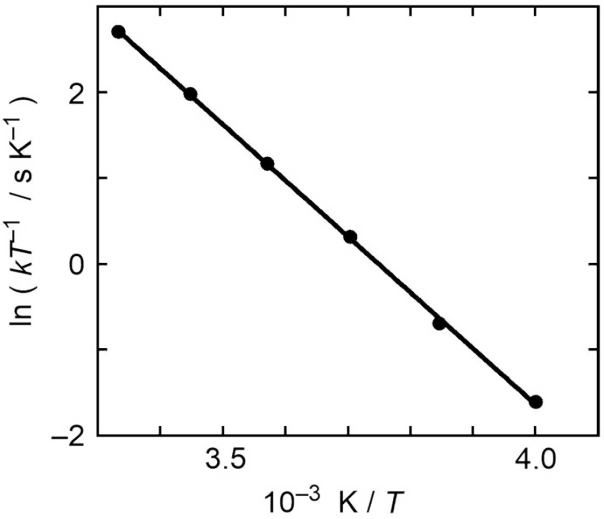

Fig. S20. Eyring plot for temperature dependent exchange rates for the rotation of the rotor in compound **C18Np**.

3. Details of X-ray Crystallography

Single-crystal X-ray crystallographic analyses were performed using a Bruker Venture diffractometer.

Table S1. Crystal Data

Compound		**C12Np**	**C14Np**
CCDC #		**2202293**	**2202294**
Temperature		100 K	123 K
Empirical formula		C34 H54 N2	C38 H62 N2
Crystal shape		prism	prism
Crystal color		colorless	colorless
Crystal size		0.420 x 0.400 x 0.280 mm^3	0.320 x 0.200 x 0.100 mm^3
Formula weight / g mol^{-1}		490.79	546.89
Crystal system		Monoclinic	Monoclinic
Space group		$P\,2_1/n$	$P\,2_1/c$
Z		4	4
Calculated density		1.080 Mg/m^3	1.063 Mg/m^3
Cell parameter	*a*	10.7668(3) Å	11.7462(14) Å
	b	18.0397(5) Å	9.5109(12) Å
	c	15.5823(5) Å	30.593(4) Å
	α	90°	90°
	β	93.8990(10)°	90.057(6)°
	γ	90°	90°
	V	3019.54(15) $Å^3$	3417.8(7) $Å^3$
F(000)		1088	1216
Absorption coefficient		0.455 mm^{-1}	0.455 mm^{-1}
***θ* range for collection (deg)**		3.753 to 75.508° (Cu)	2.889 to 75.190° (Cu)
Index ranges		-13<=h<=13, -21<=k<=22, -19<=l<=18	-14<=h<=14, -10<=k<=11, -38<=l<=38
Reflections collected		24260	35956
Independent reflections		6066 [R(int) = 0.0229]	6841 [R(int) = 0.0648]
Completeness		97.8 %	98.1 %
Goodness-of-fit on F^2		1.030	1.144
Final R indices [I>2sigma(I)]		R1 = 0.0404, wR2 = 0.1057	R1 = 0.0994, wR2 = 0.2720
R indices (all data)		R1 = 0.0413, wR2 = 0.1062	R1 = 0.1059, wR2 = 0.2750
Largest diff. peak and hole		0.282 and -0.192 $e.Å^{-3}$	0.448 and -0.412 $e.Å^{-3}$

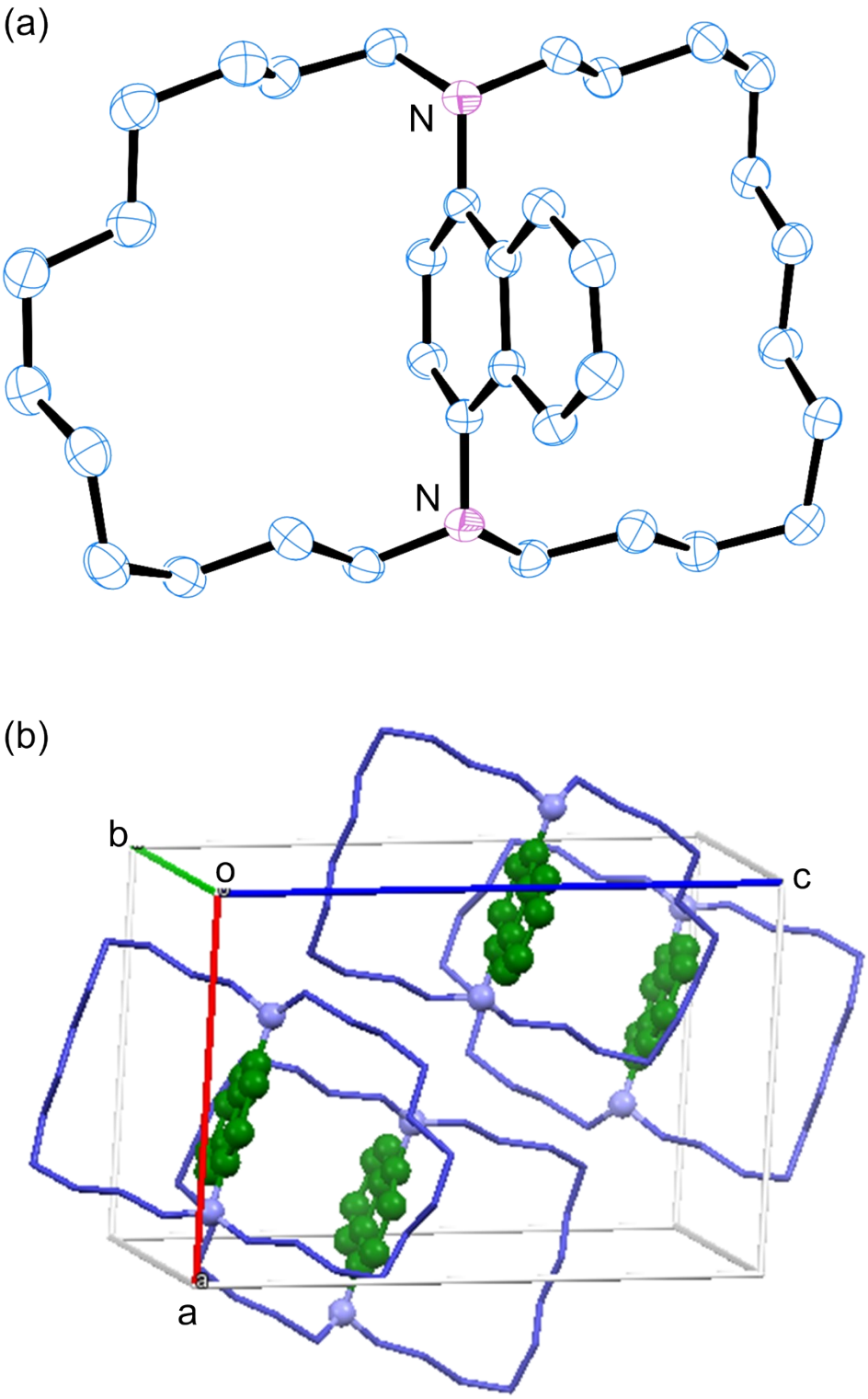

Fig. S21. (a) An ORTEP drawing (50% thermal ellipsoids) of molecular structure and (b) crystal packing structure of **C12Np** determined by X-ray crystallography.

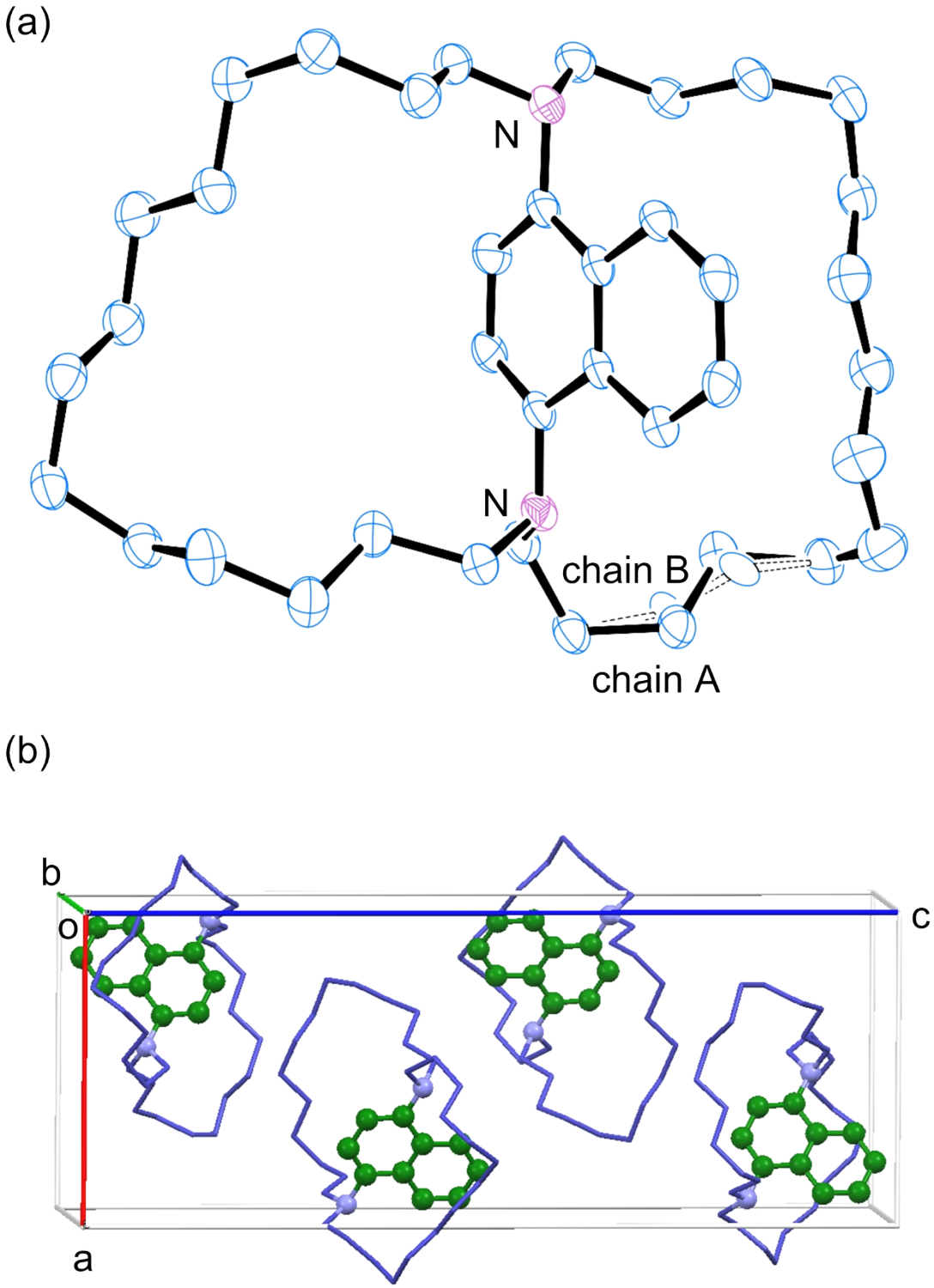

Fig. S22. (a) An ORTEP drawing (50% thermal ellipsoids) of molecular structure (the population ratio of the disordered atoms: chain A: chain B = 0.843 (10) : 0.157(10)) and (b) crystal packing structure of **C14Np** determined by X-ray crystallography.