Supplementary Information

A Pyrene-bridged Macrocage Showing No Excimer Fluorescence

Hirokuni Shionari,[a] Yusuke Inagaki,[a] Kentaro Yamaguchi,[b] and Wataru Setaka[*,a]*

[a] *Division of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan*

[b] *Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan*

1. Copies of Spectra for All New Compounds

a. Spectra of 2,7-bis(tri-9-decenylsilyl)pyrene (2)

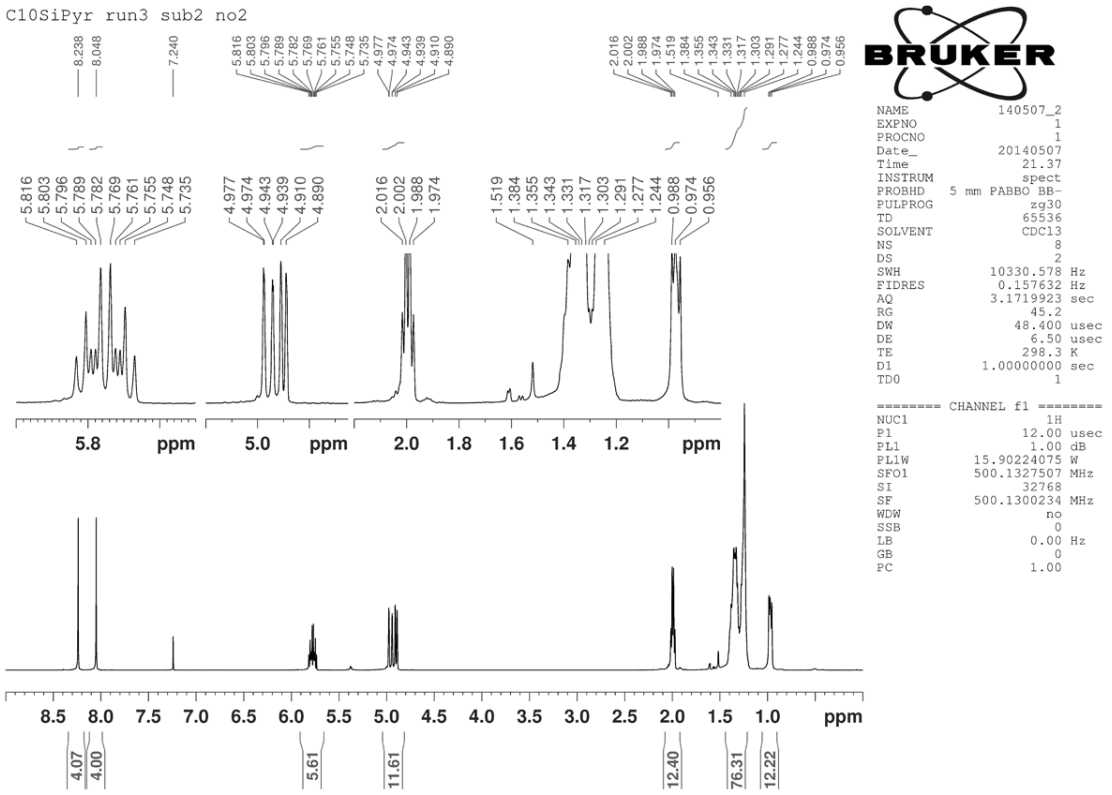

Fig. S1. ^{1}H NMR spectrum of 2,7-bis(tri-9-decenylsilyl)pyrene (**2**) in $CDCl_3$.

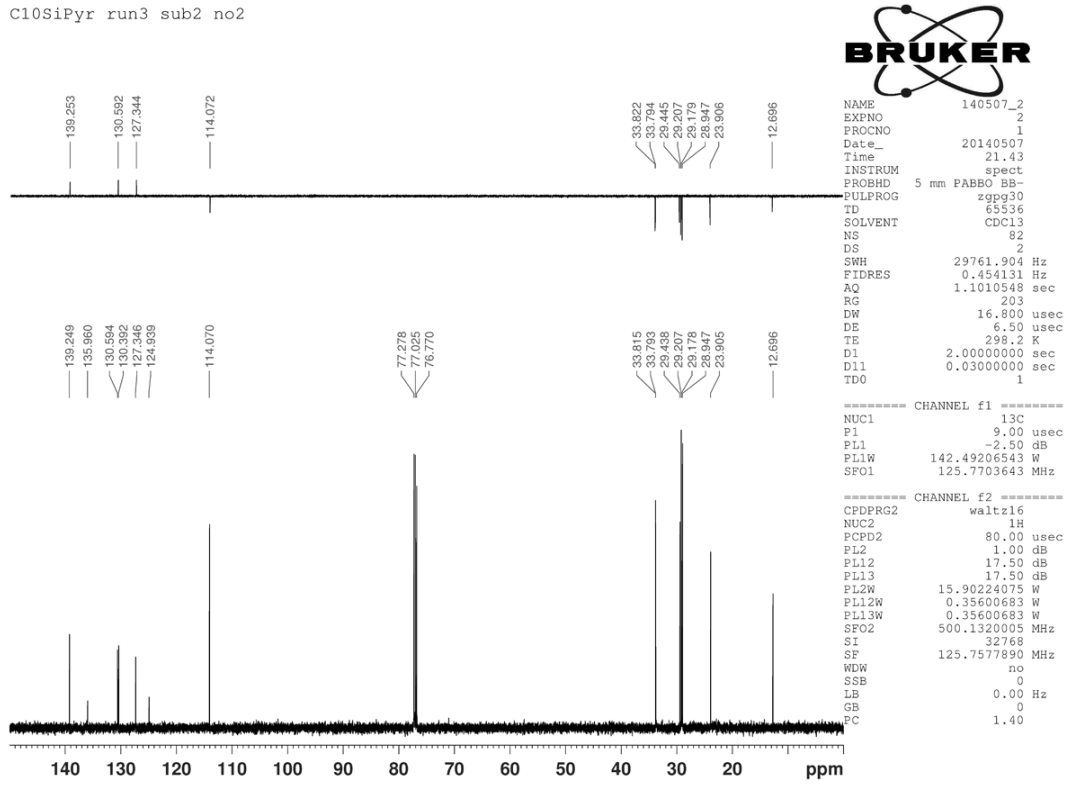

Fig. S2. ^{13}C NMR spectrum of 2,7-bis(tri-9-decenylsilyl)pyrene (**2**) in $CDCl_3$.

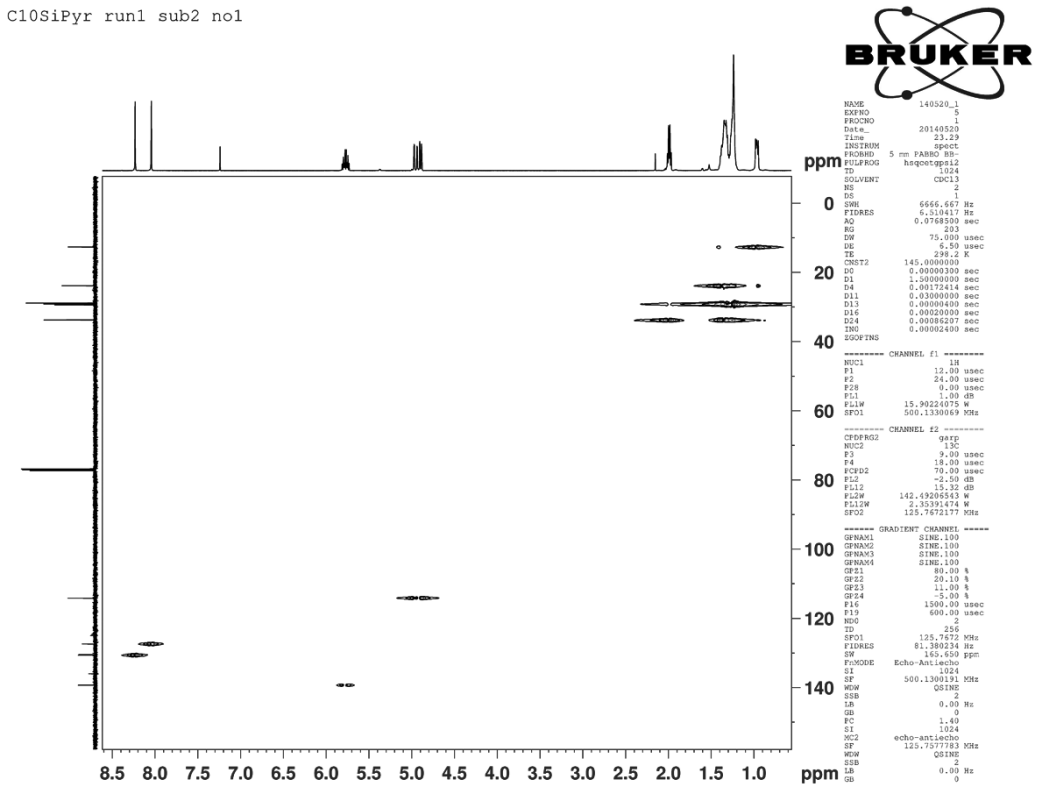

Fig. S3. ^{1}H-^{13}C hsqc NMR spectrum of 2,7-bis(tri-9-decenylsilyl)pyrene (**2**) in $CDCl_3$.

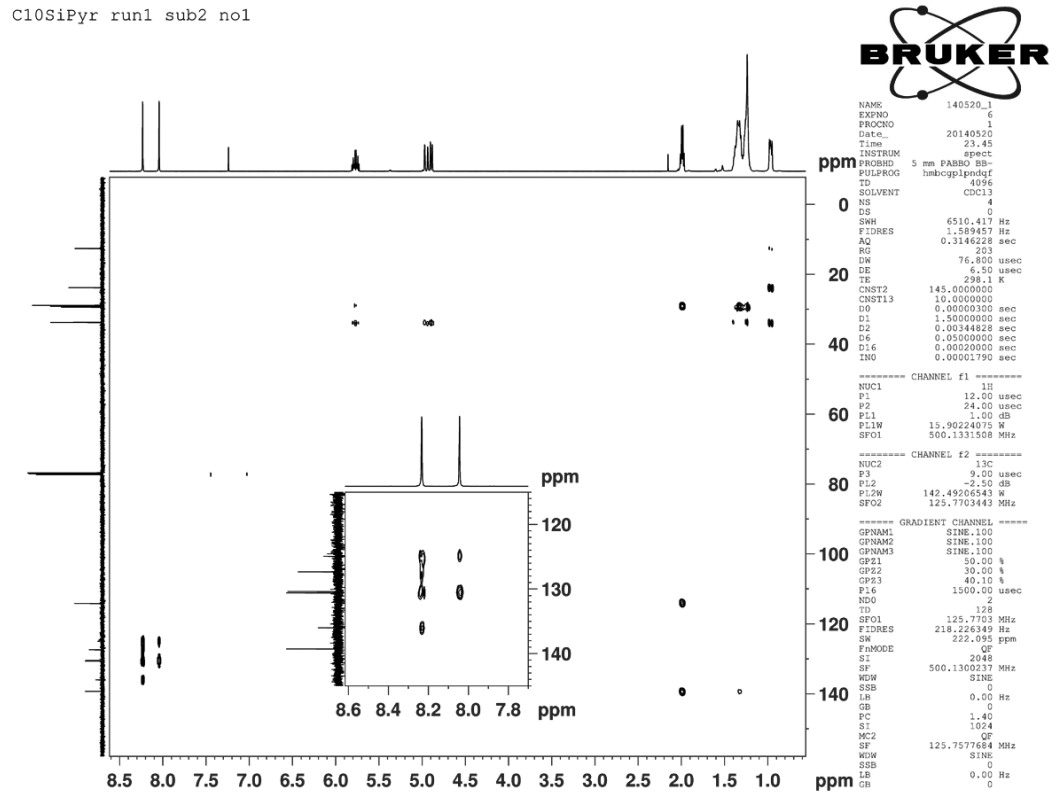

Fig. S4. ^{1}H-^{13}C hmbc NMR spectrum of 2,7-bis(tri-9-decenylsilyl)pyrene (**2**) in $CDCl_3$.

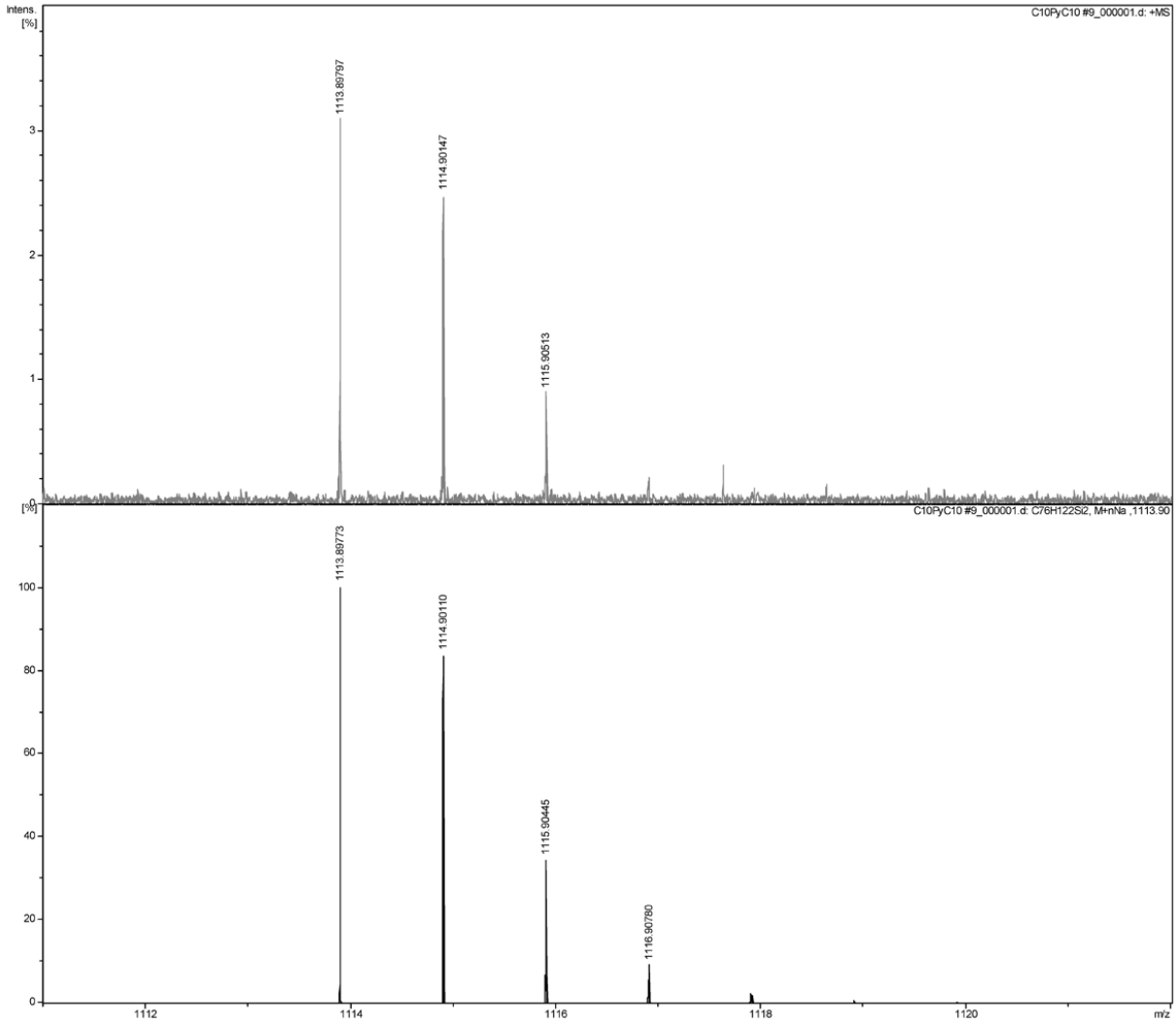

Fig. S5. HRMS(ESI, positive) spectrum of 2,7-bis(tri-9-decenylsilyl)pyrene (**2**): top; obsd., bottom; calcd.

b. Spectra of Molecular Gyrotop (1)

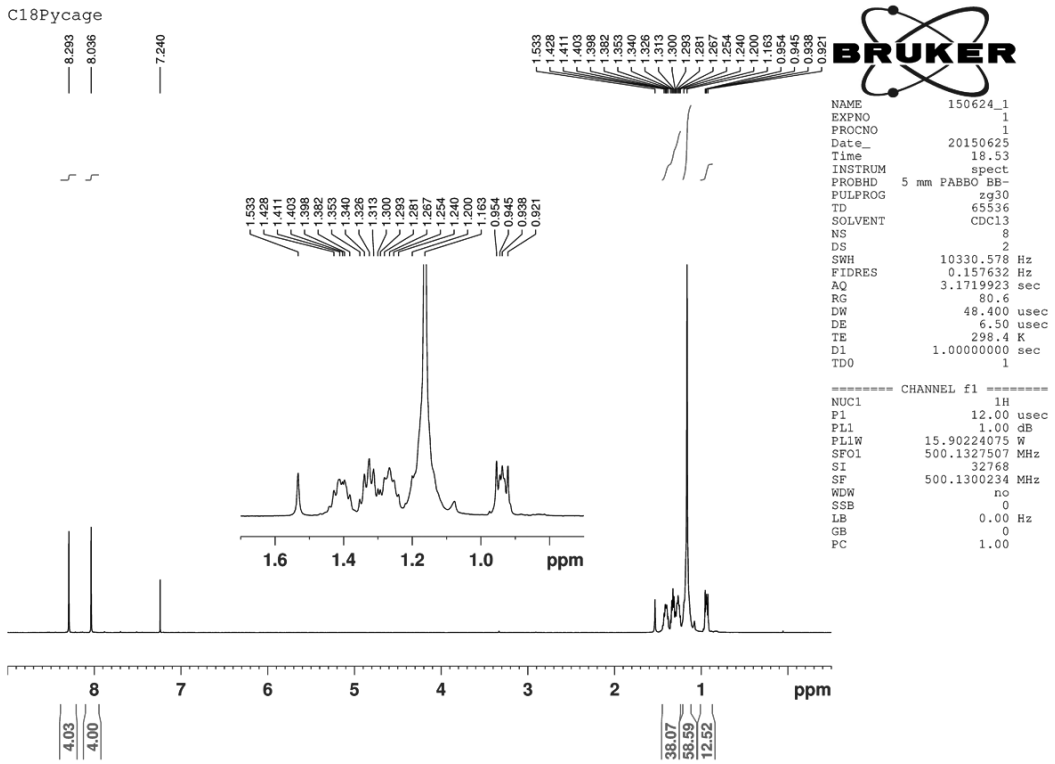

Fig. S6. ^{1}H NMR spectrum of Molecular Gyrotop (**1**) in $CDCl_3$.

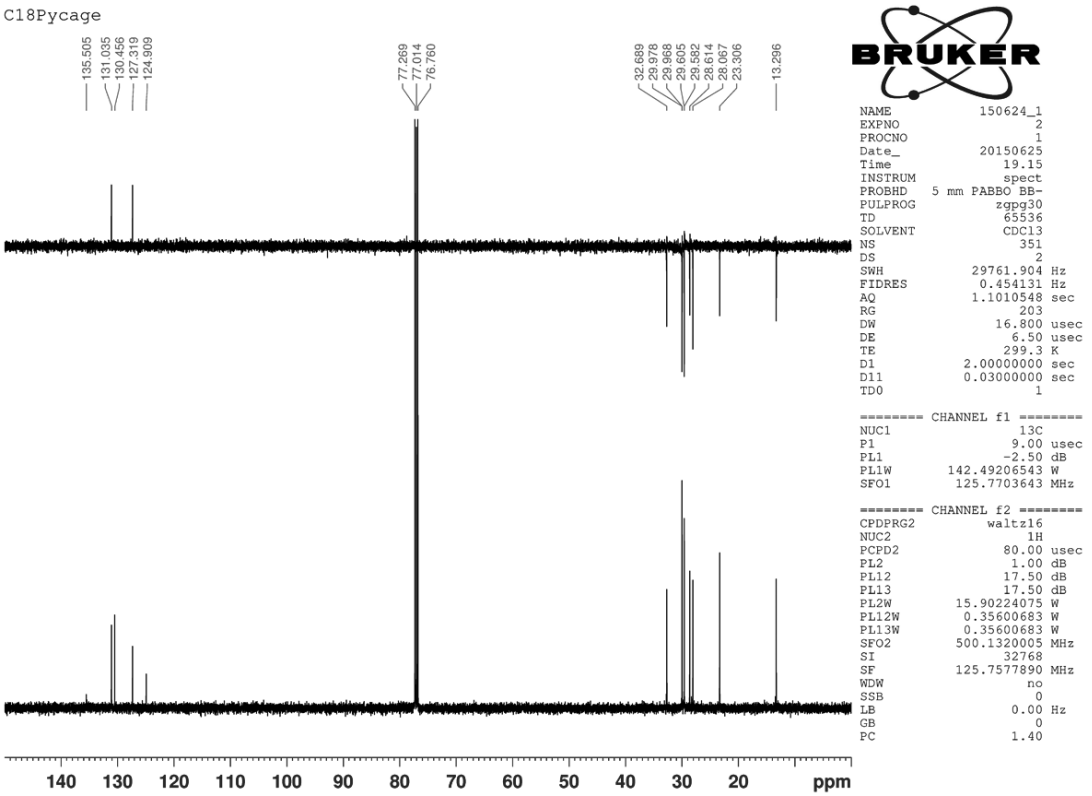

Fig. S7. ^{13}C NMR spectrum of Molecular Gyrotop (**1**) in $CDCl_3$.

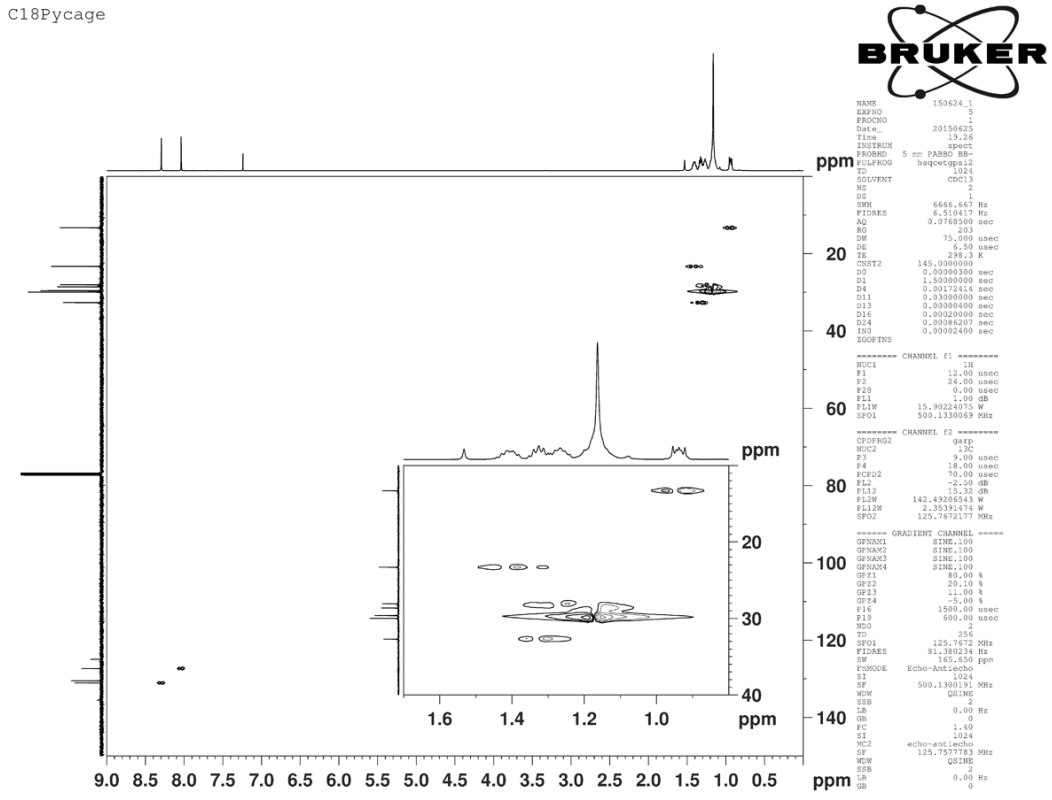

Fig. S8. ^{1}H-^{13}C hsqc NMR spectrum of Molecular Gyrotop (**1**) in $CDCl_3$.

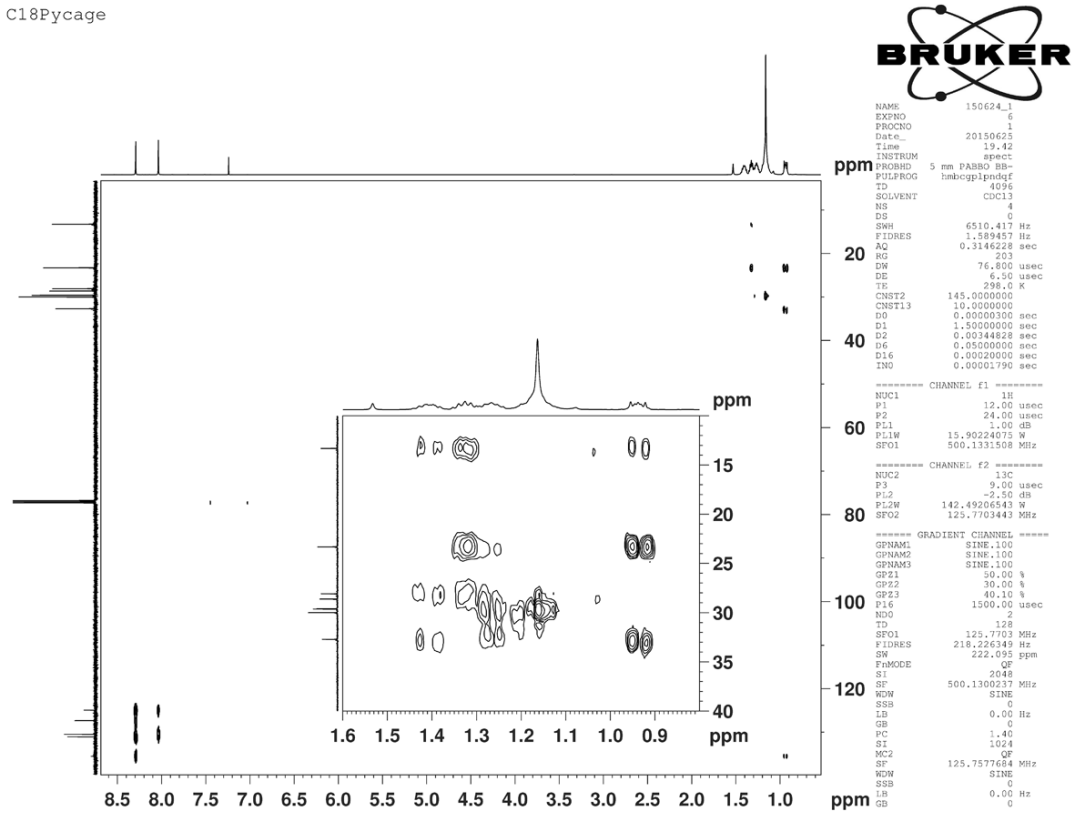

Fig. S9. ^{1}H-^{13}C hmbc NMR spectrum of Molecular Gyrotop (**1**) in $CDCl_3$.

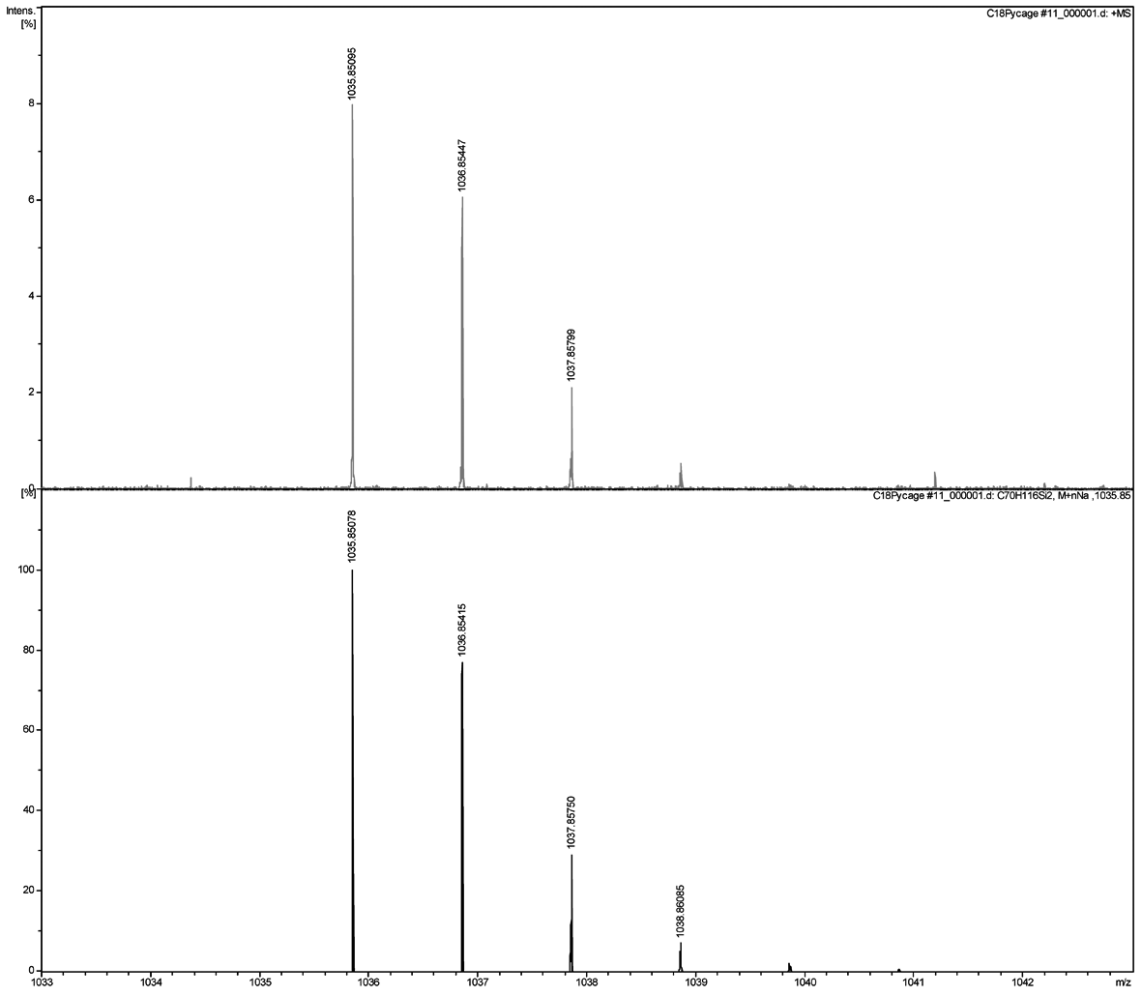

Fig. S10. HRMS(ESI, positive) spectrum of Molecular Gyrotop (**1**): top; obsd., bottom; calcd.

c. Spectra of Molecular Gyrotop Isomer (1i)

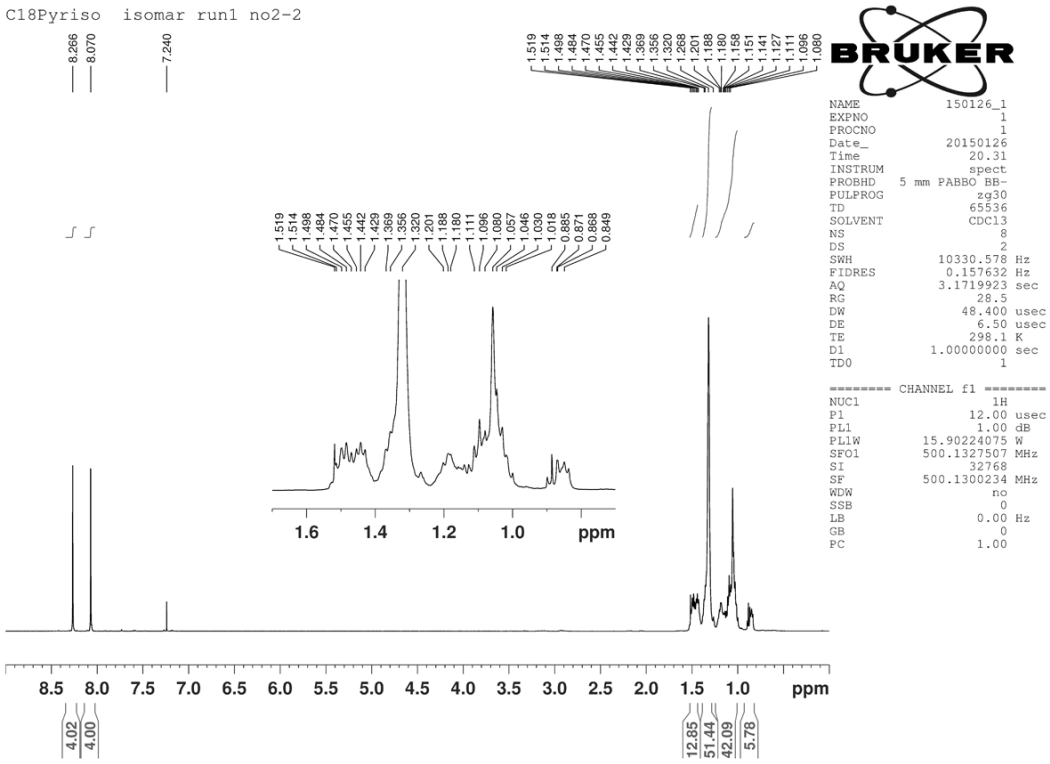

Fig. S11. ^{1}H NMR spectrum of Molecular Gyrotop Isomer (**1i**) in $CDCl_3$.

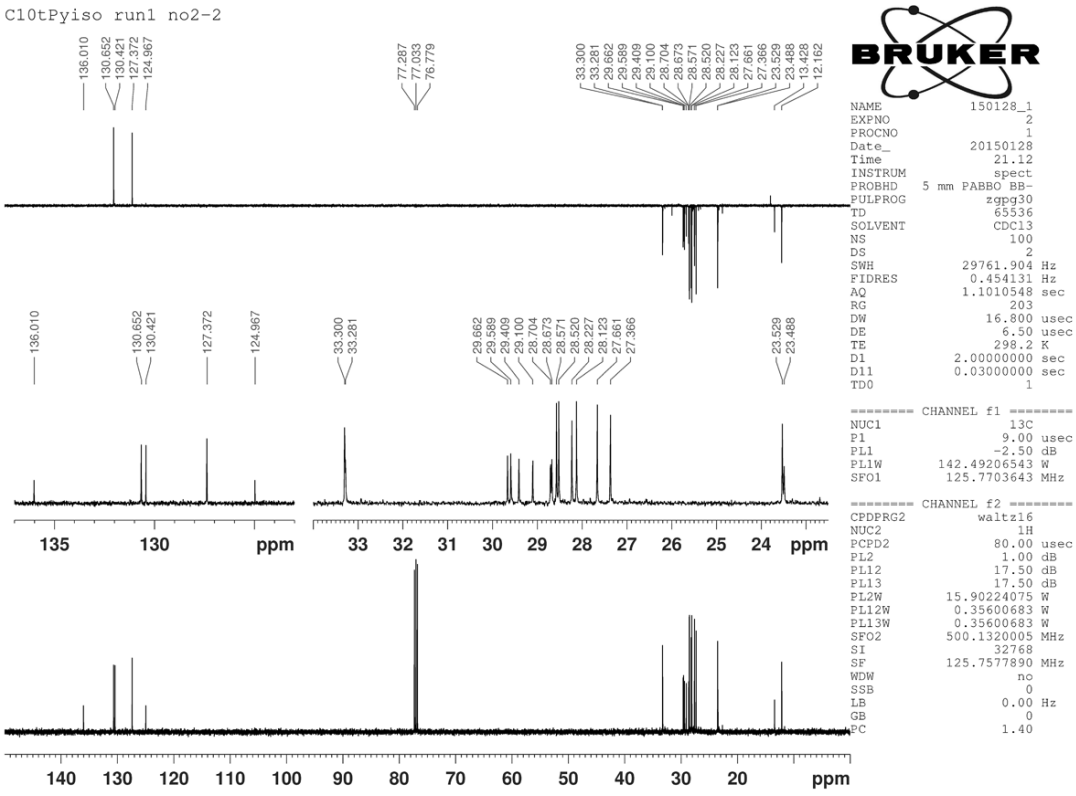

Fig. S12. ^{13}C NMR spectrum of Molecular Gyrotop Isomer (**1i**) in $CDCl_3$.

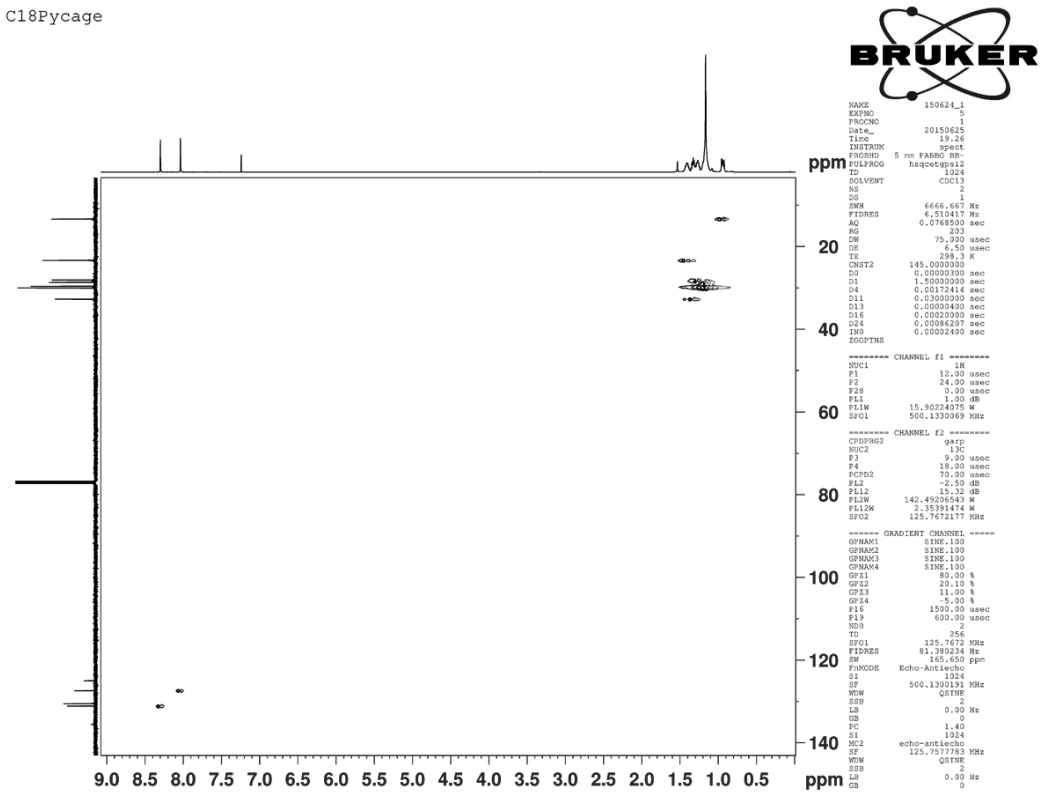

Fig. S13. ^{1}H-^{13}C hsqc NMR spectrum of Molecular Gyrotop Isomer (**1i**) in $CDCl_3$.

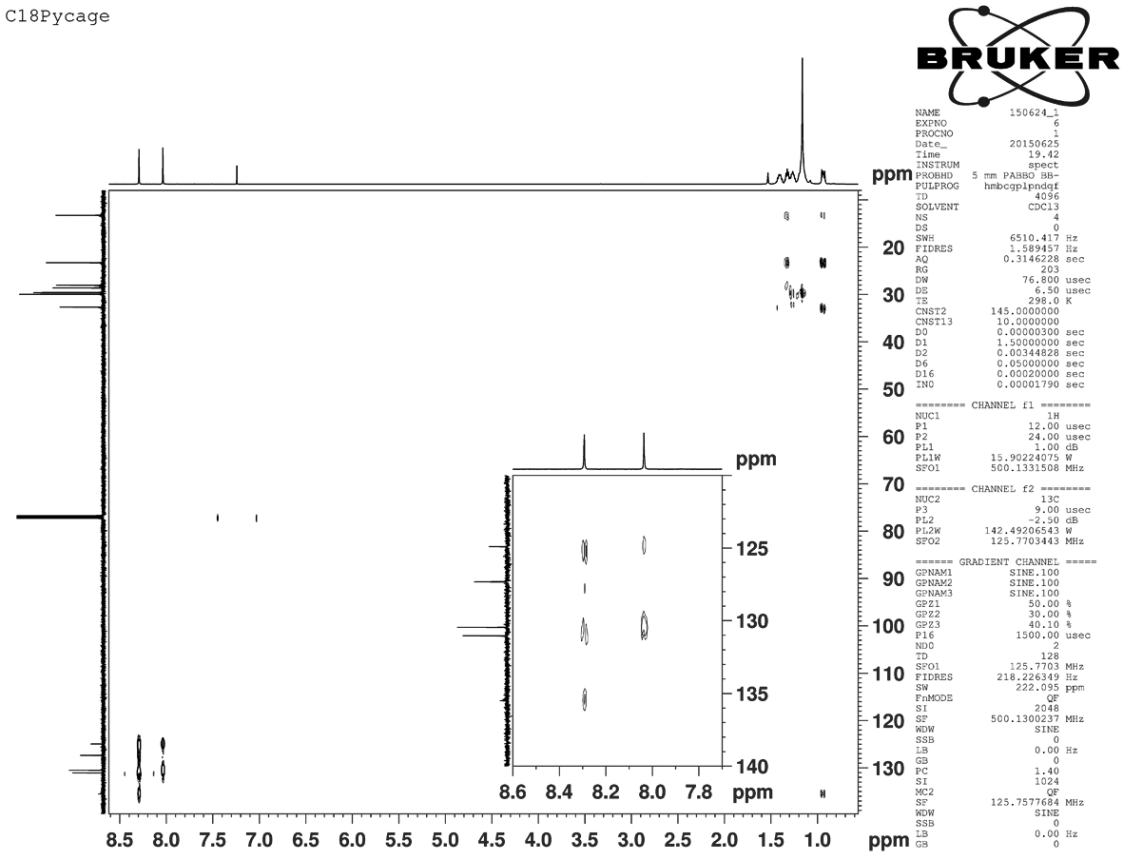

Fig. S14. ^{1}H-^{13}C hmbc NMR spectrum of Molecular Gyrotop Isomer (**1i**) in $CDCl_3$.

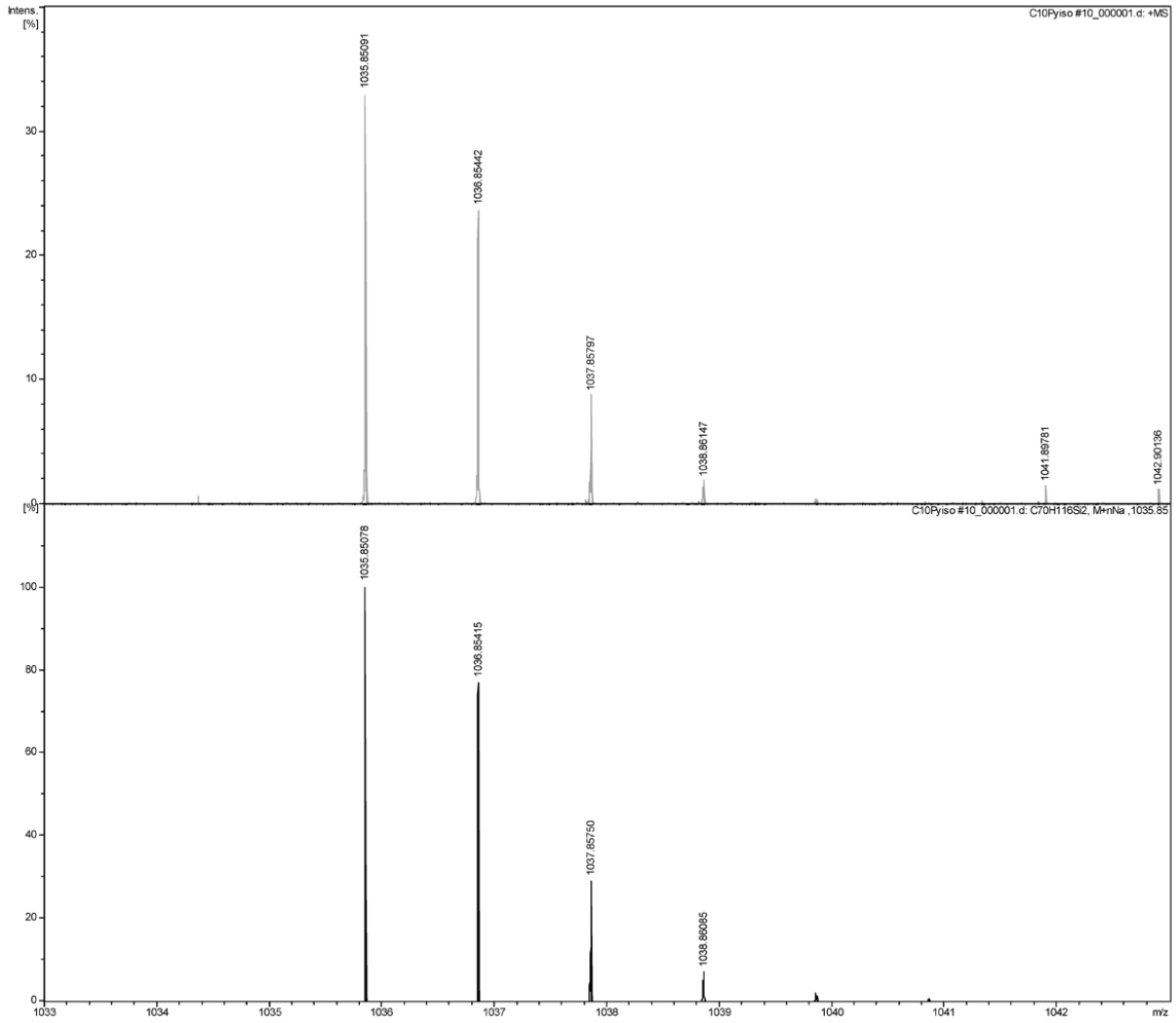

Fig. S15. HRMS(ESI, positive) spectrum of Molecular Gyrotop Isomer (**1i**): top; obsd., bottom; calcd.

d. Spectra of 2,7-bis(menylsilyl)pyrene (**3**)

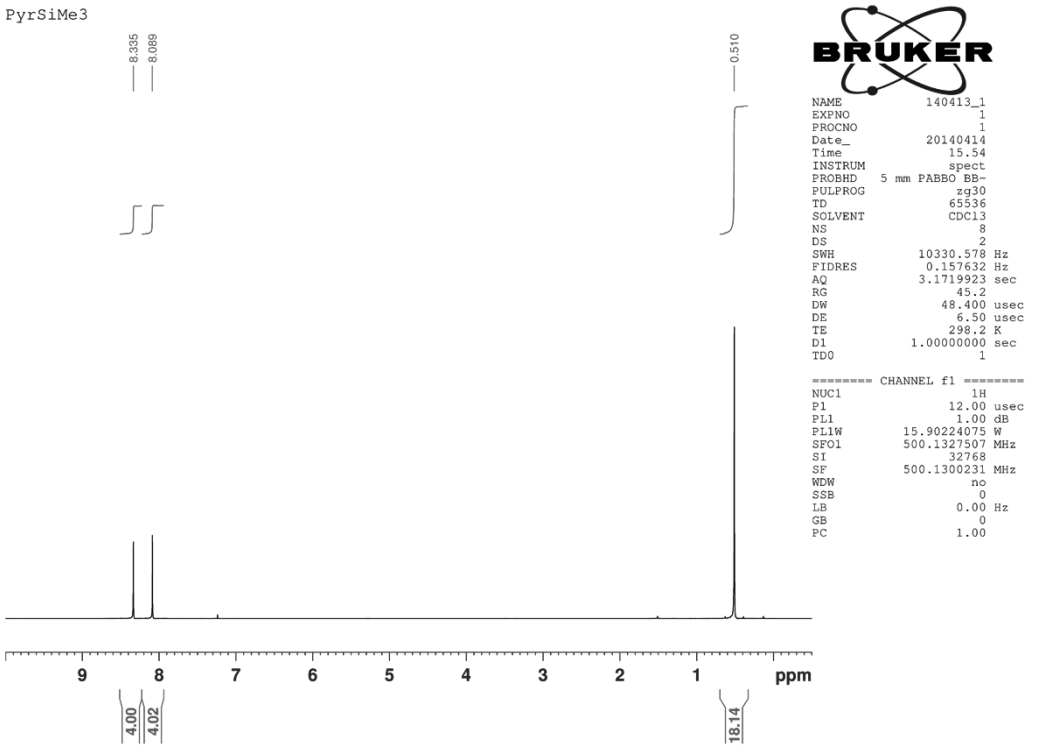

Fig. S16. ^{1}H NMR spectrum of 2,7-bis(menylsilyl)pyrene (**3**) in $CDCl_3$.

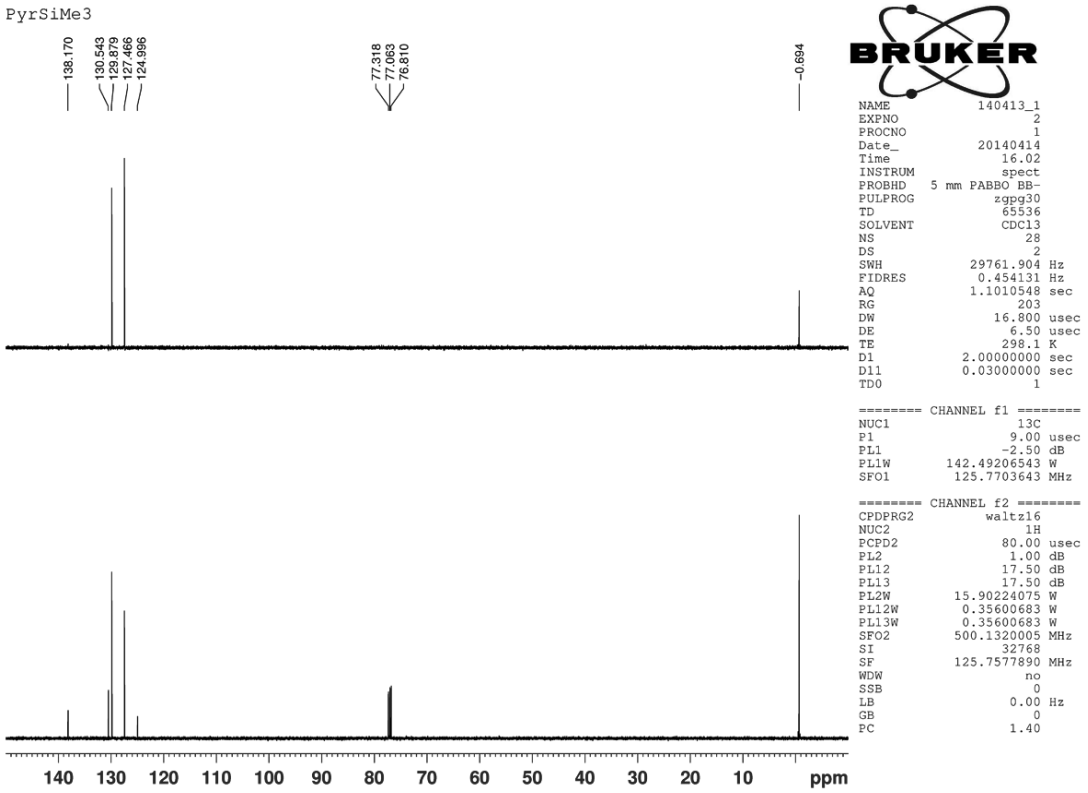

Fig. S17. ^{13}C NMR spectrum of 2,7-bis(menylsilyl)pyrene (**3**) in $CDCl_3$.

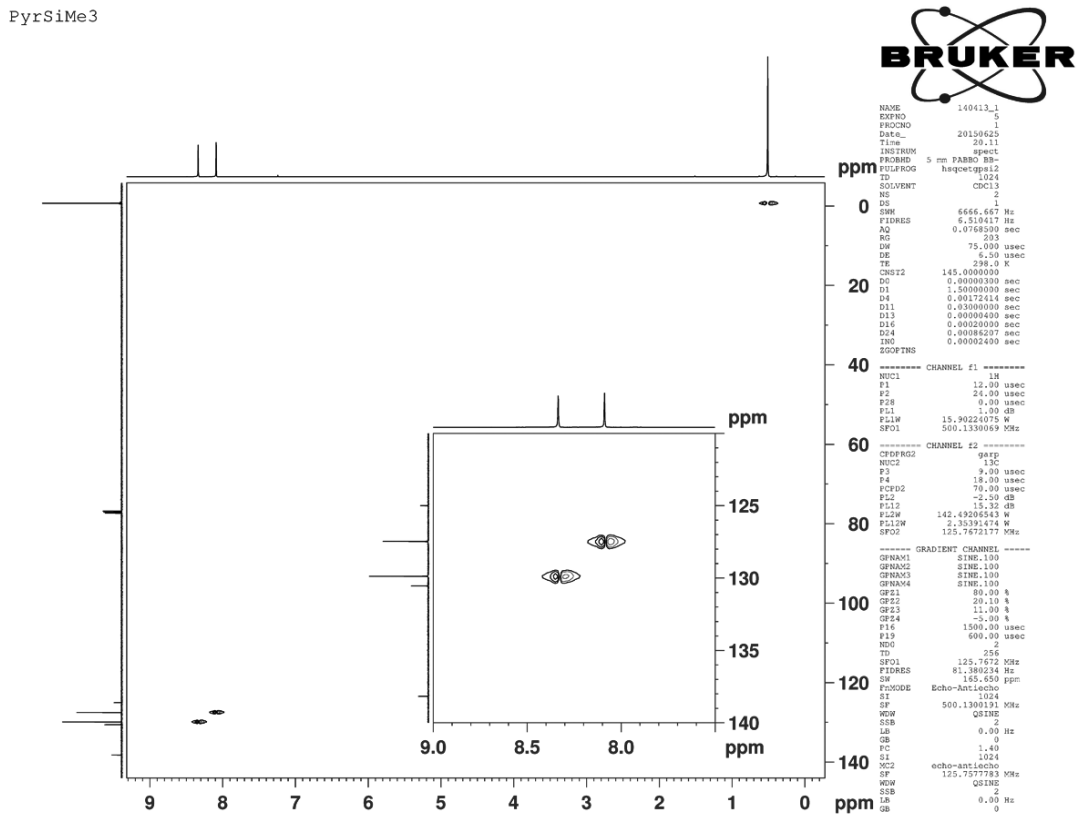

Fig. S18. ^{1}H-^{13}C hsqc NMR spectrum of 2,7-bis(menylsilyl)pyrene (**3**) in $CDCl_3$.

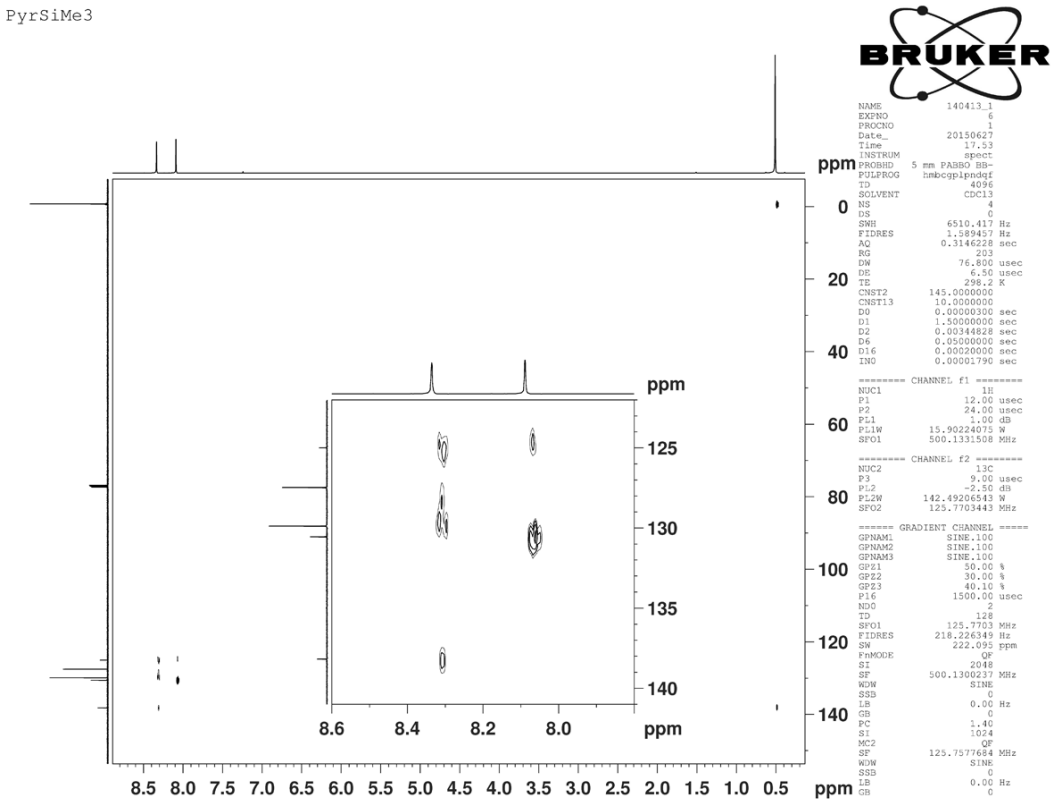

Fig. S19. ^{1}H-^{13}C hmbc NMR spectrum of 2,7-bis(menylsilyl)pyrene (**3**) in $CDCl_3$.

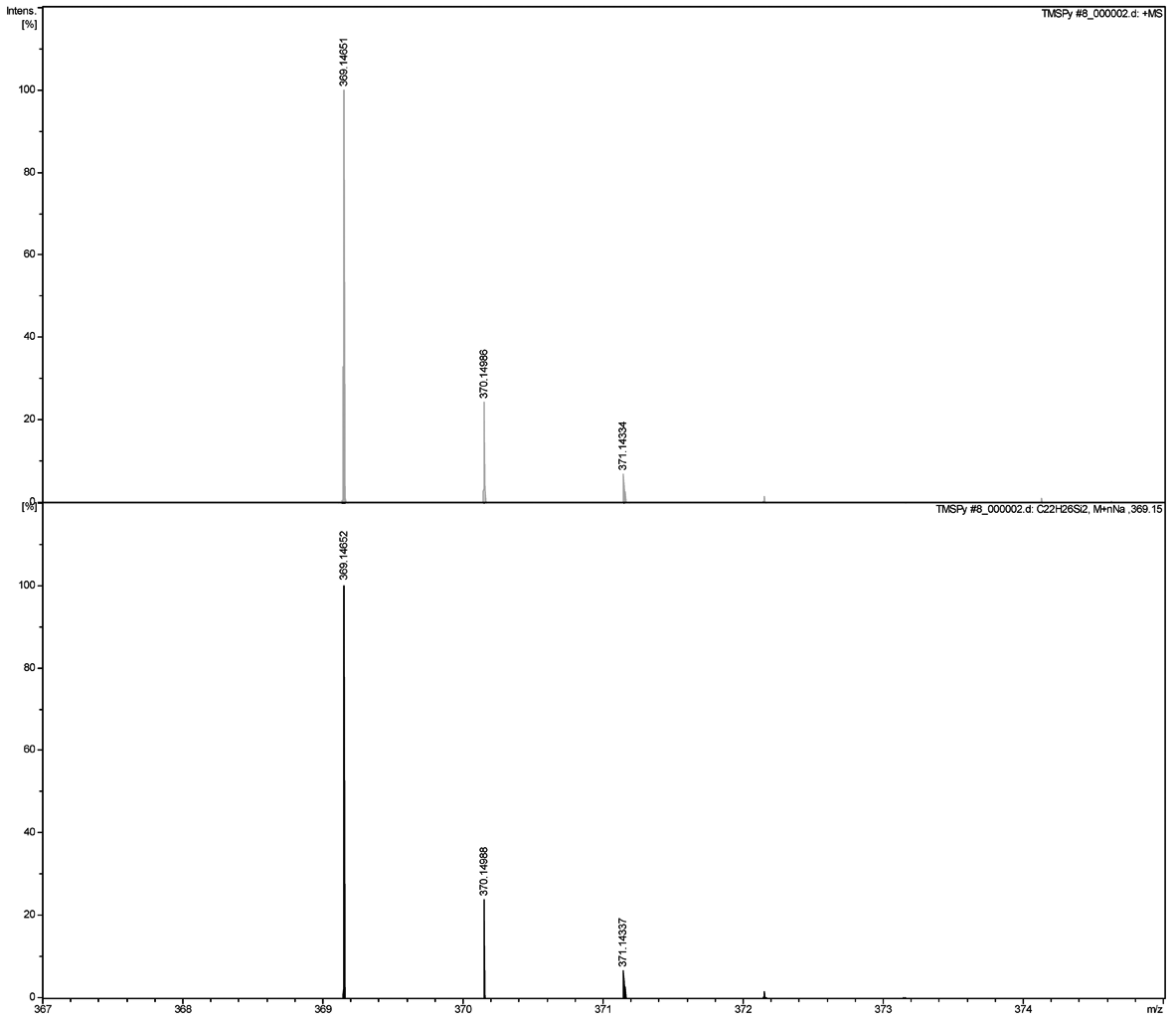

Fig. S20. HRMS(ESI, positive) spectrum of 2,7-bis(menylsilyl)pyrene (**3**): top; obsd., bottom; calcd.

3. Details of X-ray Crystallography

Table S1. Crystal Data of **1** and **3**

		1	**3**
CCDC #		1415849	1415850
Compound Name		C18 Pyrene-gyrotop	2,7-Bis(trimethylsilyl)pyrene
Empirical formula		$C_{70}H_{116}Si_2$	$C_{22}H_{26}Si_2$
Cryst shape		prism	prism
Cryst color		colorless	colorless
Cryst size		0.30 x 0.20 x 0.20 mm^3	0.50 x 0.30 x 0.20 mm^3
Formula weight / g mol^{-1}		1013.8	346.61
Crystal system		Triclinic	Monoclinic
Space group		*P*-1	$P2_1/c$
Z		2	2
Temperature / K		100	100
Cell parameter	*a*	12.173(3) Å	6.3540(12) Å
	b	17.375(4) Å	16.626(3) Å
	c	18.275(4) Å	9.3688(17) Å
	α	61.920(3)°	90°
	β	71.547(3)°	100.456(2)°
	γ	87.263(3)°	90°
	V	3211.3(14) $Å^3$	973.3(3) $Å^3$
Calculated density		1.048 Mg/m^3	1.183 Mg/m^3
F(000)		1128	372
Absorption coefficient		0.093 mm^{-1}	0.183 mm^{-1}
θ range for collecn (deg)		1.34 to 28.71°	2.45 to 28.06°
Index ranges		-14<=h<=16, -17<=k<=22, -19<=l<=23	-7<=h<=8, -15<=k<=21, -9<=l<=11
Reflections collected		18533	5274
Independent reflections		14243 [R(int) = 0.0210]	2118 [R(int) = 0.0188]
Completeness		97.8 %	99.7 %
Goodness-of-fit on F^2		1.043	1.056
Final R indices [I>2sigma(I)]		R1 = 0.0575, wR2 = 0.1454	R1 = 0.0331, wR2 = 0.0875
R indices (all data)		R1 = 0.0688, wR2 = 0.1553	R1 = 0.0375, wR2 = 0.0905
Largest diff. peak and hole		0.602 and -0.356 e.$Å^{-3}$	0.361 and -0.195 e.$Å^{-3}$

Table S2. Parameters for Weighted Least-Squares Planes through the Starred Atoms for **1**

(Nardelli, Musatti, Domiano & Andreetti Ric.Sci.(1965),15(II-A),807).
Equation of the plane: m1*X+m2*Y+m3*Z=d

Plane 1

m1 = -0.99836(0.00000)
m2 = 0.04105(0.00031)
m3 = -0.04002(0.00007)
D = -8.69372(0.00246)

Atom		d	s	d/s	(d/s)**2
C01	*	0.0032	0.0017	1.882	3.544
C02	*	0.0327	0.0018	17.854	318.761
C03	*	0.0546	0.0018	29.838	890.302
C04	*	0.0536	0.0017	31.210	974.078
C05	*	0.0324	0.0018	17.692	313.012
C06	*	-0.0012	0.0018	-0.669	0.448
C07	*	0.0533	0.0017	31.067	965.153
C08	*	0.0356	0.0018	19.464	378.842
C09	*	-0.0087	0.0020	-4.430	19.628
C10	*	-0.0293	0.0018	-16.016	256.498
C11	*	0.0142	0.0018	7.689	59.123
C12	*	0.0507	0.0018	27.719	768.343
C13	*	0.0596	0.0022	27.206	740.184
C14	*	0.0472	0.0022	21.569	465.230
C15	*	0.0573	0.0021	27.632	763.513
C16	*	0.0399	0.0021	19.222	369.478
Si01	*	-0.0272	0.0006	-44.650	1993.658
Si02	*	-0.0234	0.0006	-38.429	1476.806
					==========
				Sum((d/s)**2) for starred atoms	10756.598

Chi-squared at 95% for 15 degrees of freedom: 25.00
The group of atoms deviates significantly from planarity

4. Details of Fluorescence Study

a. Fluorescence lifetime measurement

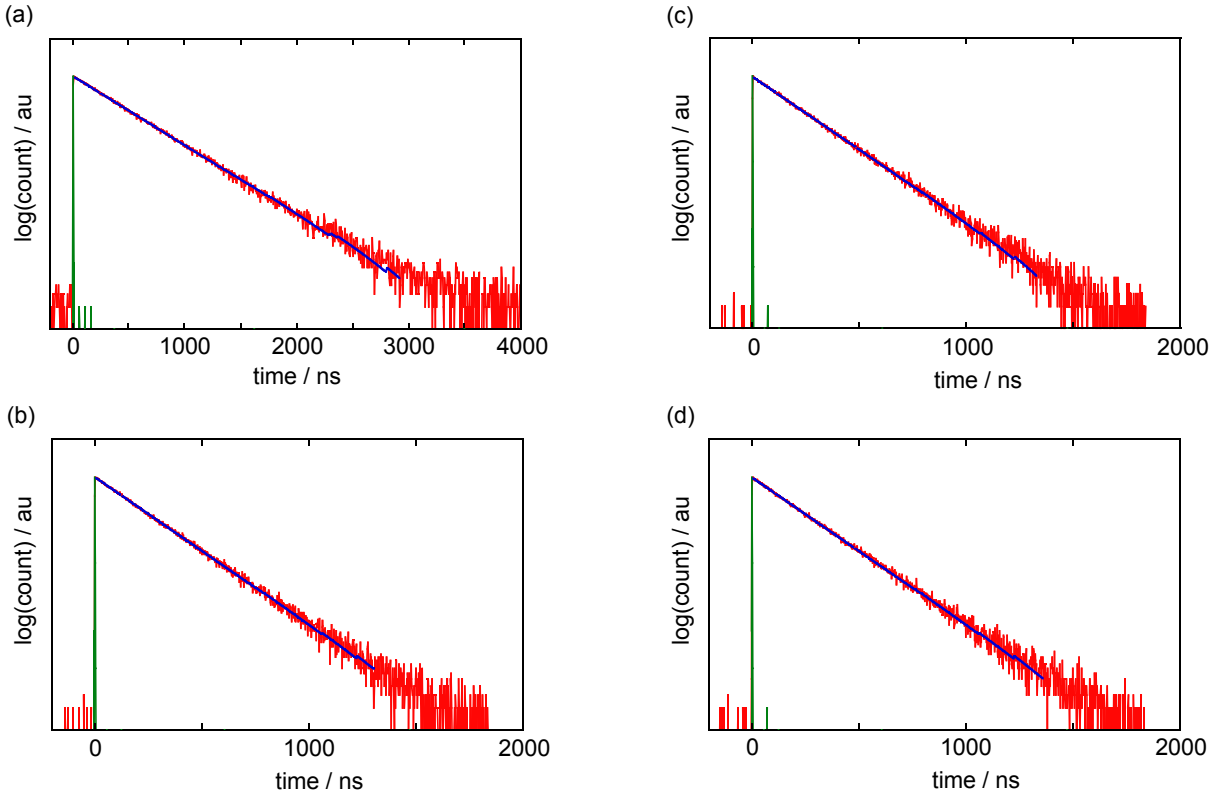

Fig. S21. Normalized fluorescence decay traces of pyrenes [red line; observed intensity, green line; light pulse, blue line, line fitting] (conditions: 1 μM, 296 K, ex. 340 nm, obs. 383 - 385 nm) : (a) pyrene; (b) **3**; (c) **1**; (d) **1i**.

b. Fluorescence quenching by nitrobenzene

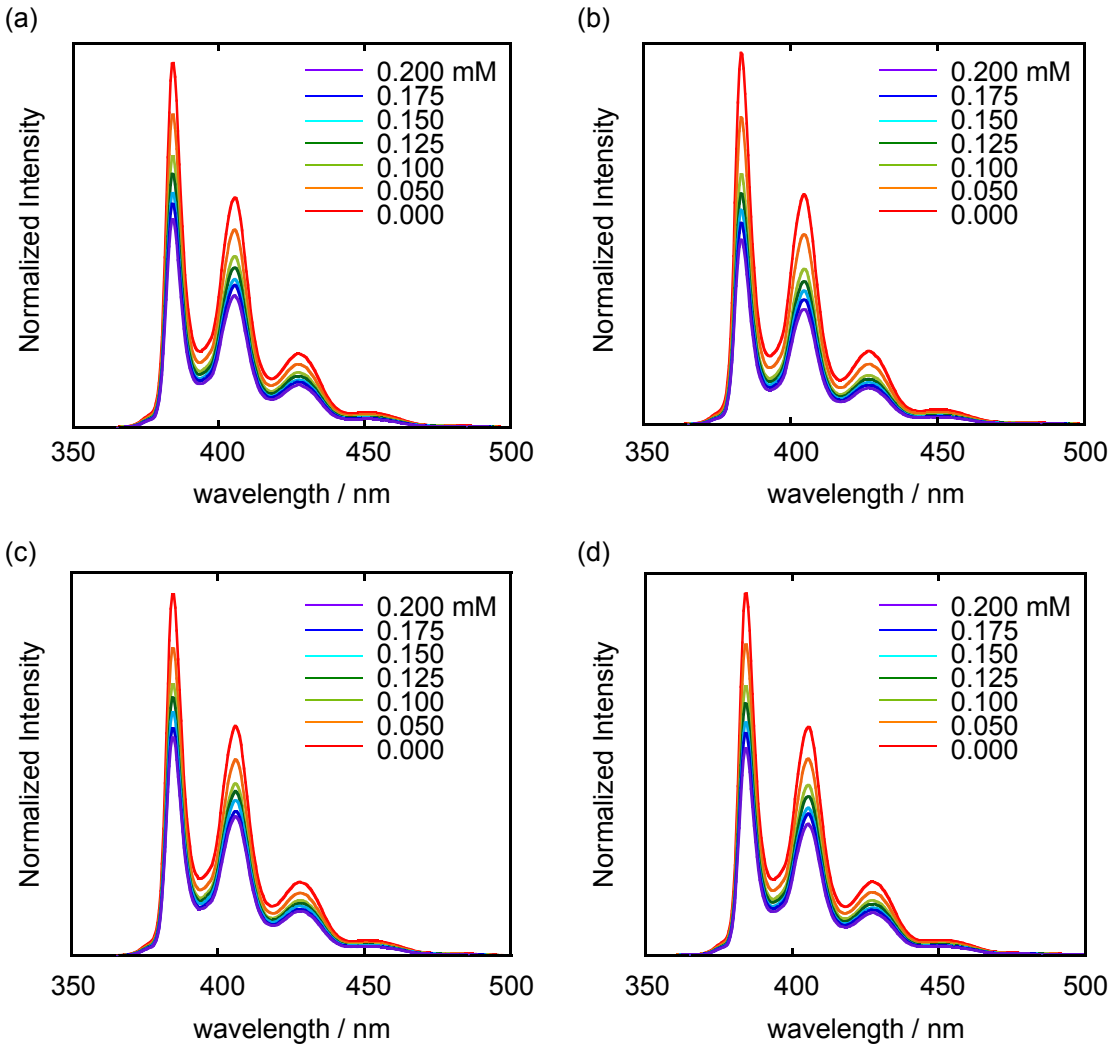

Fig. S22. Fluorescence spectra of 10×10^{-6} M pyrenes in hexane at rt in the presence of increasing concentrations of nitrobenzene: (a) pyrene, (b) **3**, (c) **1**, (d) **1i**.

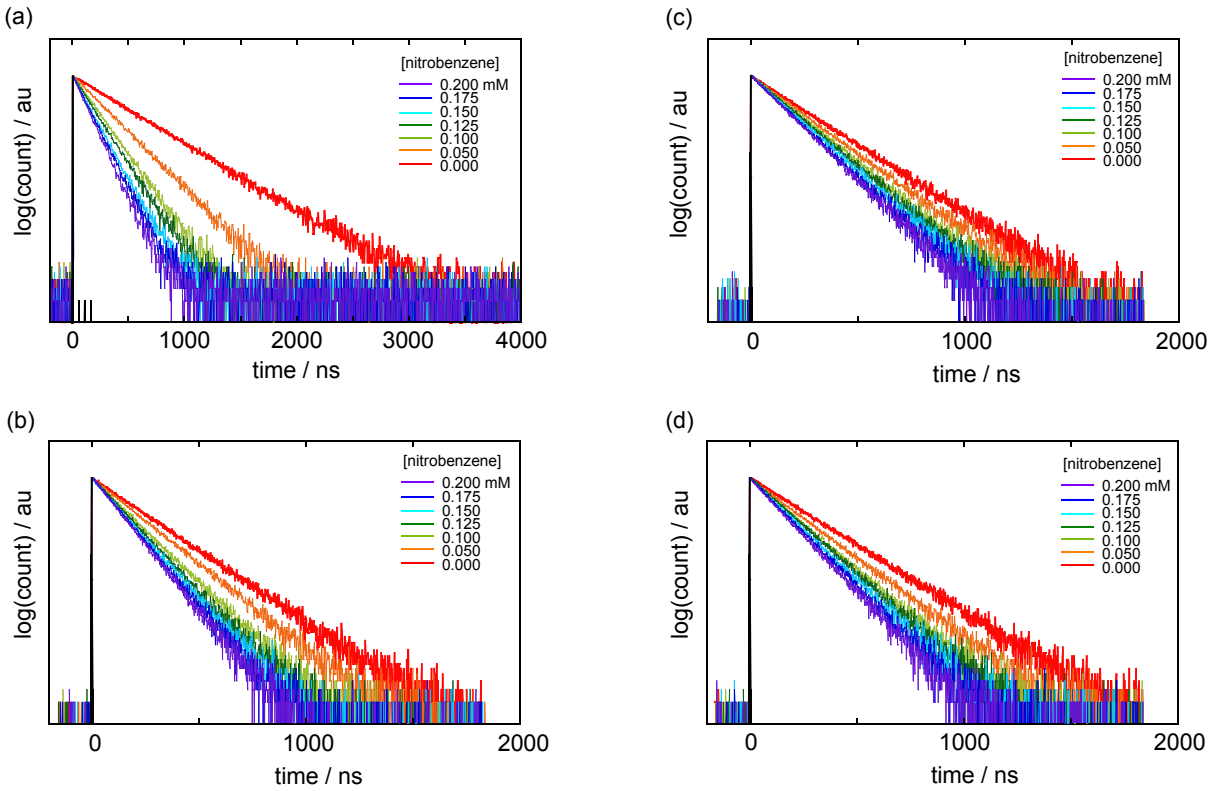

Fig. S23. Normalized fluorescence decay traces of pyrenes in the presence of nitrobenzene as a quencher [black line; light pulse] (concentrations of substrates 1 μM): (a) pyrene, (b) **3**, (c) **1**, (d) **1i**.