Supplementary Information

Synthesis and fluorescence properties of 9,9-dimethylfluorene-diyl bridged molecular gyrotops: Effects of slight fluorophore motion on fluorescence efficiency in a solid-state

Reina Yoshizawa,[a] Yusuke Inagaki,[a] Hiroyuki Momma,[b] Eunsang Kwon,[b] Kazuaki Ohara,[c] Kentaro Yamaguchi,[c] and Wataru Setaka*[a]

a. Division of Applied Chemistry, Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

b. Faculty of Pharmaceutic Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Aoba-ku, Sendai, 980-8578, Japan.

c. Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan.

E-mail: wsetaka@tmu.ac.jp

(Total 26 pages including this cover page)

1. Copies of NMR and HRMS Spectra for New Compounds

a. Spectra of C10FluC10

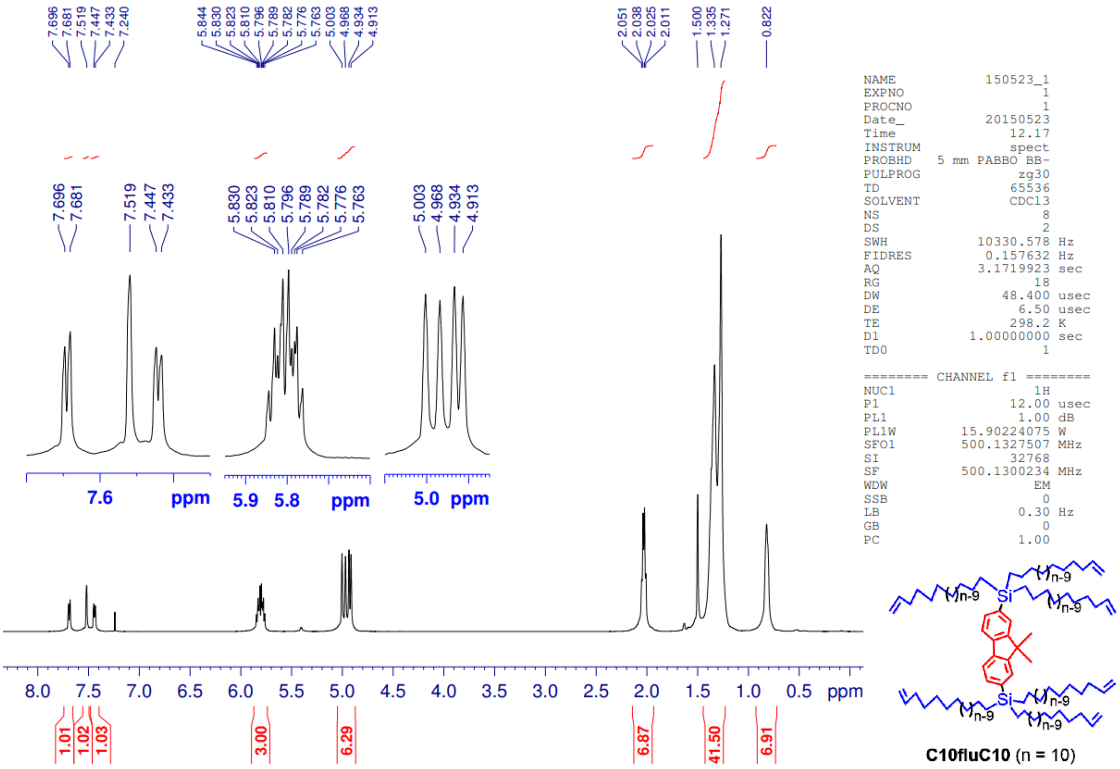

Fig. S1. ^{1}H NMR spectrum of **C10FluC10** in $CDCl_3$.

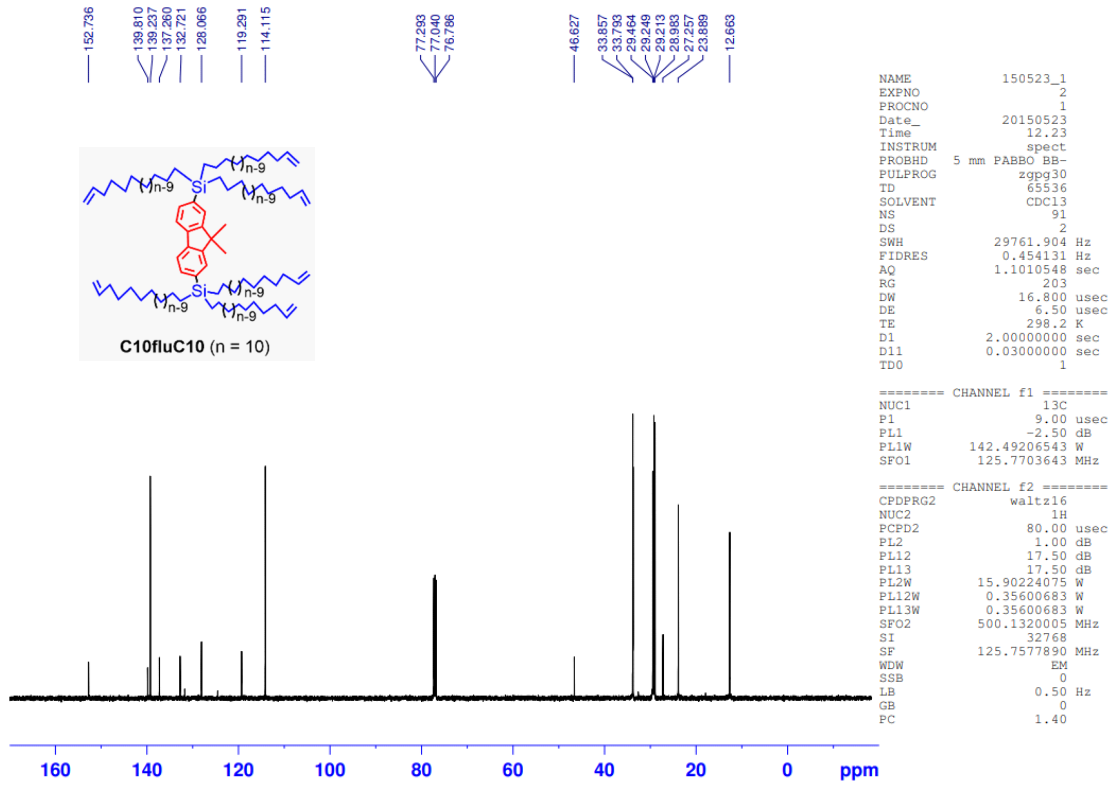

Fig. S2. ^{13}C NMR spectrum of **C10FluC10** in $CDCl_3$.

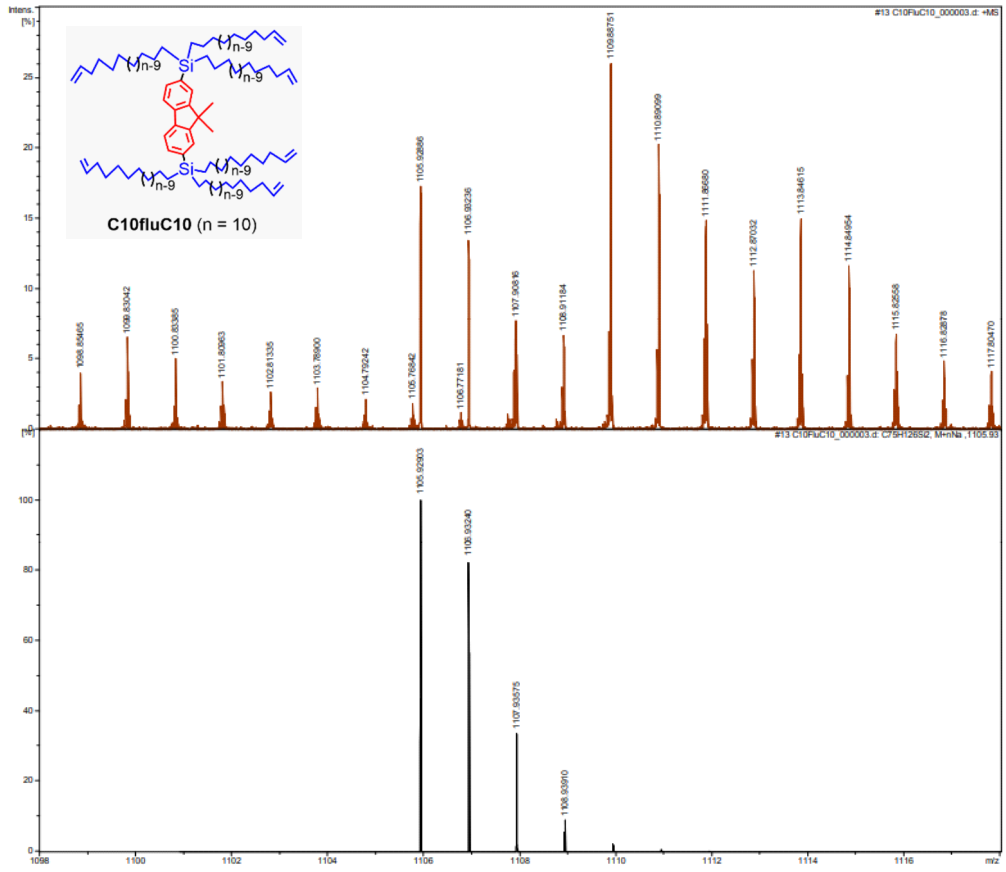

Fig. S3. HRMS spectrum of **C10FluC10** (ESI, positive). Top: obsd. Bottom: sim.

b. Spectra of C12FluC12

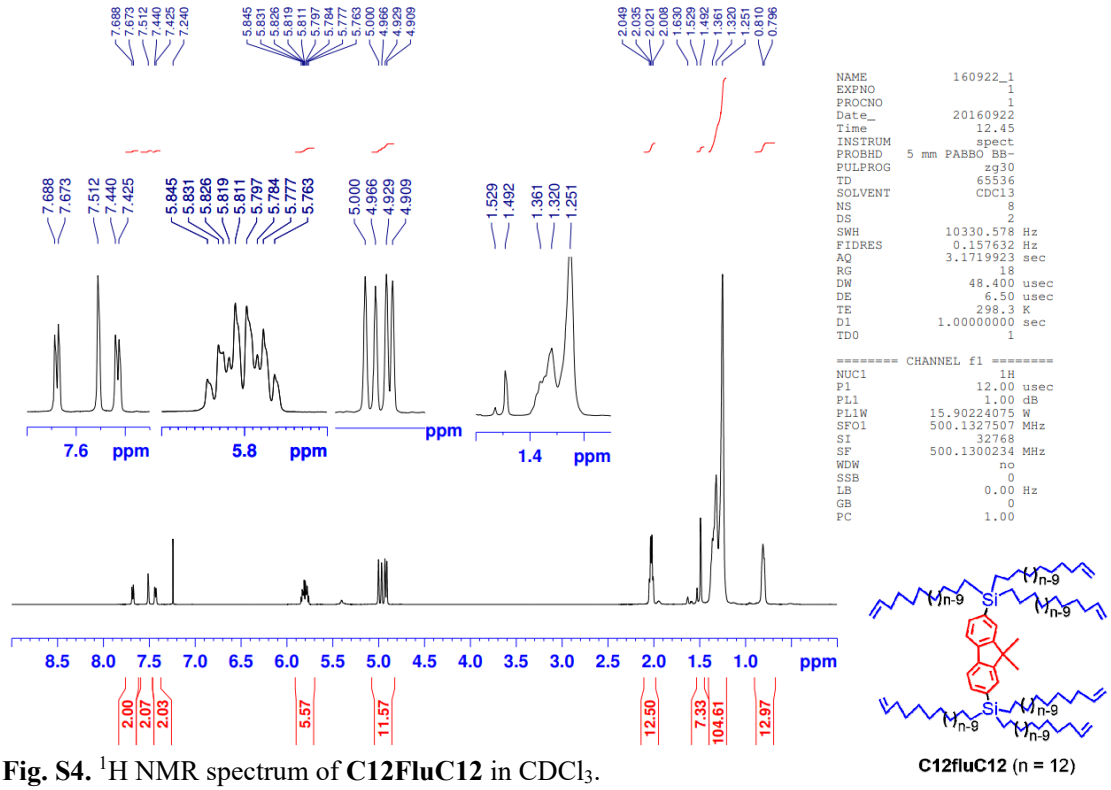

Fig. S4. ^{1}H NMR spectrum of **C12FluC12** in $CDCl_3$.

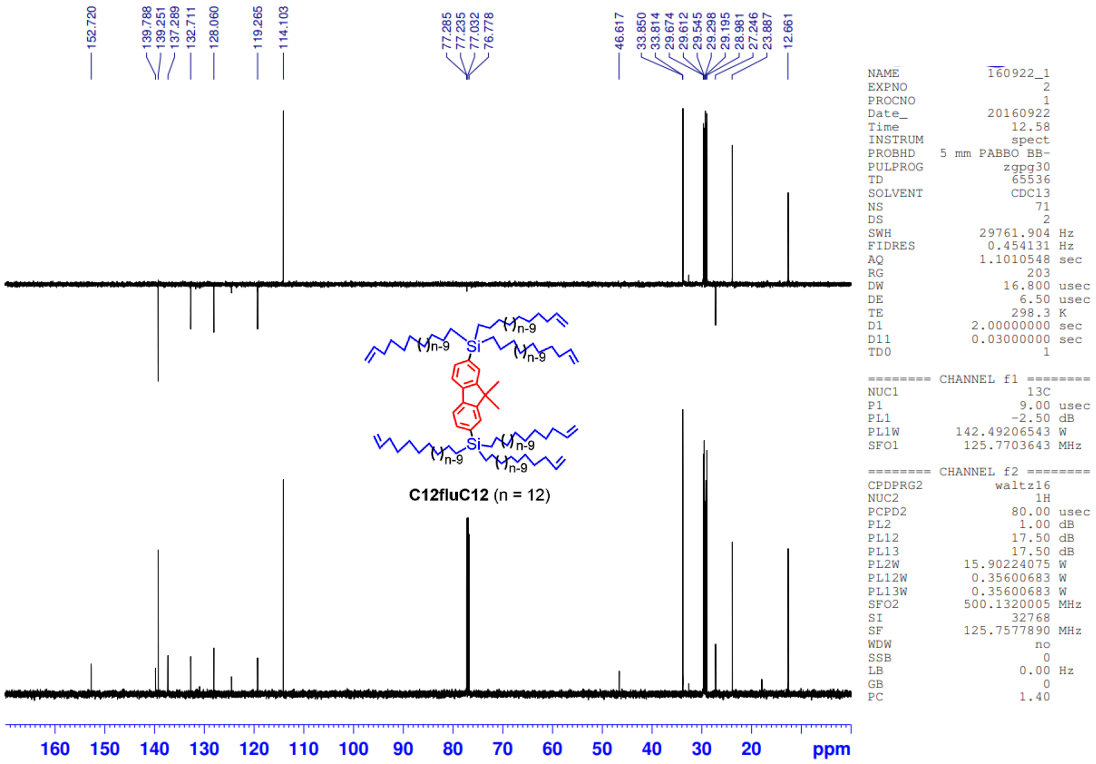


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Fig. S5. ^{13}C NMR spectrum of **C12FluC12** in $CDCl_3$.

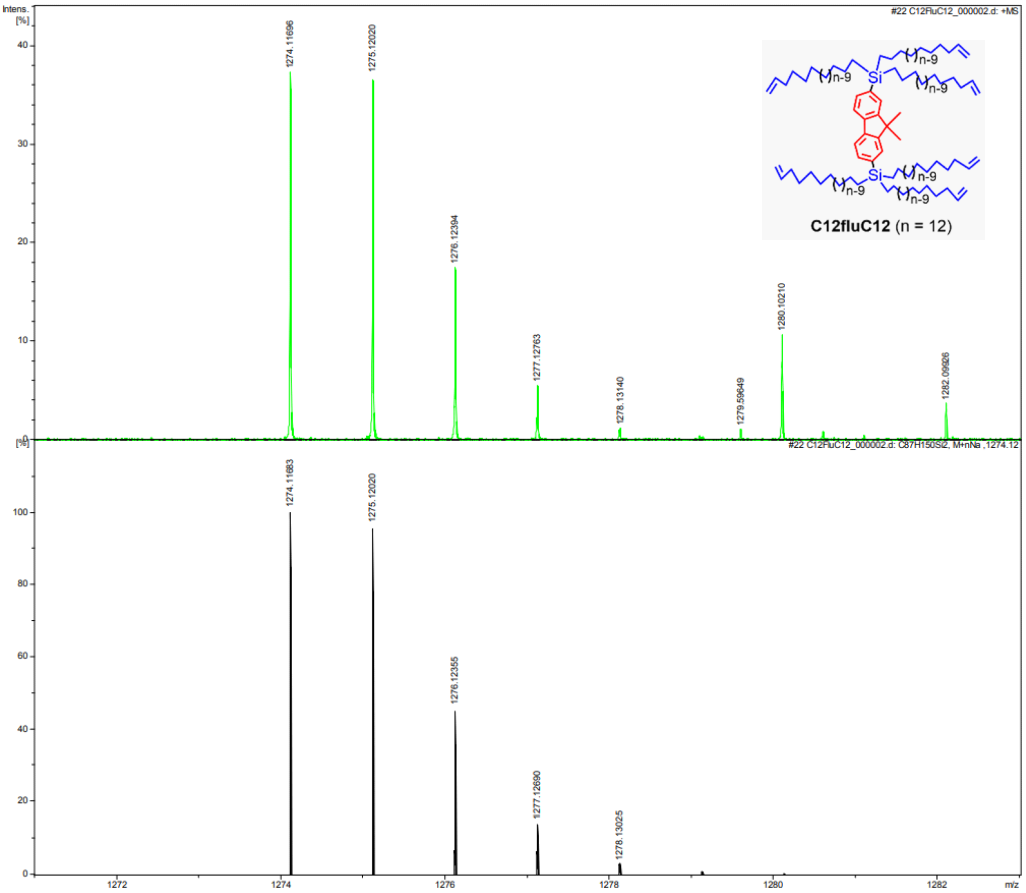


Fig. S6. HRMS spectrum of **C12FluC12** (ESI, positive). Top: obsd. Bottom: sim.

c. Spectra of C18

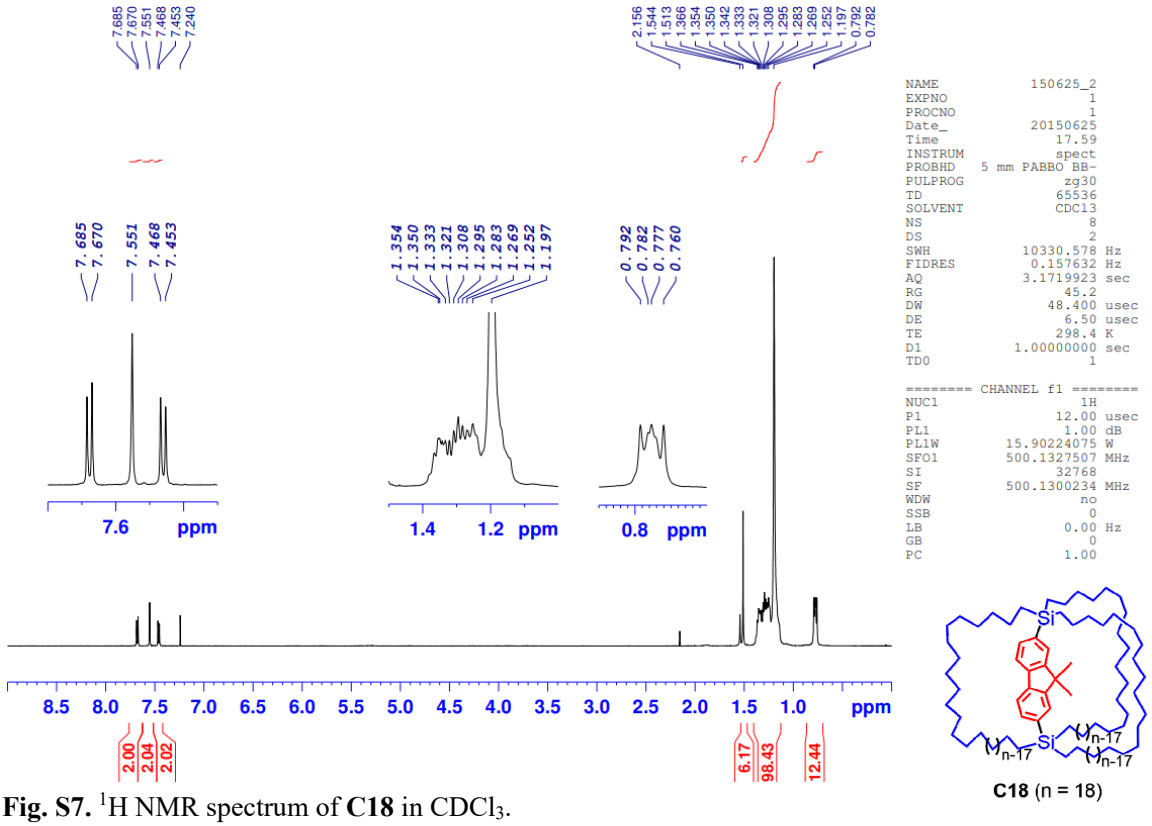


Fig. S7. ^{1}H NMR spectrum of **C18** in $CDCl_3$.

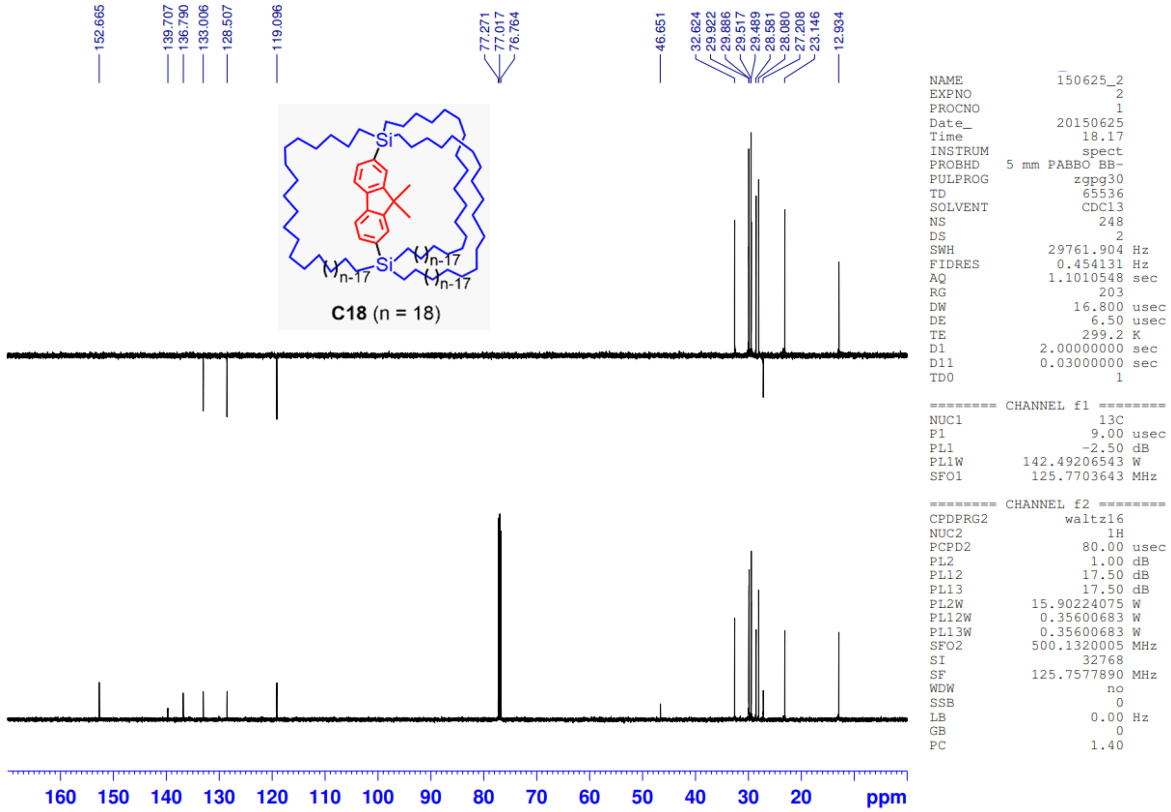


Fig. S8. ^{13}C NMR spectrum of **C18** in $CDCl_3$.

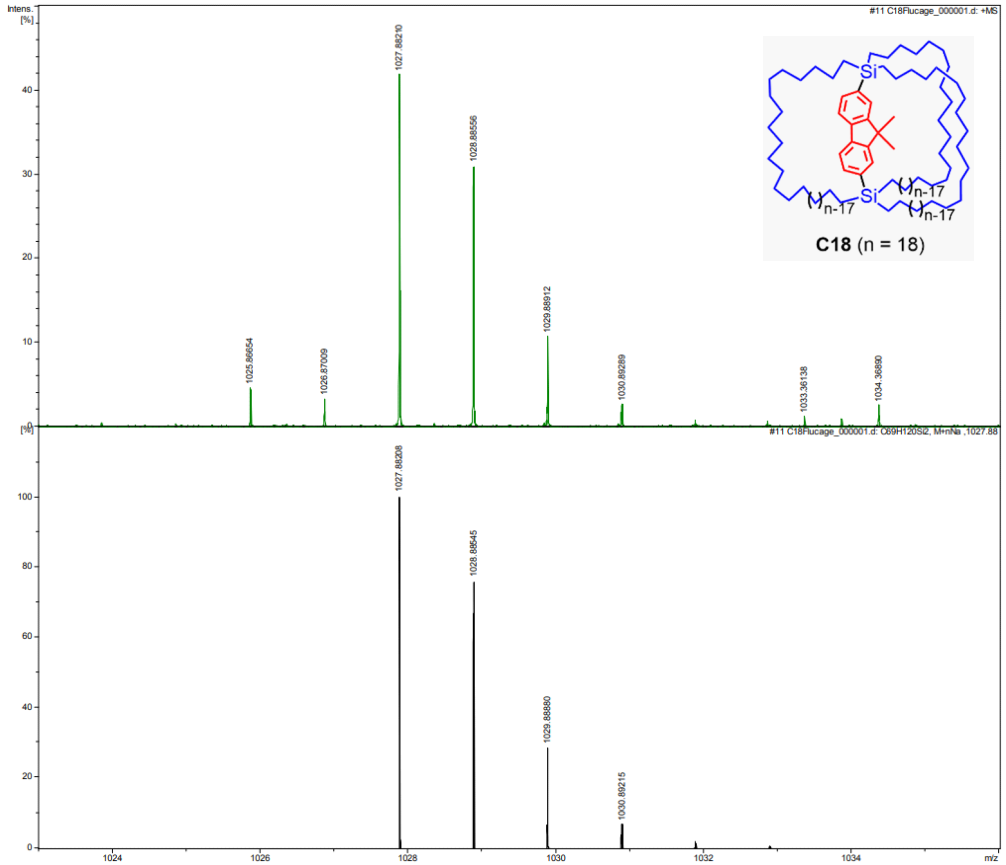


Fig. S9. HRMS spectrum of **C18** (ESI, positive). Top: obsd. Bottom: sim.

d. Spectra of C18i

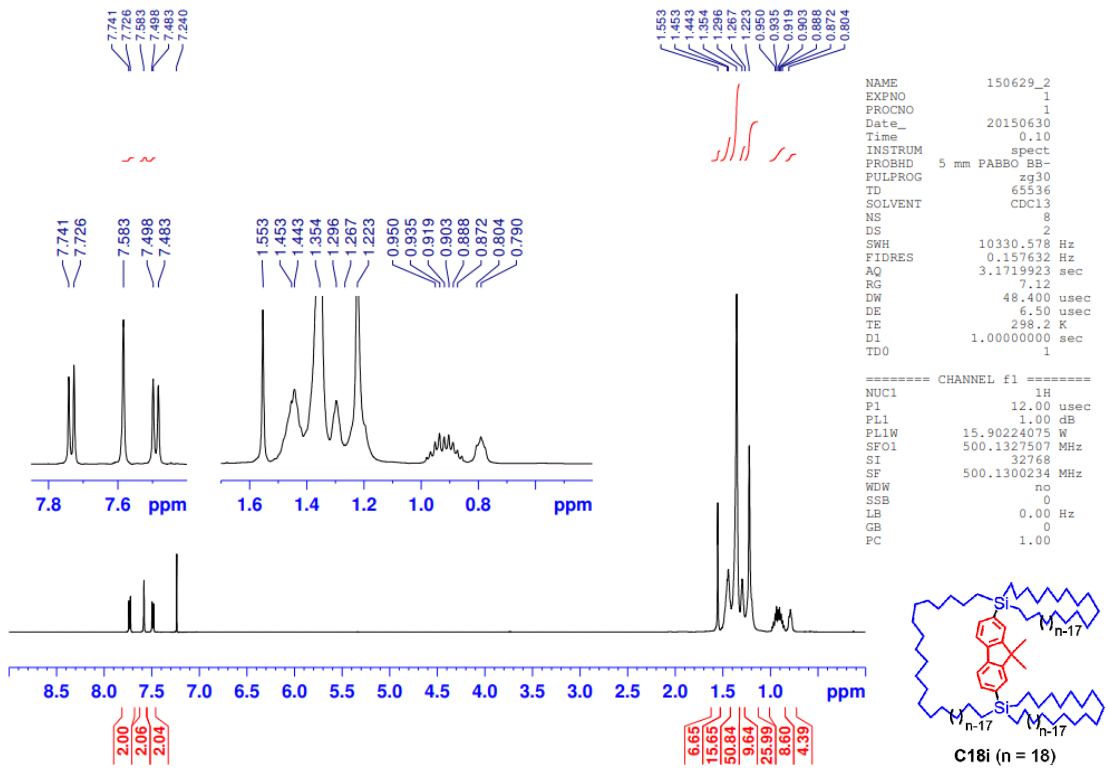


Fig. S10. ^{1}H NMR spectrum of **C18i** in $CDCl_3$.

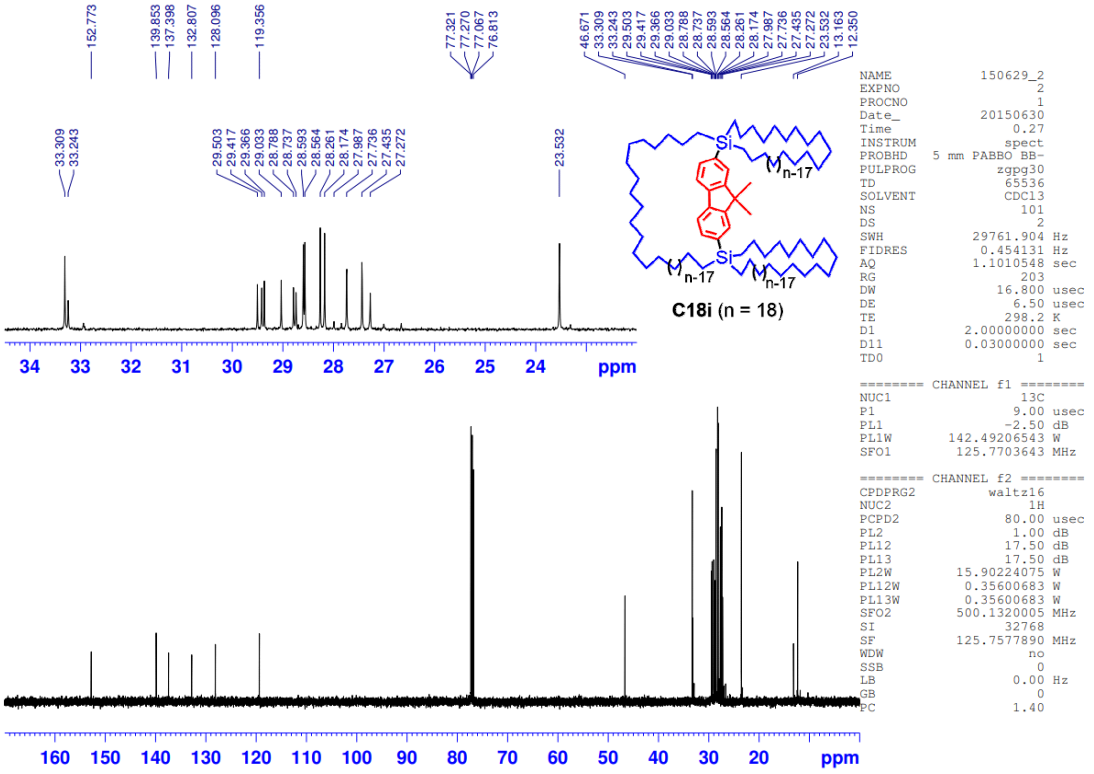


Fig. S11. ^{13}C NMR spectrum of **C18i** in $CDCl_3$.

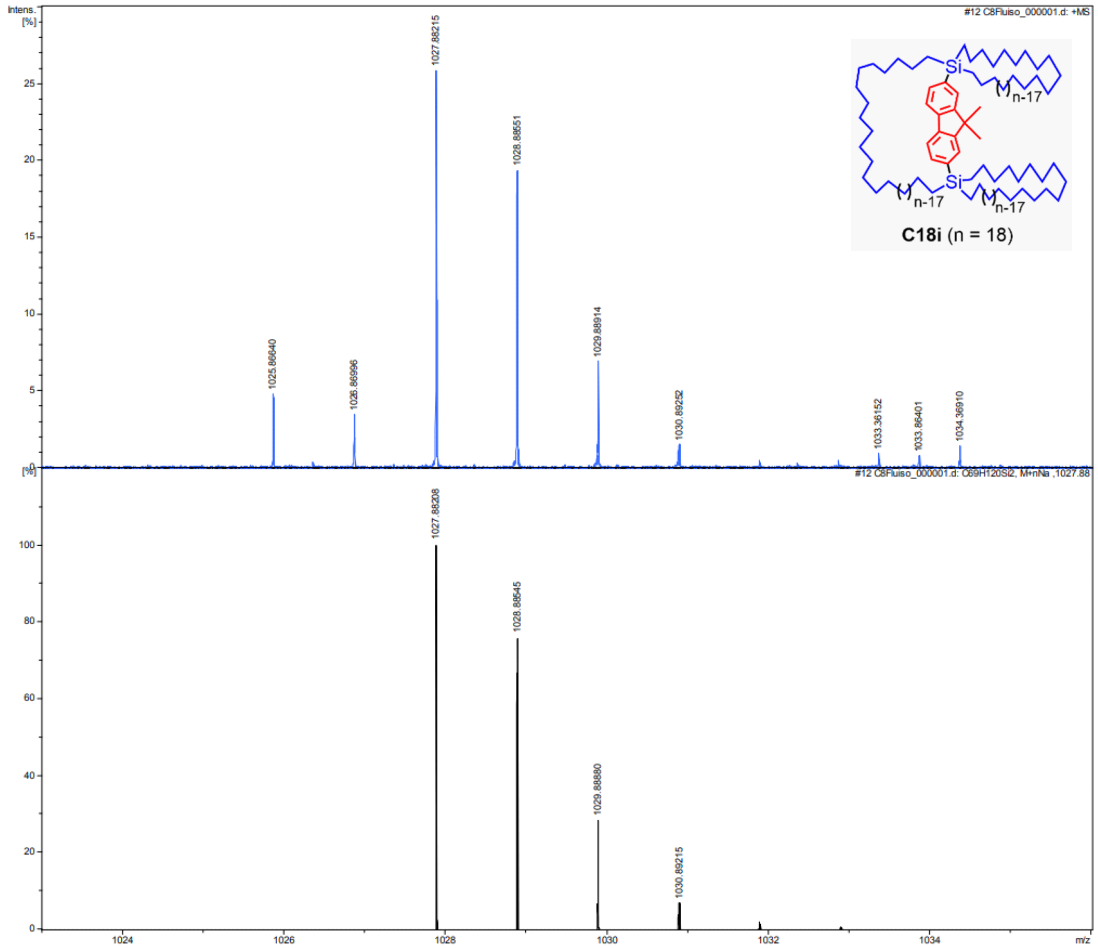


Fig. S12. HRMS spectrum of **C18i** (ESI, positive). Top: obsd. Bottom: sim.

e. Spectra of C22

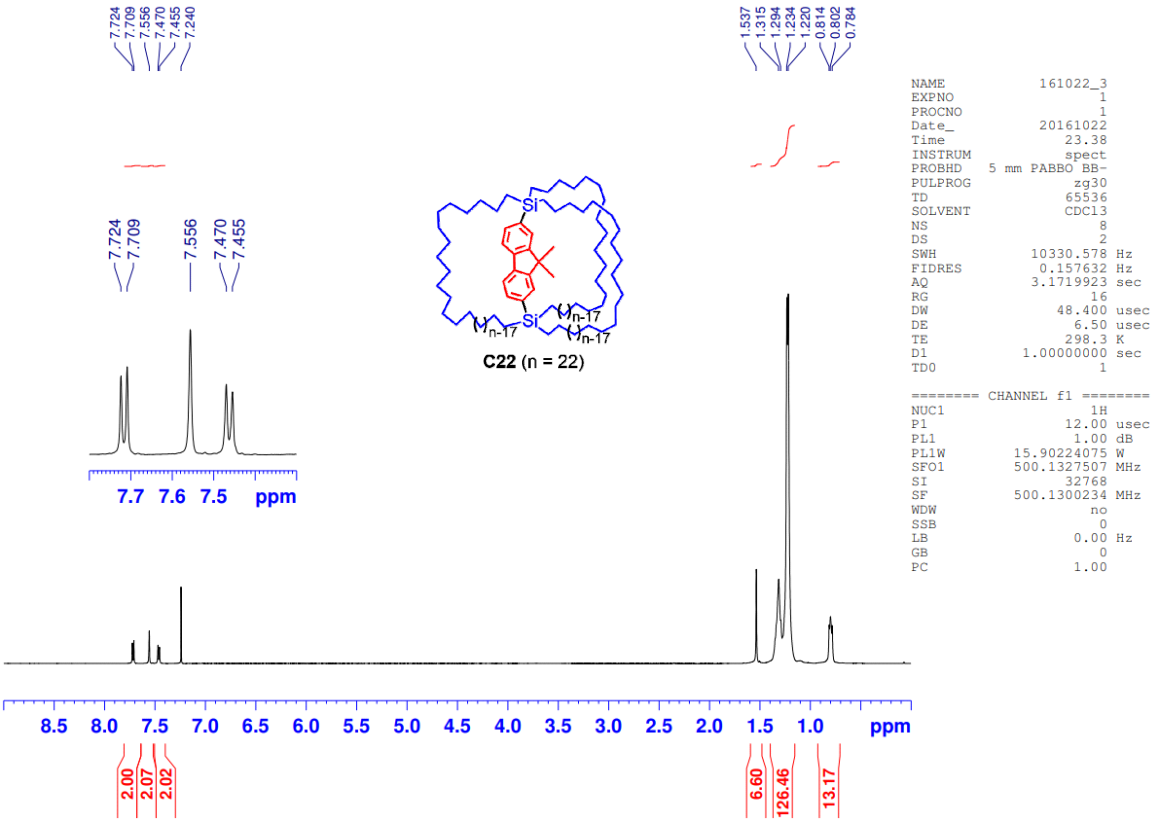


Fig. S13. ^{1}H NMR spectrum of **C22** in $CDCl_3$.

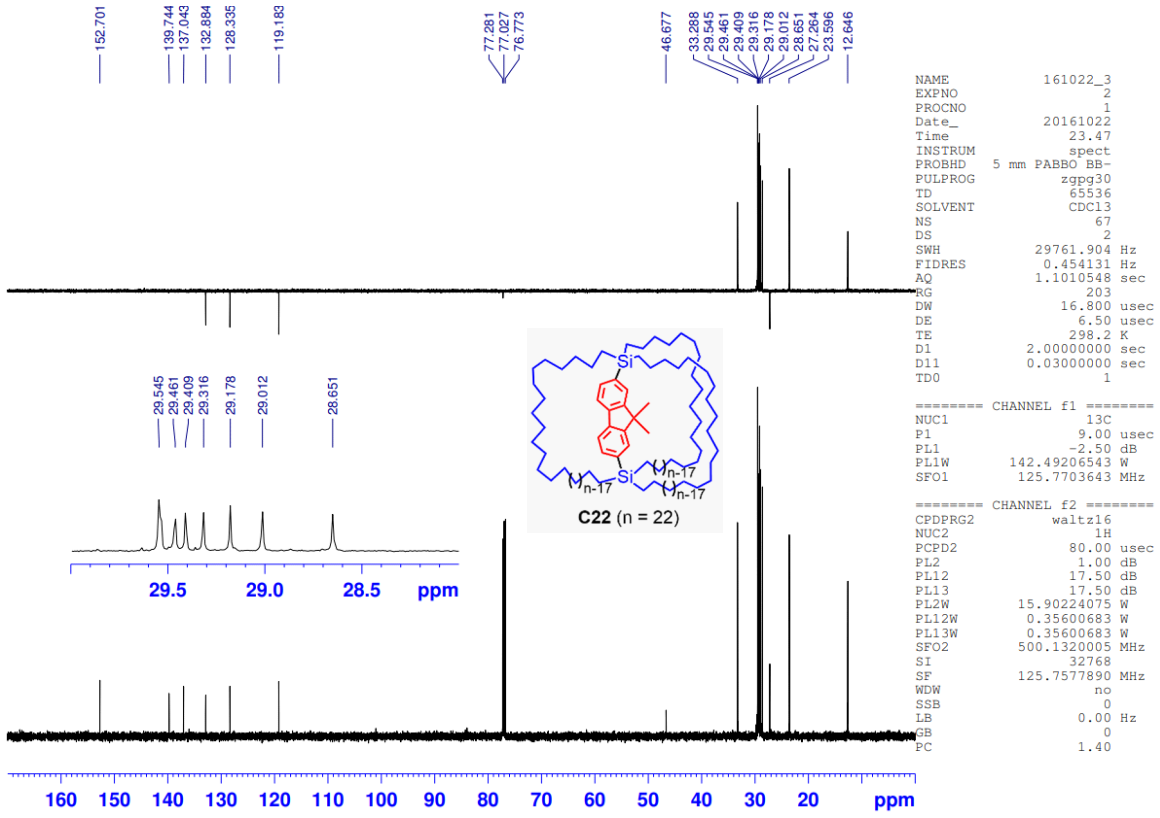


Fig. S14. ^{13}C NMR spectrum of **C22** in $CDCl_3$.

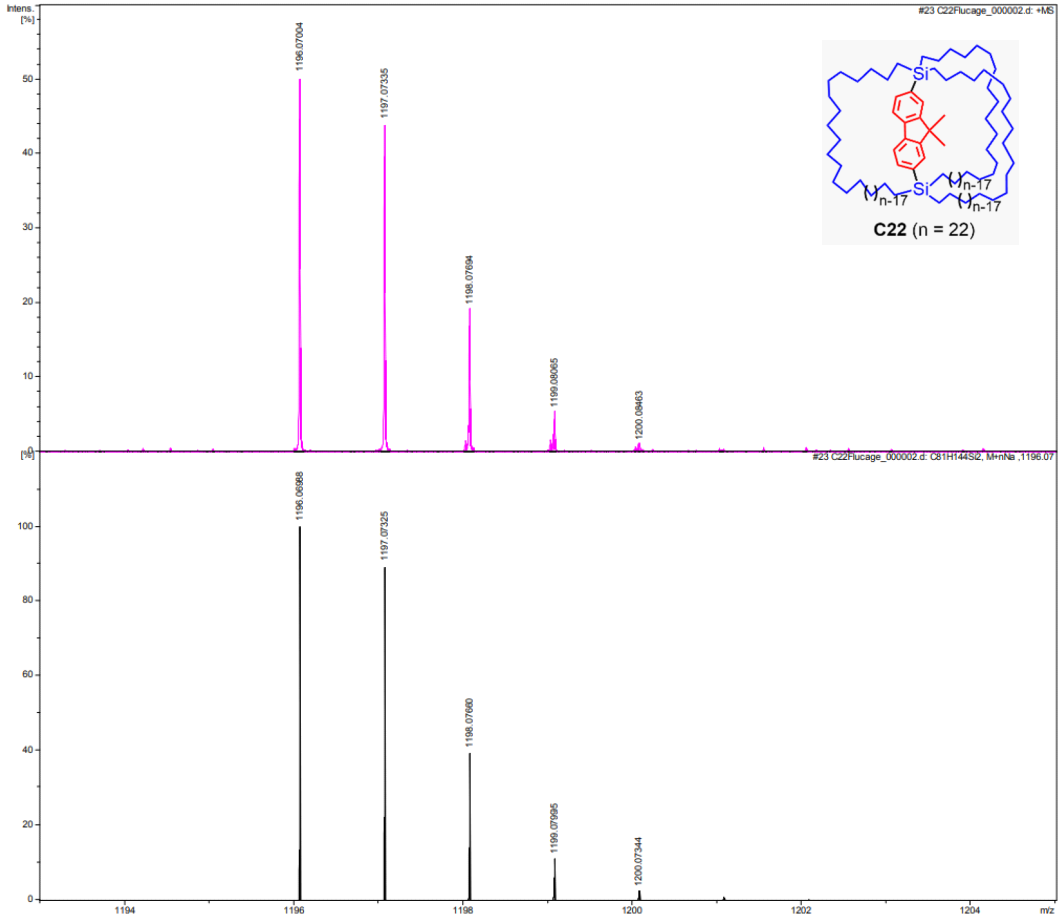


Fig. S15. HRMS spectrum of **C22** (ESI, positive). Top: obsd. Bottom: sim.

f. Spectra of C22i

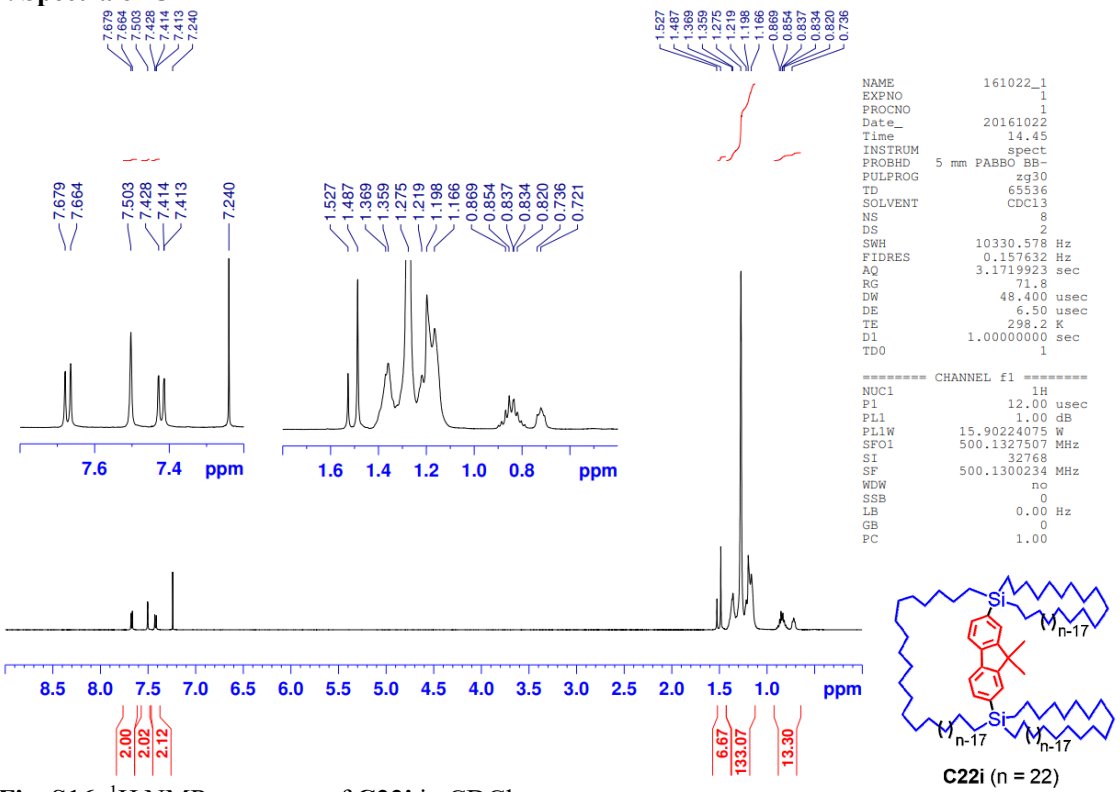
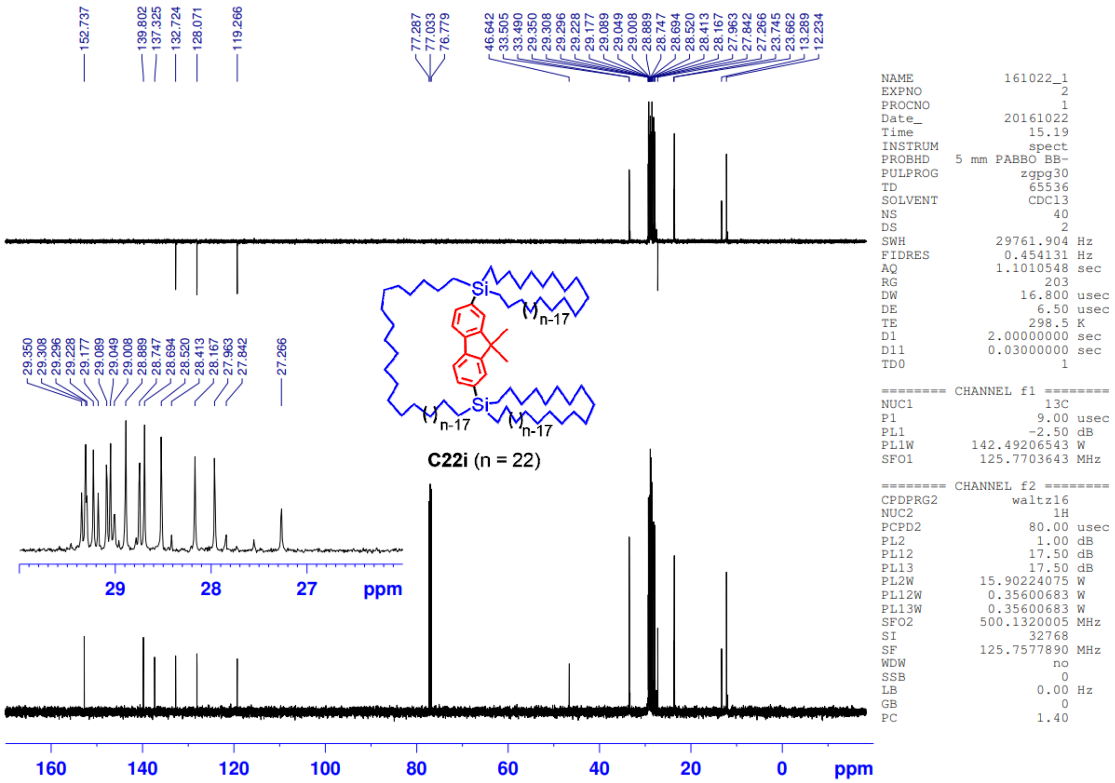


Fig. S16. ^{1}H NMR spectrum of **C22i** in $CDCl_3$.

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PL1W       142.49206543 W
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PL12W       0.35600683 W
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Fig. S17. ^{13}C NMR spectrum of **C22i** in $CDCl_3$.

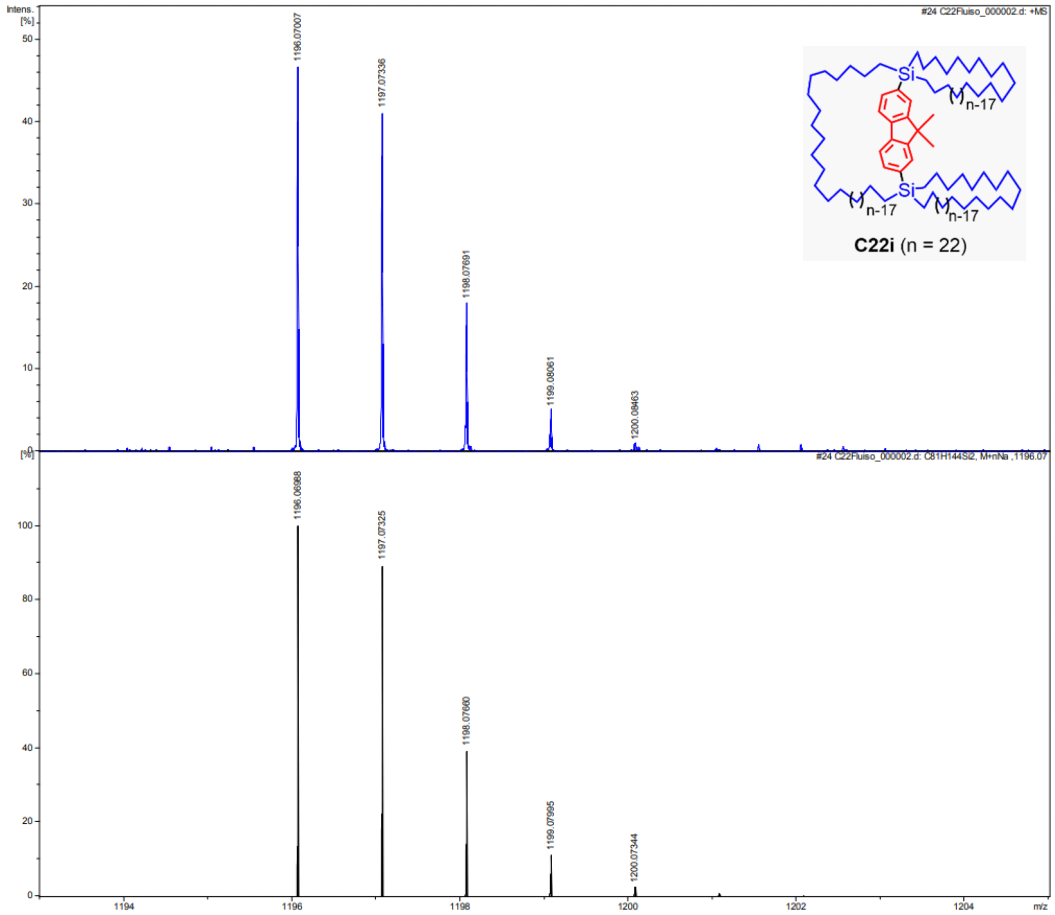


Fig. S18. HRMS spectrum of **C22i** (ESI, positive). Top: obsd. Bottom: sim.

g. Spectra of Flu-d_4

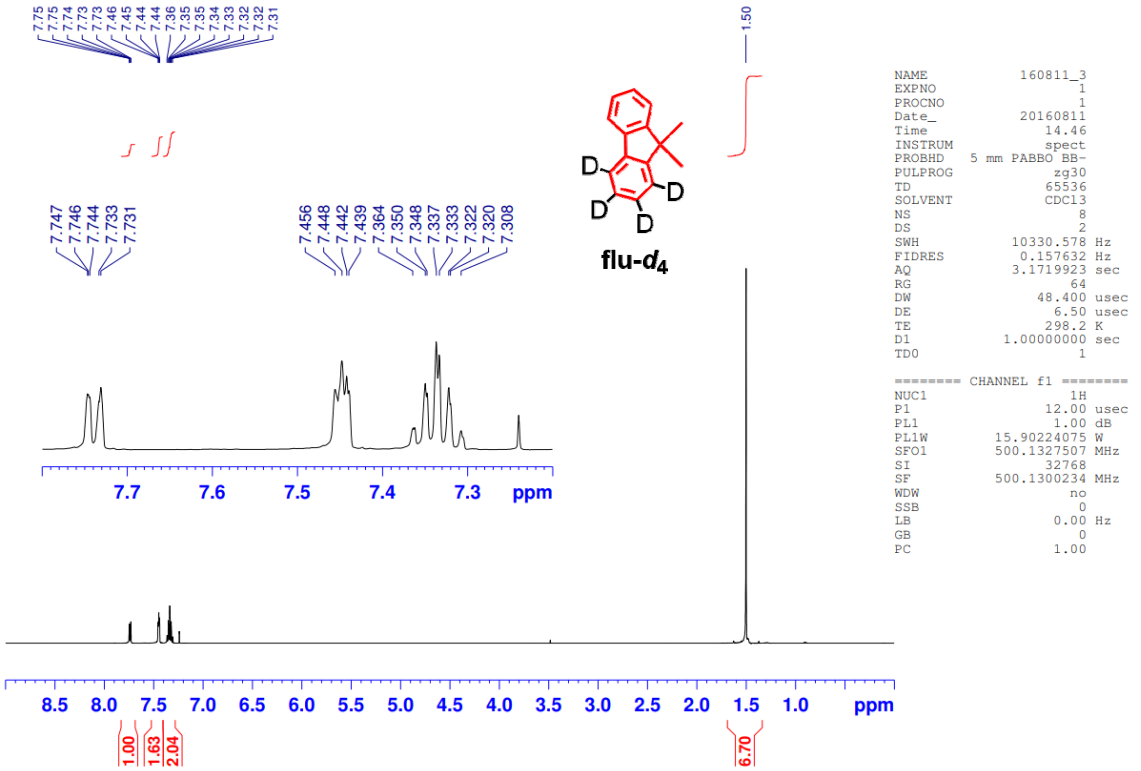


Fig. S19. ^{1}H NMR spectrum of **Flu-d_4** in $CDCl_3$.

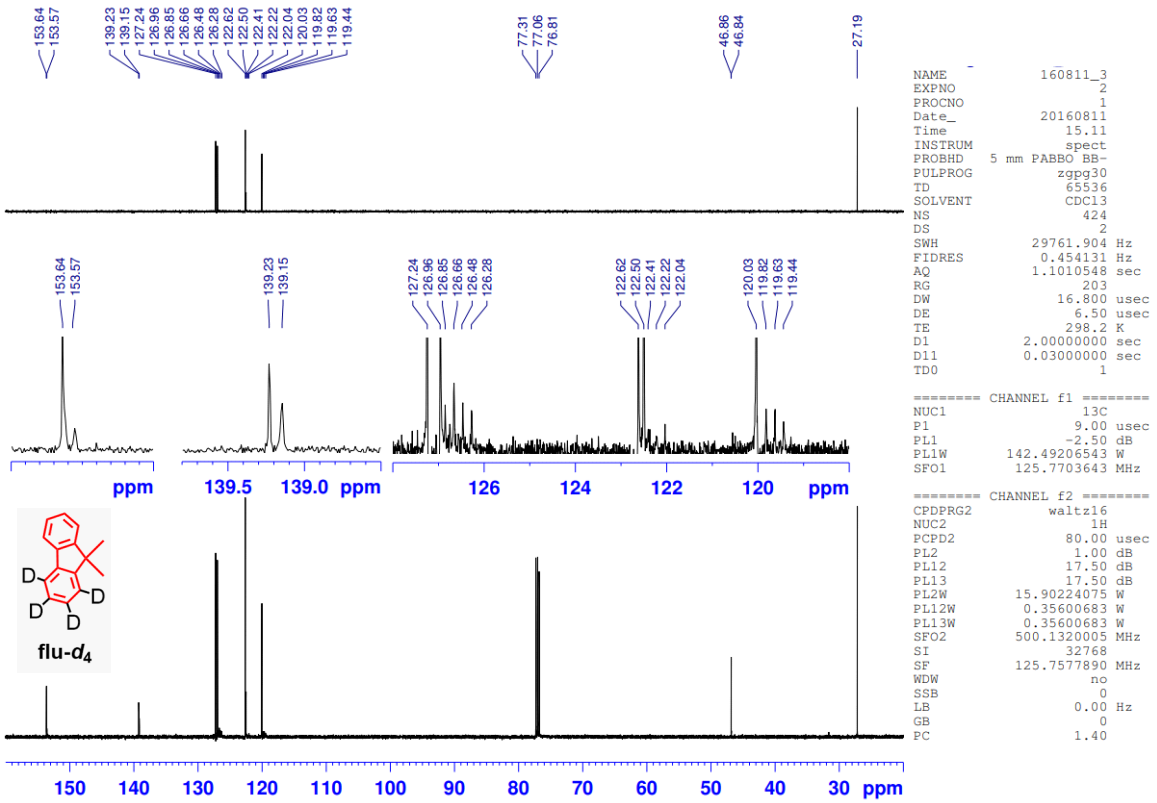


Fig. S20. ^{13}C NMR spectrum of **Flu-d_4** in $CDCl_3$.

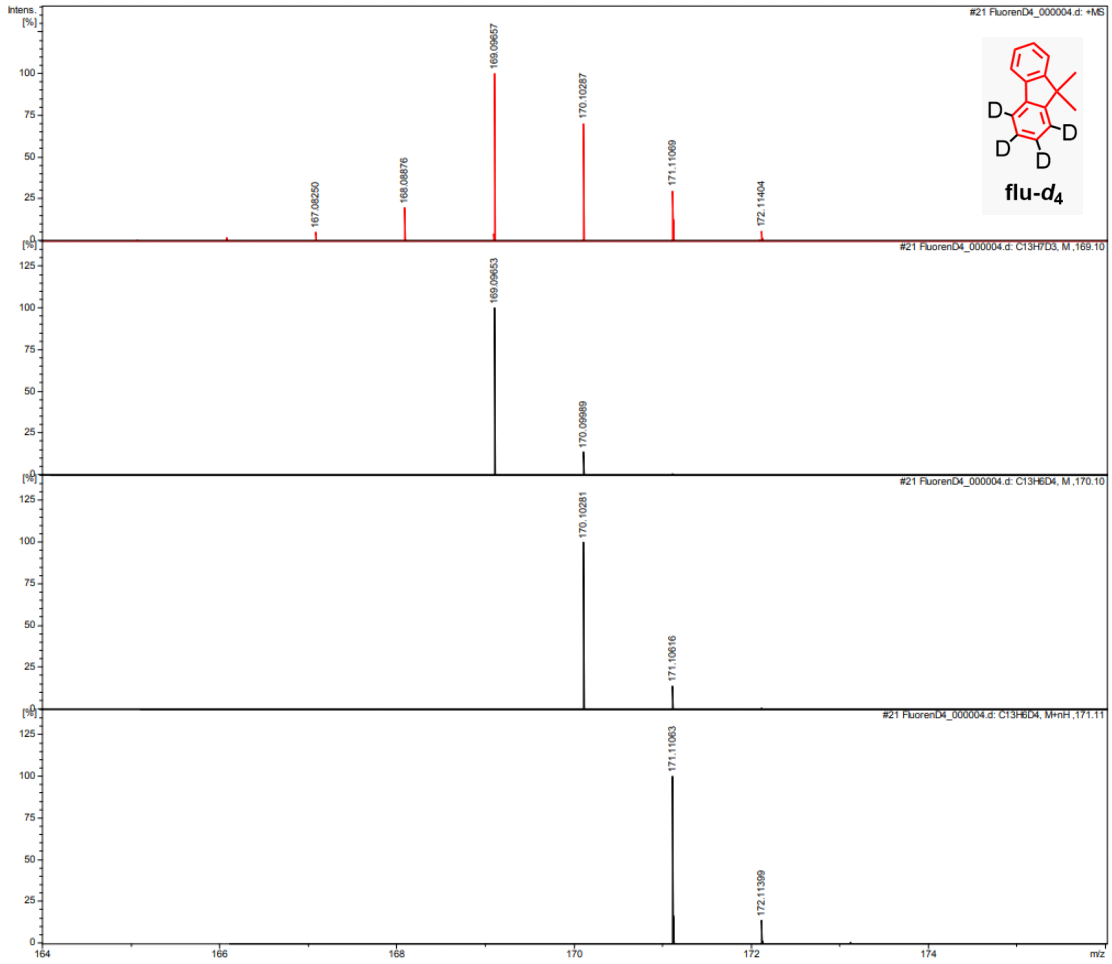


Fig. S21. HRMS spectrum of **Flu-d_4** (ESI, positive). Top: obsd. Bottom: sim.

h. Spectra of BrFluBr-d_3

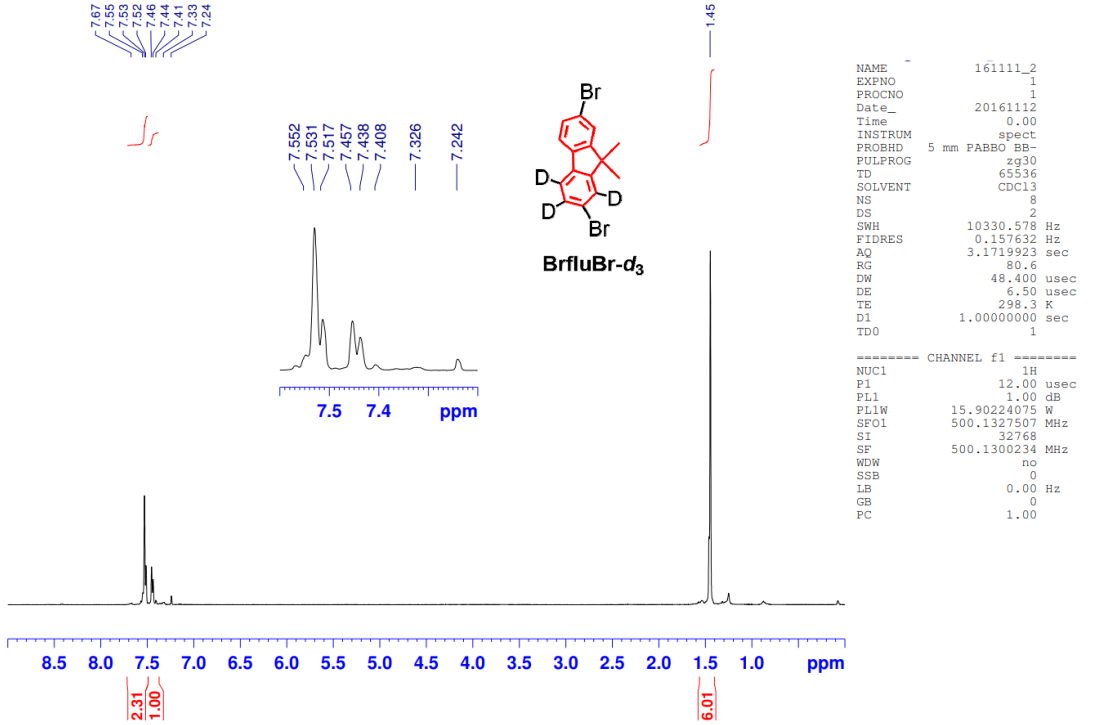


Fig. S22. ^{1}H NMR spectrum of **BrFluBr-d_3** in $CDCl_3$.

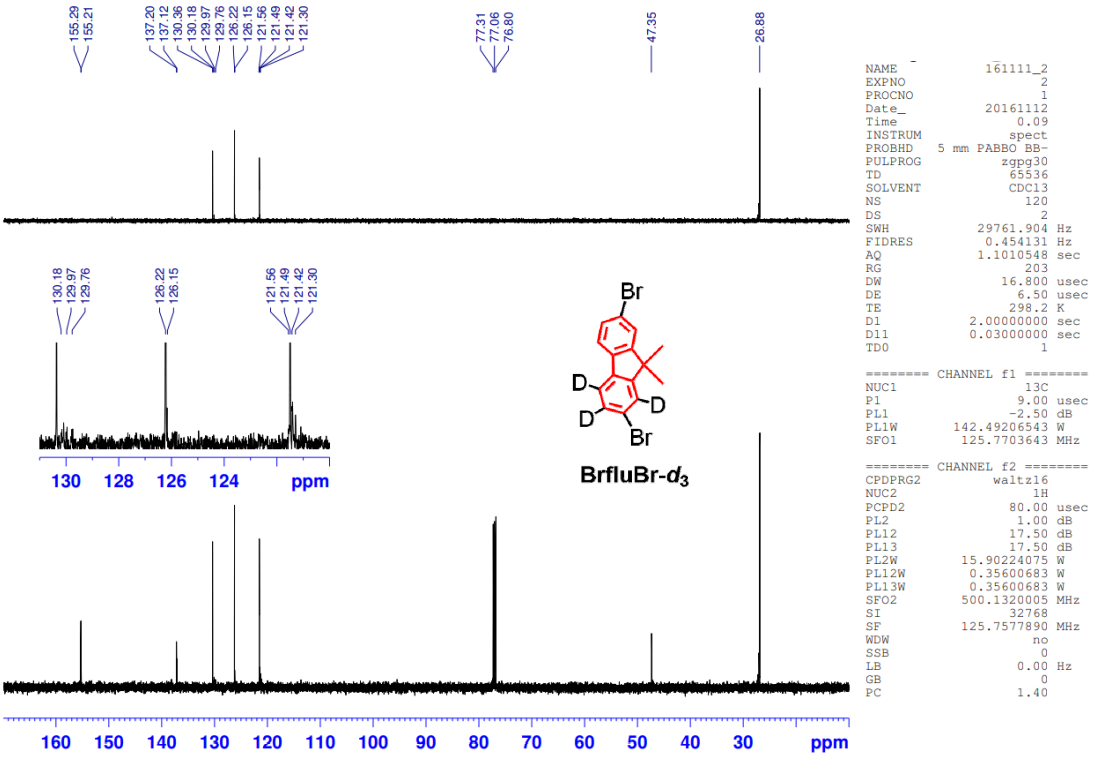


Fig. S23. ^{13}C NMR spectrum of **BrFluBr-*d*$_3$** in $CDCl_3$.

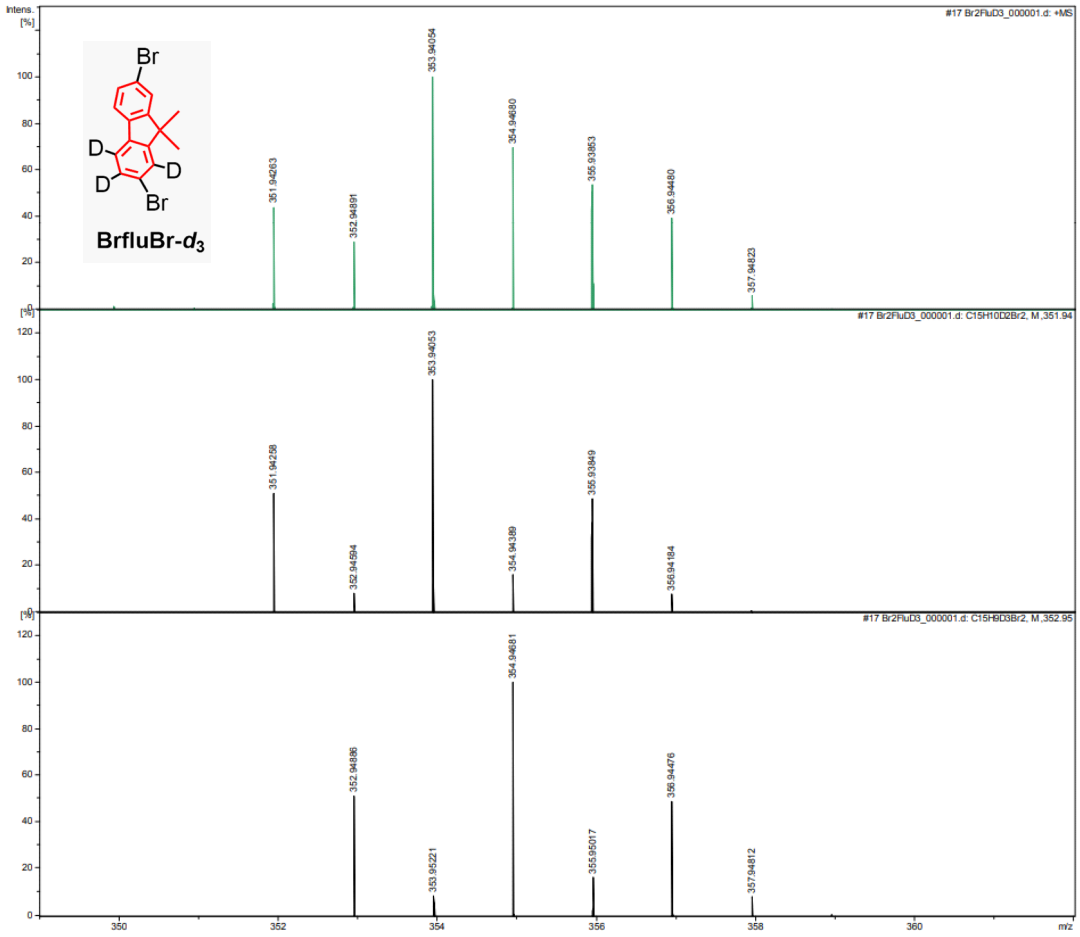


Fig. S24. HRMS spectrum of **BrFluBr-*d*$_3$** (ESI, positive). Top: obsd. Bottom: sim.

i. Spectra of C10FluC10-d_3

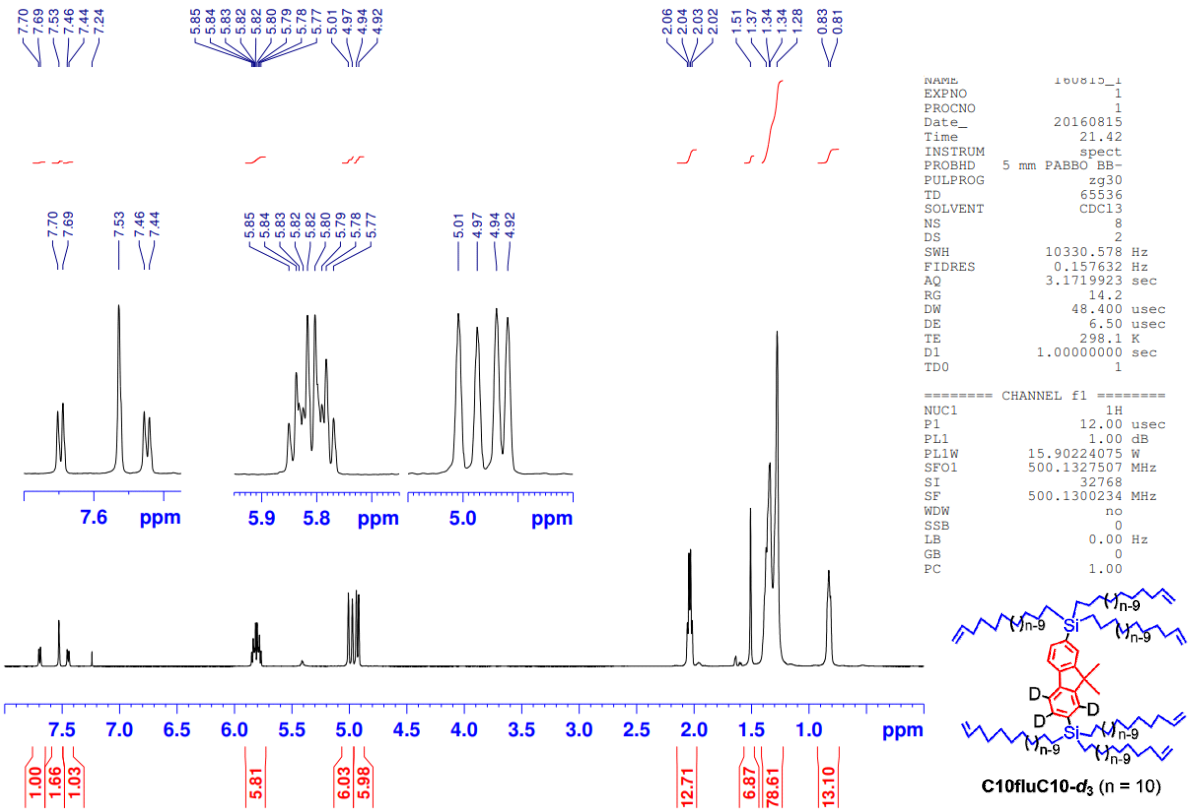


Fig. S25. ^{1}H NMR spectrum of **C10FluC10-d_3** in $CDCl_3$.

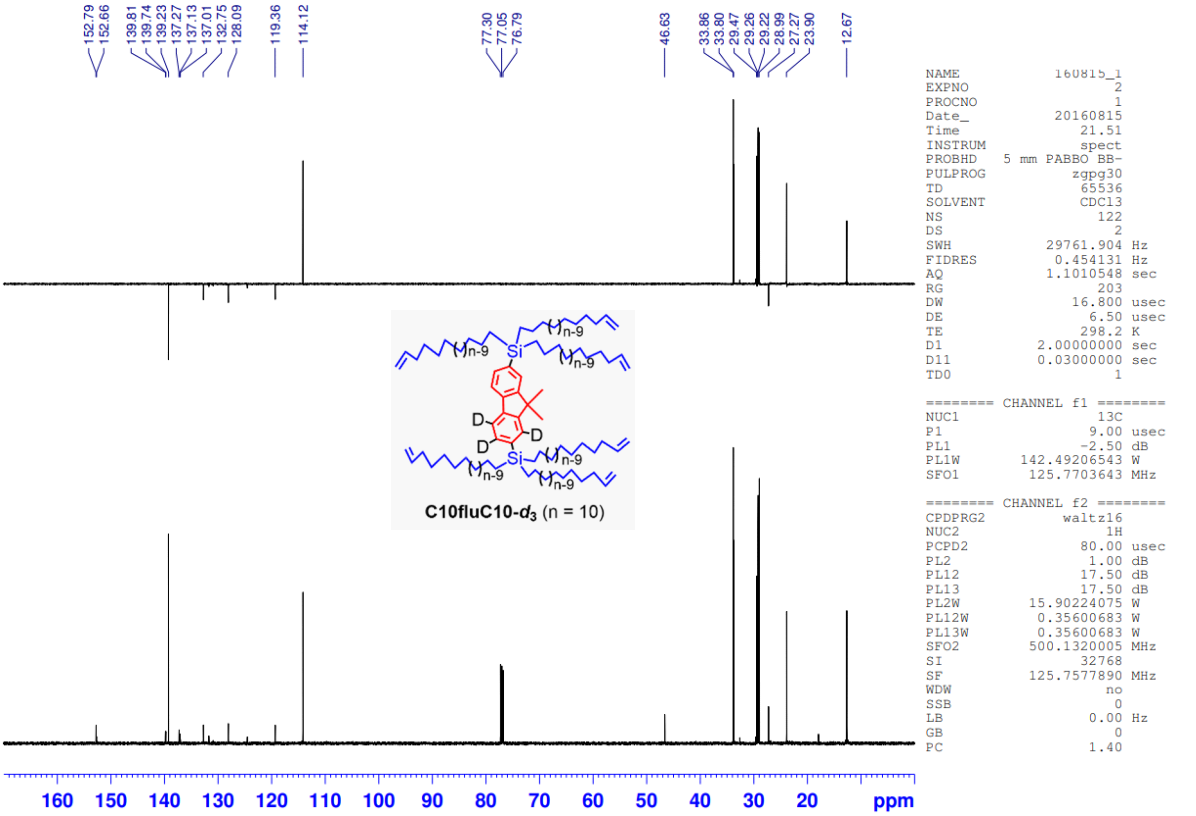


Fig. S26. ^{13}C NMR spectrum of **C10FluC10-d_3** in $CDCl_3$.

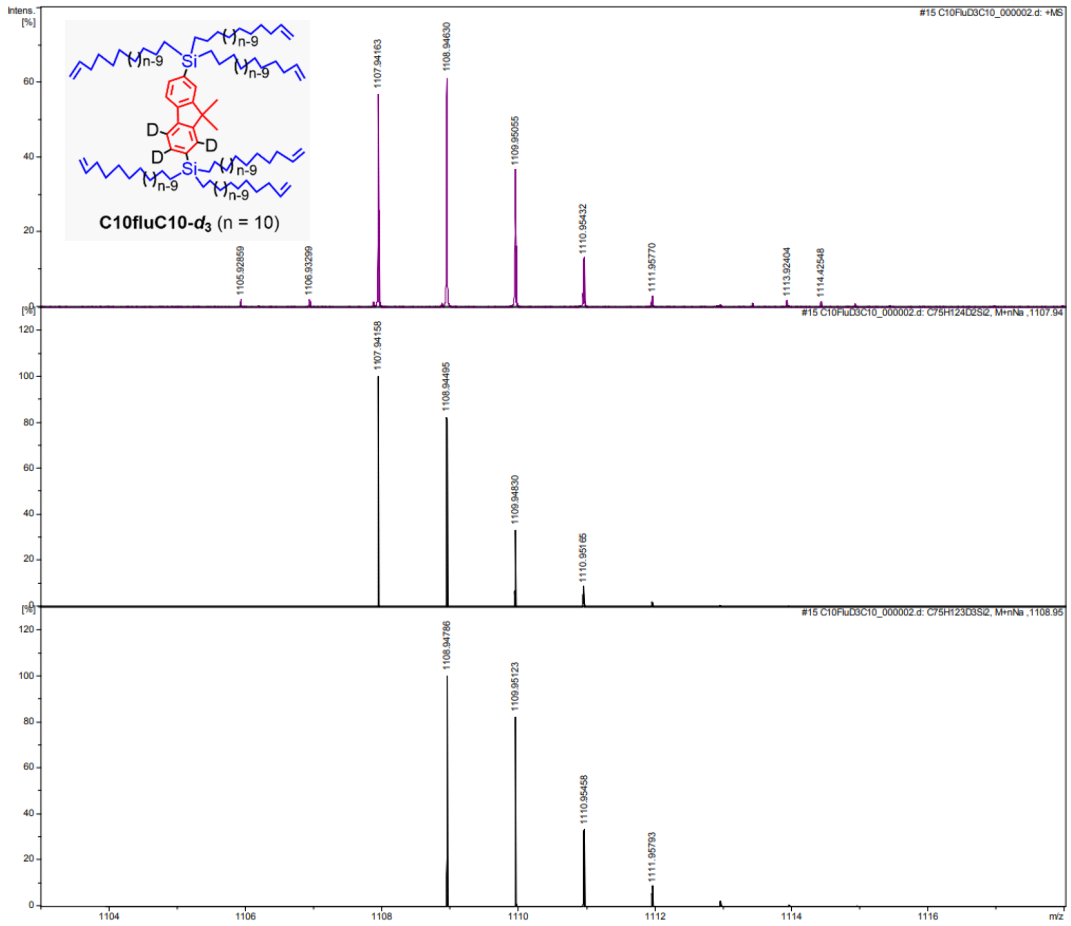


Fig. S27. HRMS spectrum of **C10FluC10-d_3** (ESI, positive). Top: obsd. Bottom: sim.

k. Spectra of C18-d_3

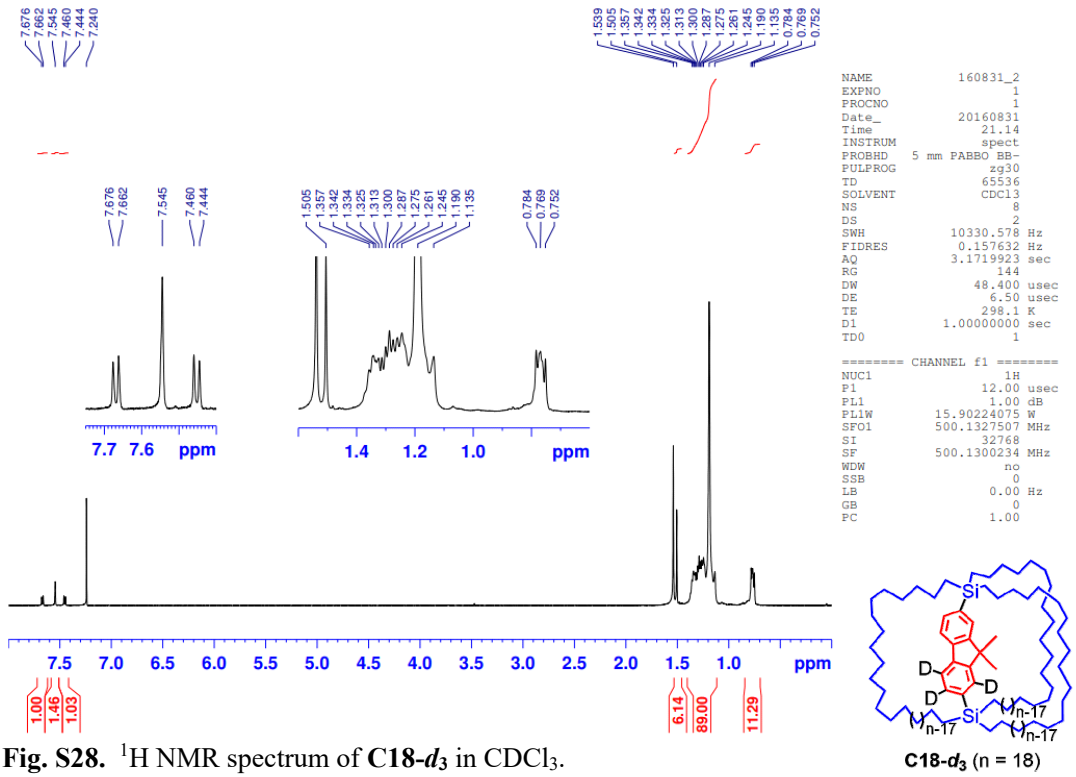


Fig. S28. ^{1}H NMR spectrum of **C18-d_3** in $CDCl_3$.

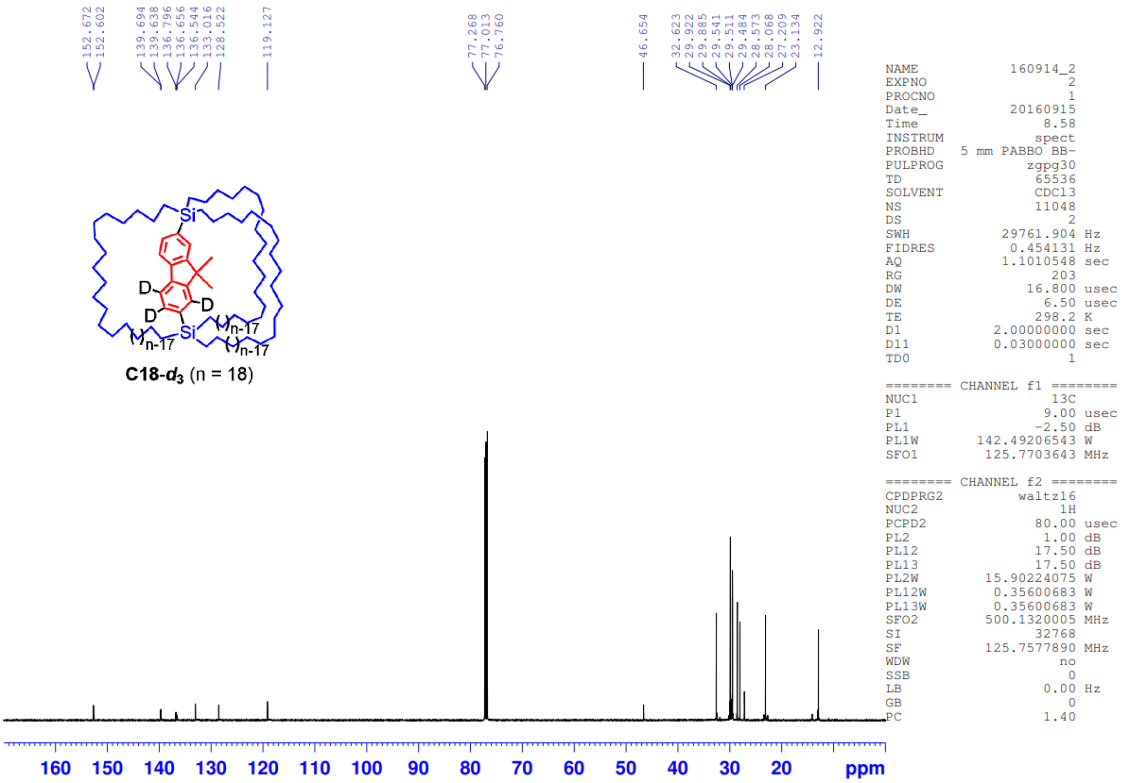


Fig. S29. ^{13}C NMR spectrum of **C18-*d*$_3$** in $CDCl_3$.

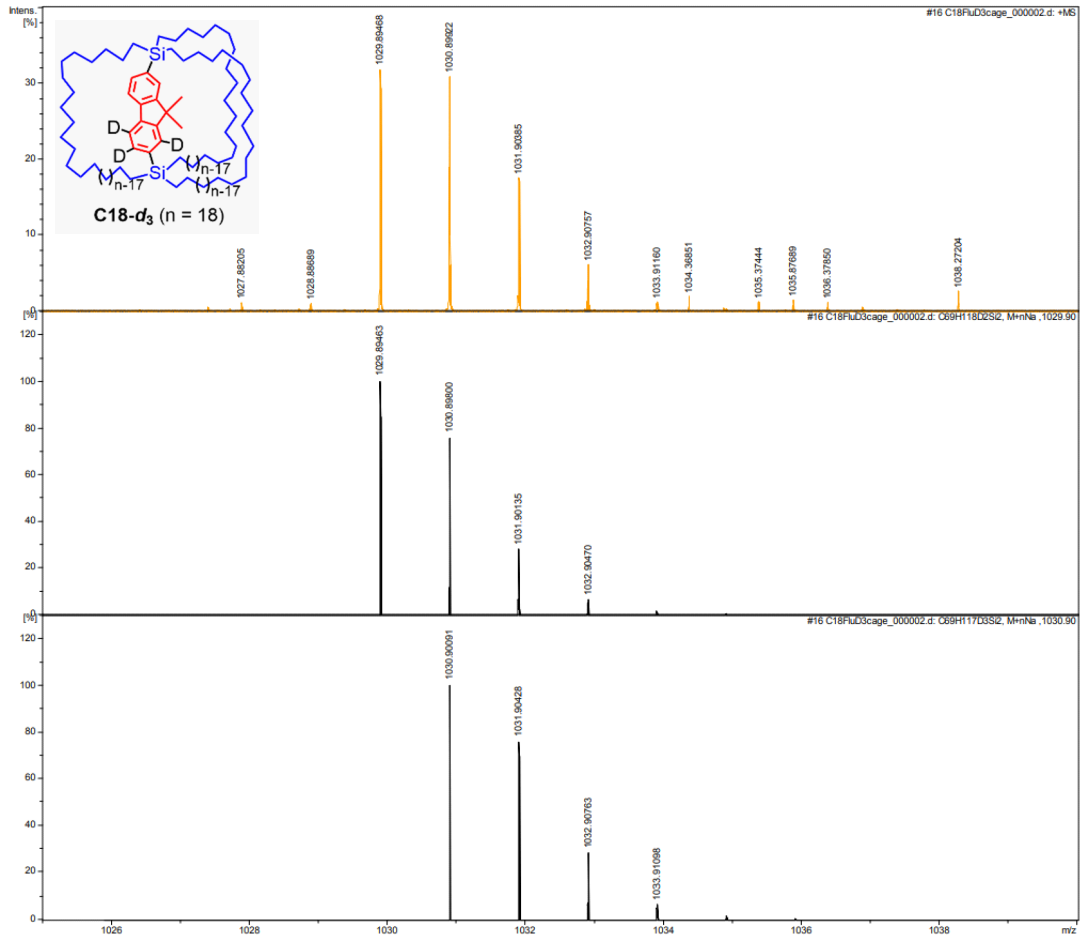


Fig. S30. HRMS spectrum of **C18-*d*$_3$** (ESI, positive). Top: obsd. Bottom: sim.

j. Spectra of C12FluC12-d_3

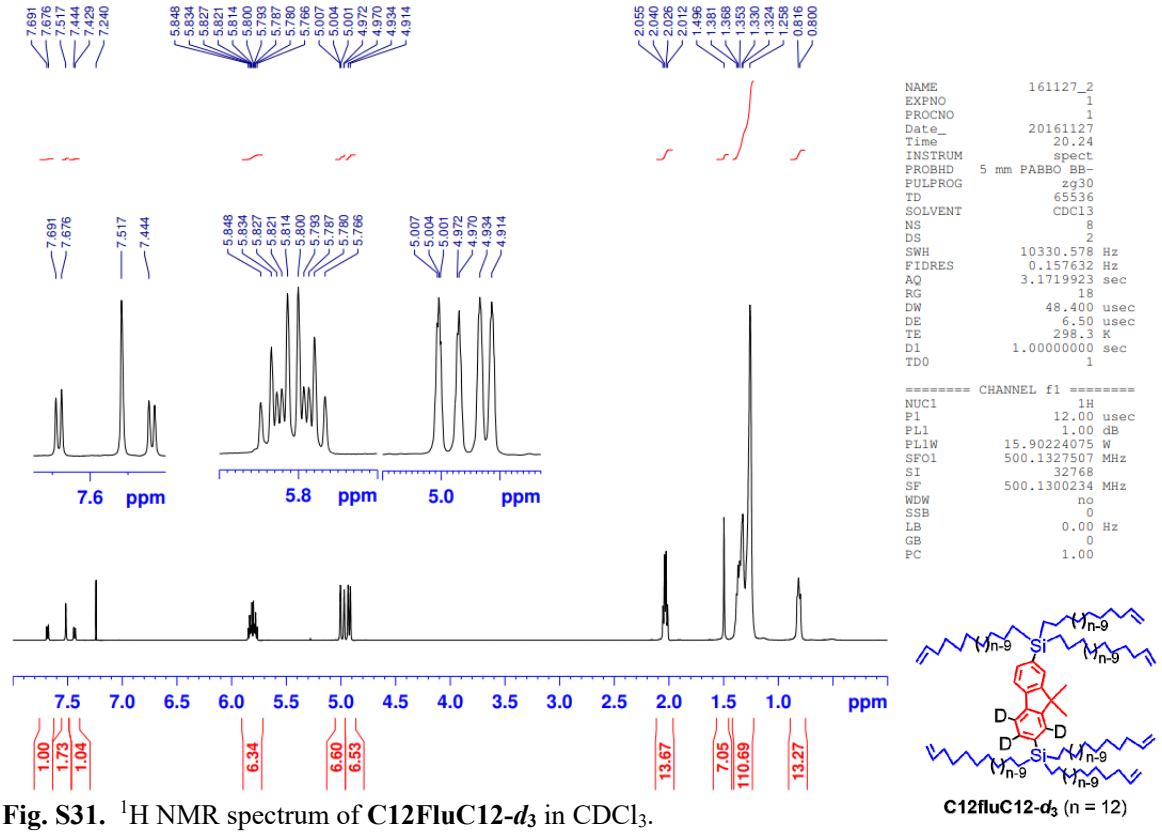


Fig. S31. ^{1}H NMR spectrum of **C12FluC12-d_3** in $CDCl_3$.

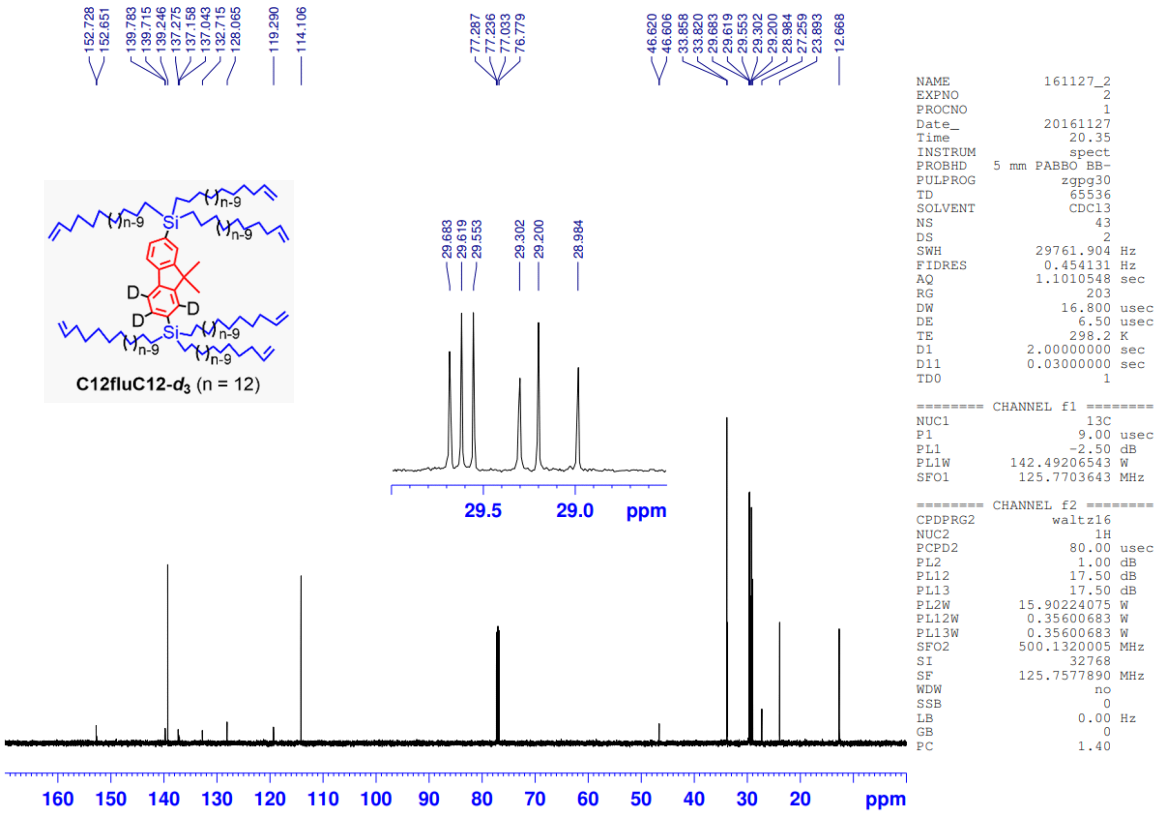


Fig. S32. ^{13}C NMR spectrum of **C12FluC10-d_3** in $CDCl_3$.

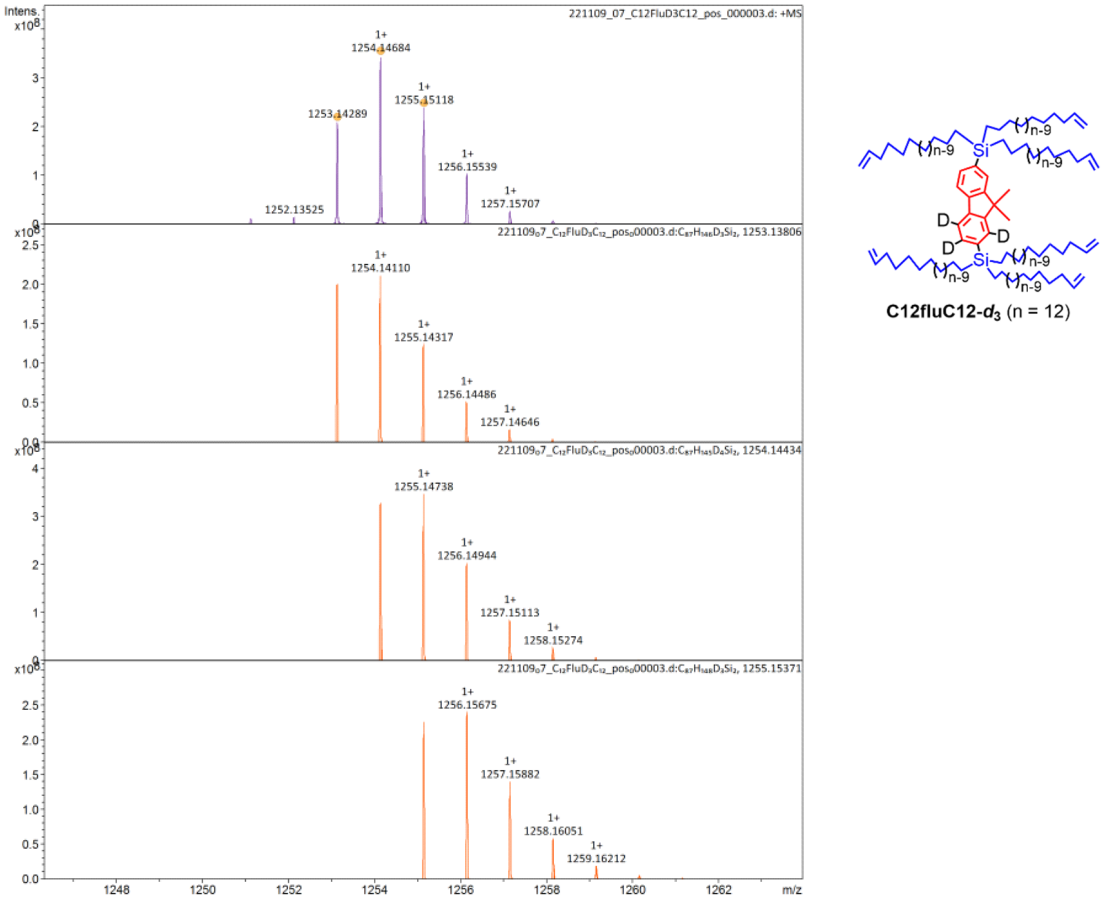
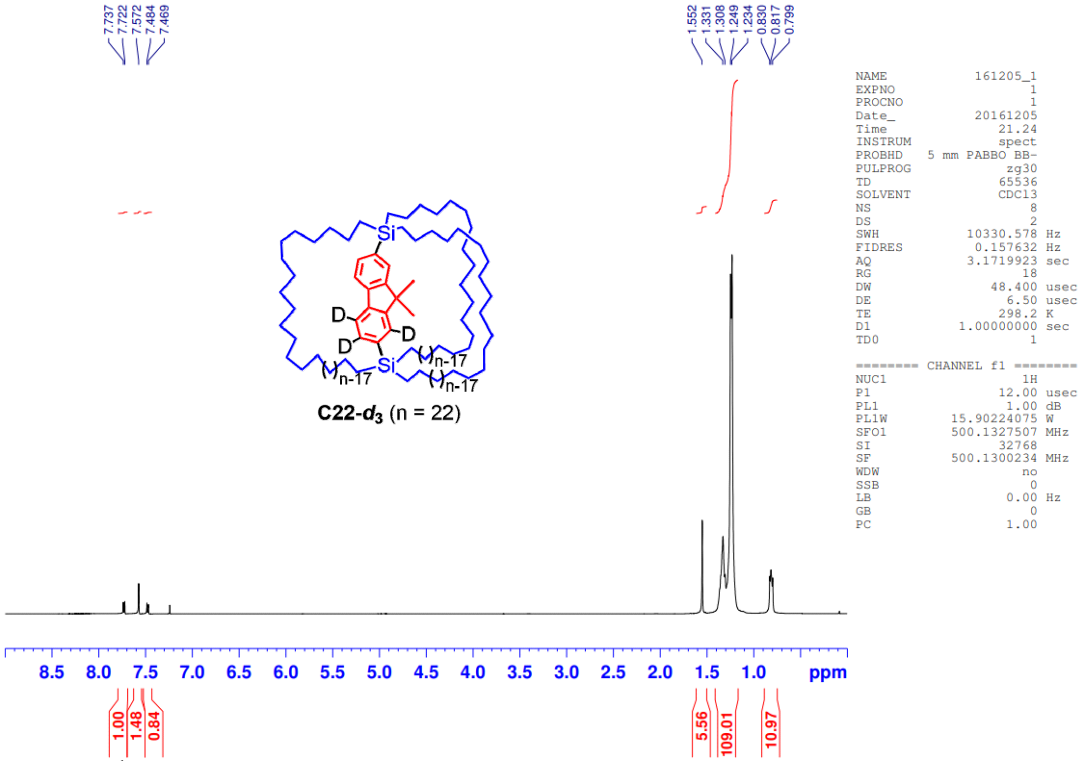


Fig. S33. HRMS spectrum of **C12FluC12-*d*$_3$** (ESI, positive). Top: obsd. Bottom: sim.

l. Spectra of C22-*d*$_3$

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D1            1.00000000 sec
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Fig. S34. ^{1}H NMR spectrum of **C22-*d*$_3$** in $CDCl_3$.

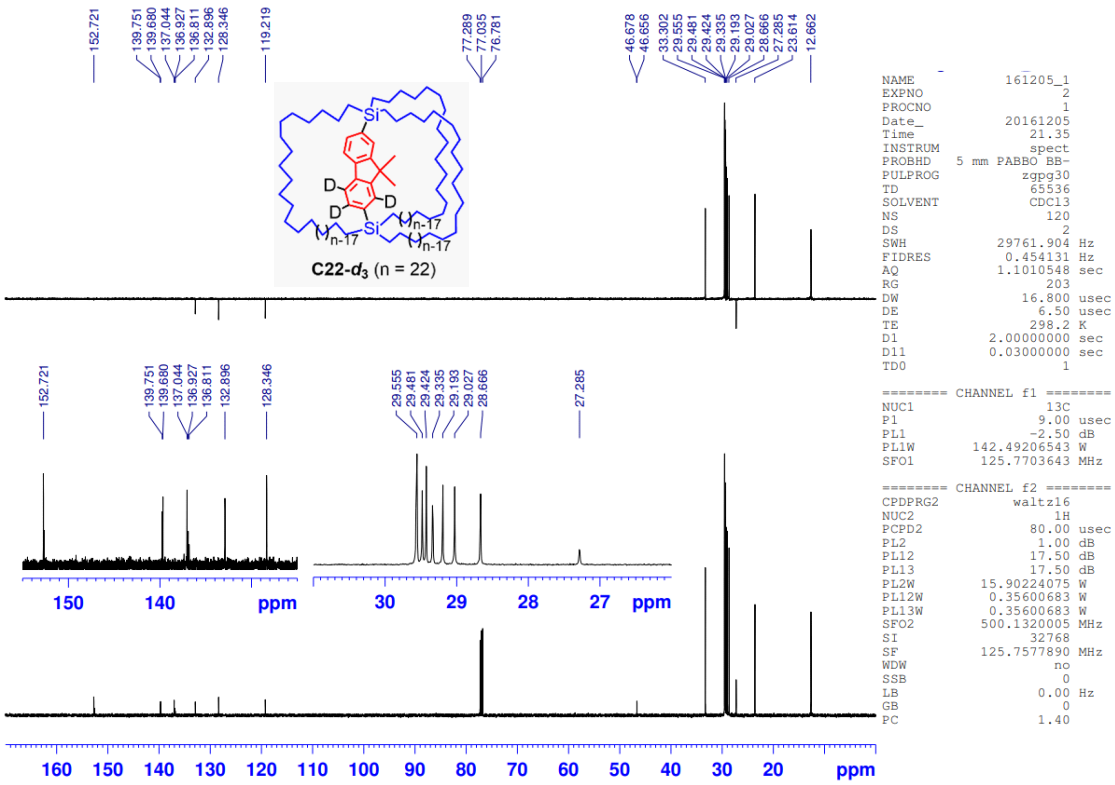

Fig. S35. ^{13}C NMR spectrum of **C22-*d*$_3$** in $CDCl_3$.

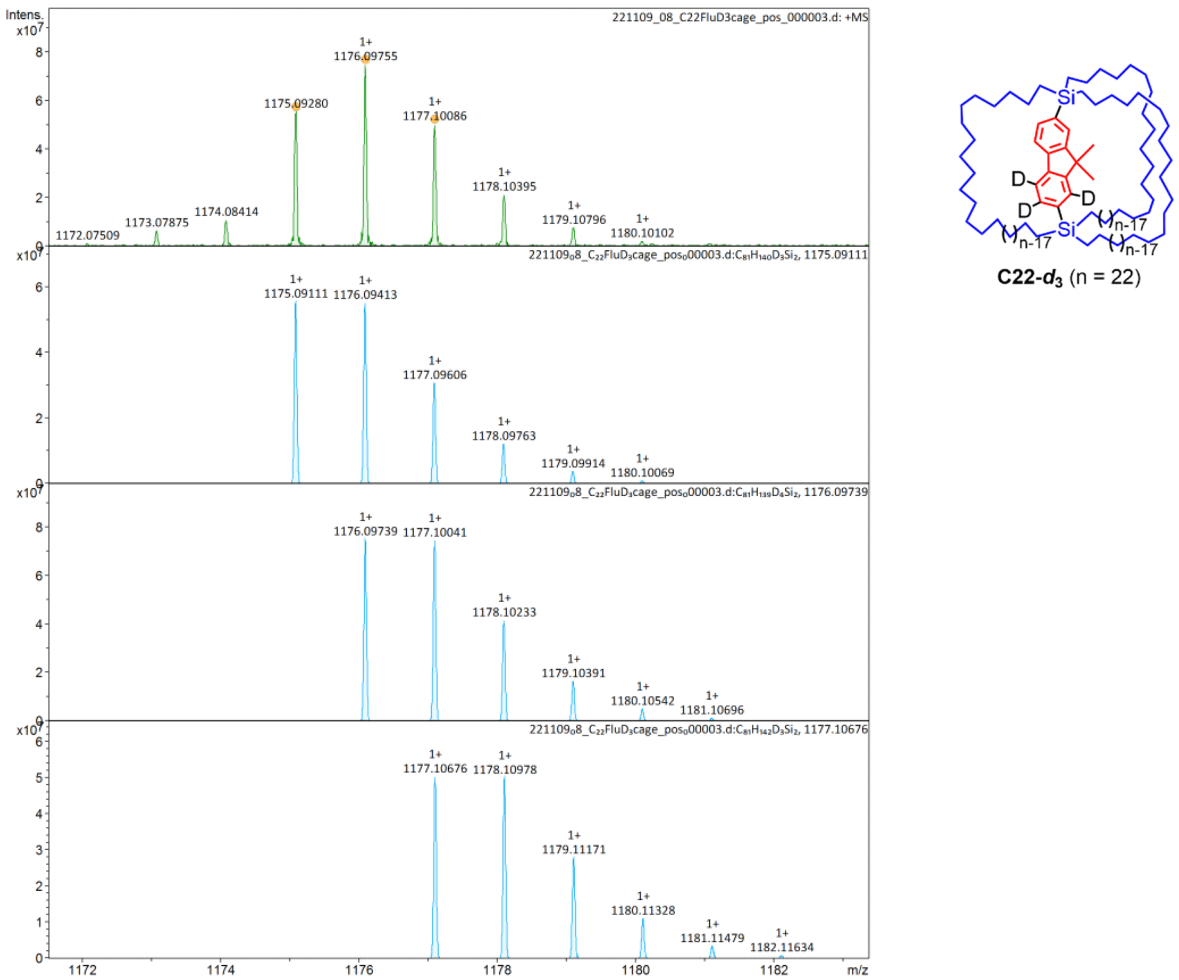

Fig. S36. HRMS spectrum of **C22-*d*$_3$** (ESI, positive). Top: obsd. Bottom: sim.

2. Appended Data of X-ray Crystallography

2-1. Crystal Data

Table S1. Crystal Data

Compound		C18	C22•2EtOH	Flu	TMS
CCDC #		2223164	2223165	2239859	2239860
Empirical formula		C69 H120 Si2	C81 H144 Si2, 2(C2 H6 O)	C15 H14	C21 H30 Si2
Temperature		200(2) K	180(2) K	200(2) K	200(2) K
Crystal shape & Color		Prism, colorless	Prism, colorless	Prism, colorless	Prism, colorless
Crystal size		0.150 x 0.140 x 0.100 mm^3	0.200 x 0.100 x 0.080 mm^3	0.400 x 0.200 x 0.100 mm^3	0.300 x 0.150 x 0.100 mm^3
Formula weight / g mol^{-1}		1005.82	1266.27	194.26	338.63
Crystal system		Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group		*P*-1	*C*2/*c*	$I4_1/a$	$P2_1/c$
Z		2	8	16	4
Calculated density		0.995 Mg/m^3	0.994 Mg/m^3	1.130 Mg/m^3	1.068 Mg/m^3
Cell parameter	*a*	11.6403(14) Å	34.1454(8) Å	21.6843(2) Å	14.1329(3) Å
	b	18.4301(10) Å	24.9090(6) Å	21.6843(2) Å	6.59460(10) Å
	c	18.5637(16) Å	22.8091(5) Å	9.7108(2) Å	23.4684(5) Å
	α	60.565(11)°	90°	90°	90°
	β	80.343(15)°	119.3180(10)°	90°	105.6690(10)°
	γ	75.890(15)°	90°	90°	90°
	V	3358.3(8) $Å^3$	16915.0(7) $Å^3$	4566.10(13) $Å^3$	2105.99(7) $Å^3$
F(000)		1124	1140	1664	736
Absorption coefficient		0.089 mm^{-1}	0.676 mm^{-1}	0.476 mm^{-1}	1.491 mm^{-1}
***θ* range for collection**		3.020 to 25.000° (MoKα)	2.313 to 67.998° (CuKα)	6.450 to 77.434° (CuKα)	3.912 to 77.432° (CuKα)
Index ranges		-13<=h<=13, -21<=k<=21, -22<=l<=22	-40<=h<=41, -29<=k<=29, -27<=l<=27	-27<=h<=24, -26<=k<=26, -12<=l<=11	-16<=h<=17, -7<=k<=6, -29<=l<=28
Reflections collected		51256	70491	18692	17125
Independent reflections		11729 [R(int) = 0.1803]	15353 [R(int) = 0.1011]	2400 [R(int) = 0.0372]	4309 [R(int) = 0.0296]
Completeness		99.3 %	99.6 %	99.6 %	98.7 %
Goodness-of-fit on F^2		1.060	1.434	1.078	1.082
Final R indices [I>2sigma(I)]		R1 = 0.1248, wR2 = 0.3516	R1 = 0.1390, wR2 = 0.3924	R1 = 0.0536, wR2 = 0.1285	R1 = 0.0410, wR2 = 0.1049
R indices (all data)		R1 = 0.2064, wR2 = 0.3847	R1 = 0.1921, wR2 = 0.4429	R1 = 0.0564, wR2 = 0.1311	R1 = 0.0420, wR2 = 0.1059

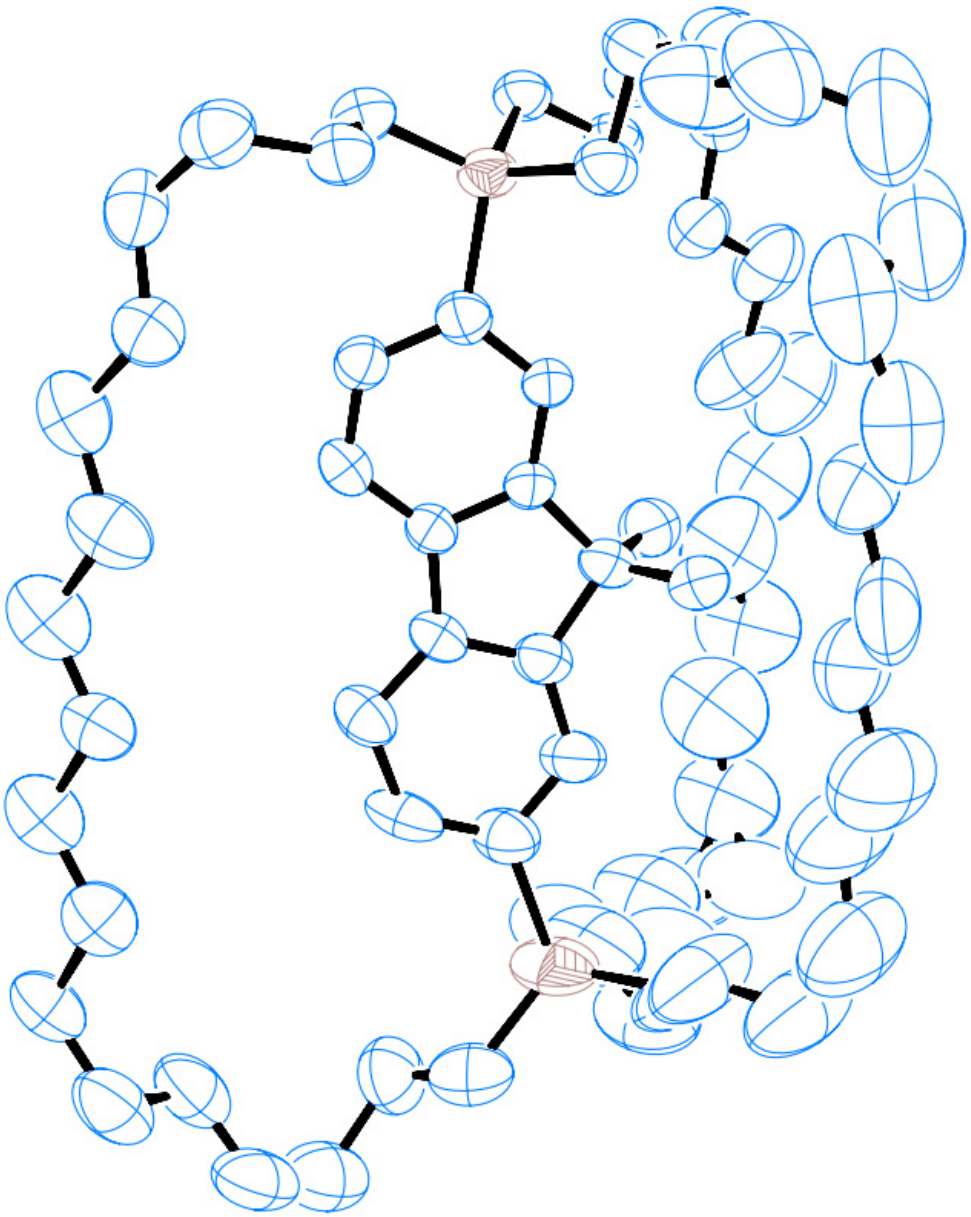

Fig. S37. An ORTEP drawing (30% thermal ellipsoids) of molecular structure of **C18** determined by X-ray crystallography.

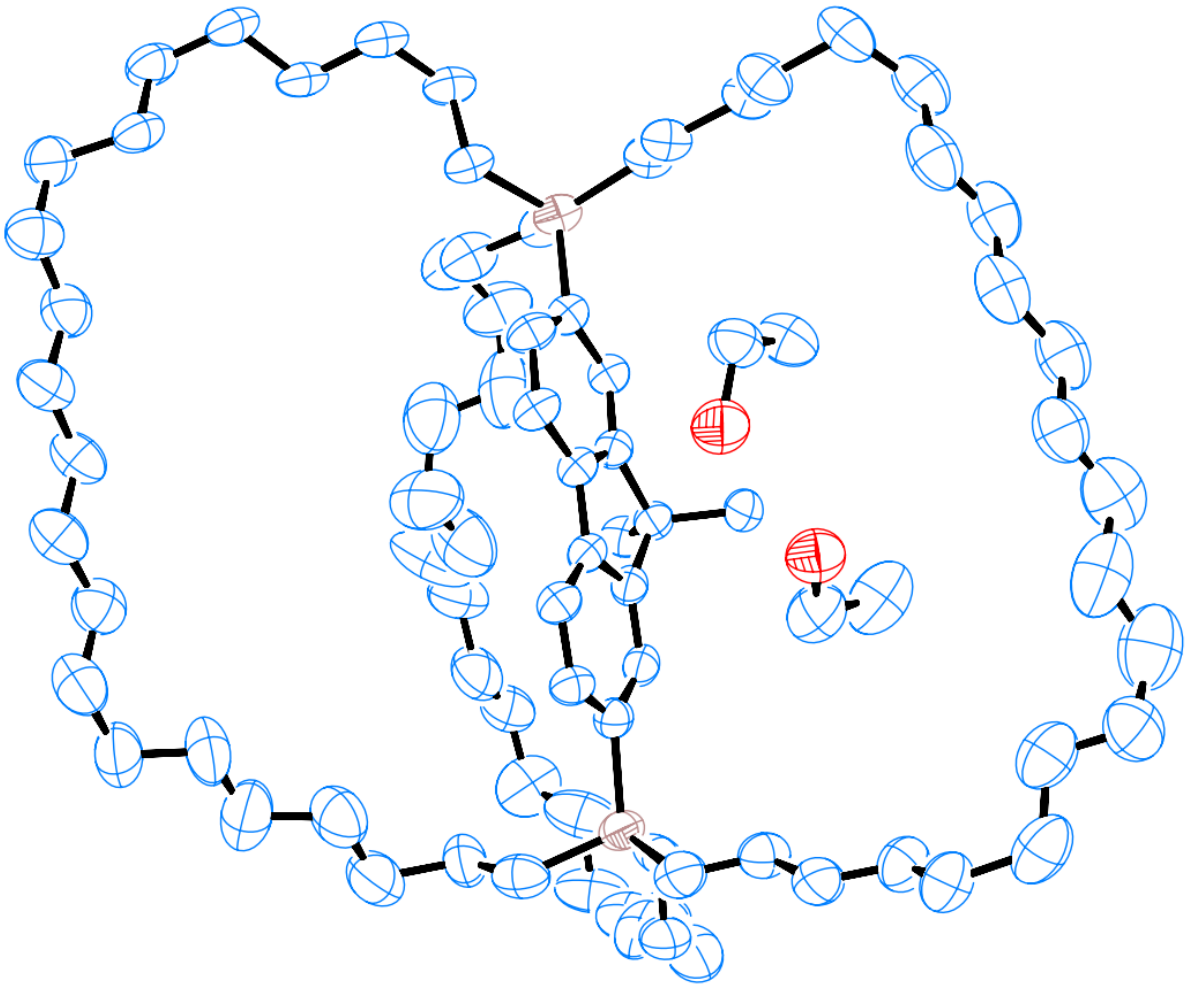

Fig. S38. An ORTEP drawing (30% thermal ellipsoids) of molecular structure of **C22•2EtOH** determined by X-ray crystallography.

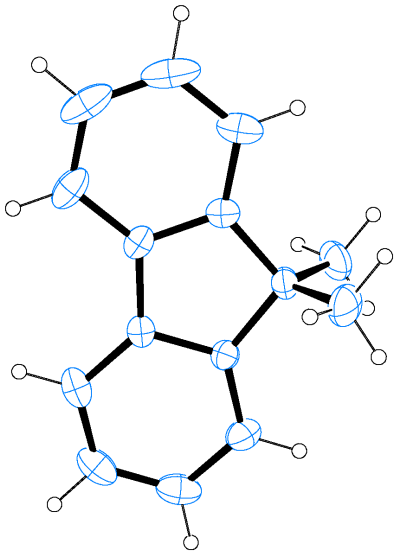

Fig. S39. An ORTEP drawing (30% thermal ellipsoids) of molecular structure of **Flu** determined by X-ray crystallography.

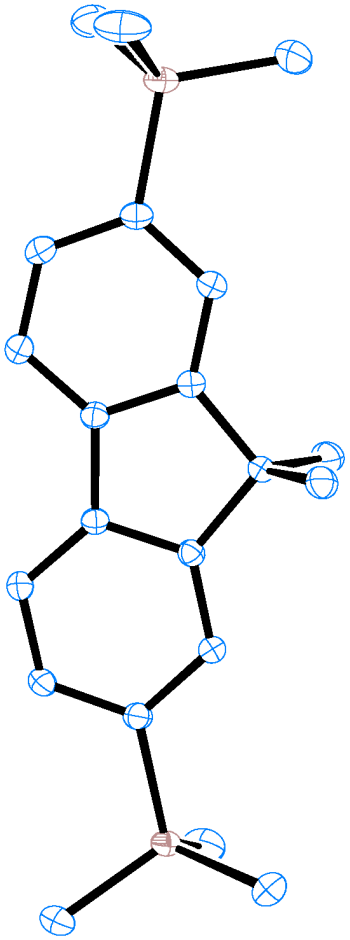

Fig. S40. An ORTEP drawing (30% thermal ellipsoids) of molecular structure of **TMS** determined by X-ray crystallography.

3. Appended Data of Fluorescence Measurements

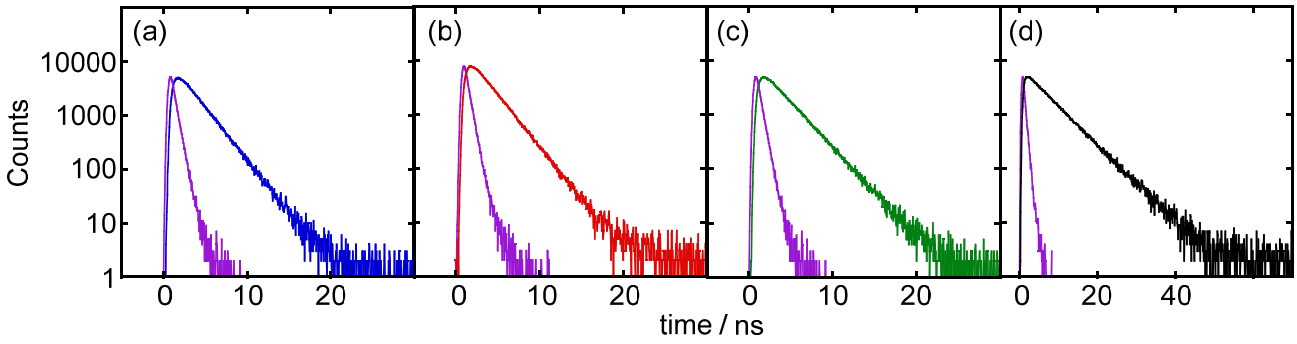

Fig. S41. Fluorescence life-time measurements for fluorenes in hexane (The excitation pulse was indicated with purple line.) : (a) **C18**, (b) **C22**, (c) **TMS**, and (d) **Flu**.

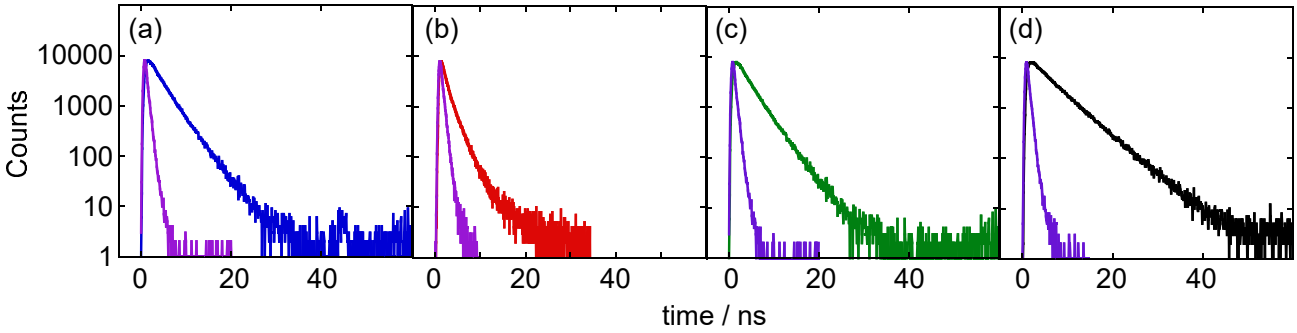

Fig. S42. Fluorescence life-time measurements for fluorenes in solid-states (The excitation pulse was indicated with purple line.): (a) **C18**, (b) **C22**, (c) **TMS**, and (d) **Flu**.

4. Appended Data of Solid-state ^{2}H NMR Study

a. Analysis of ^{2}H NMR spin-lattice relaxation (T_1) measurements

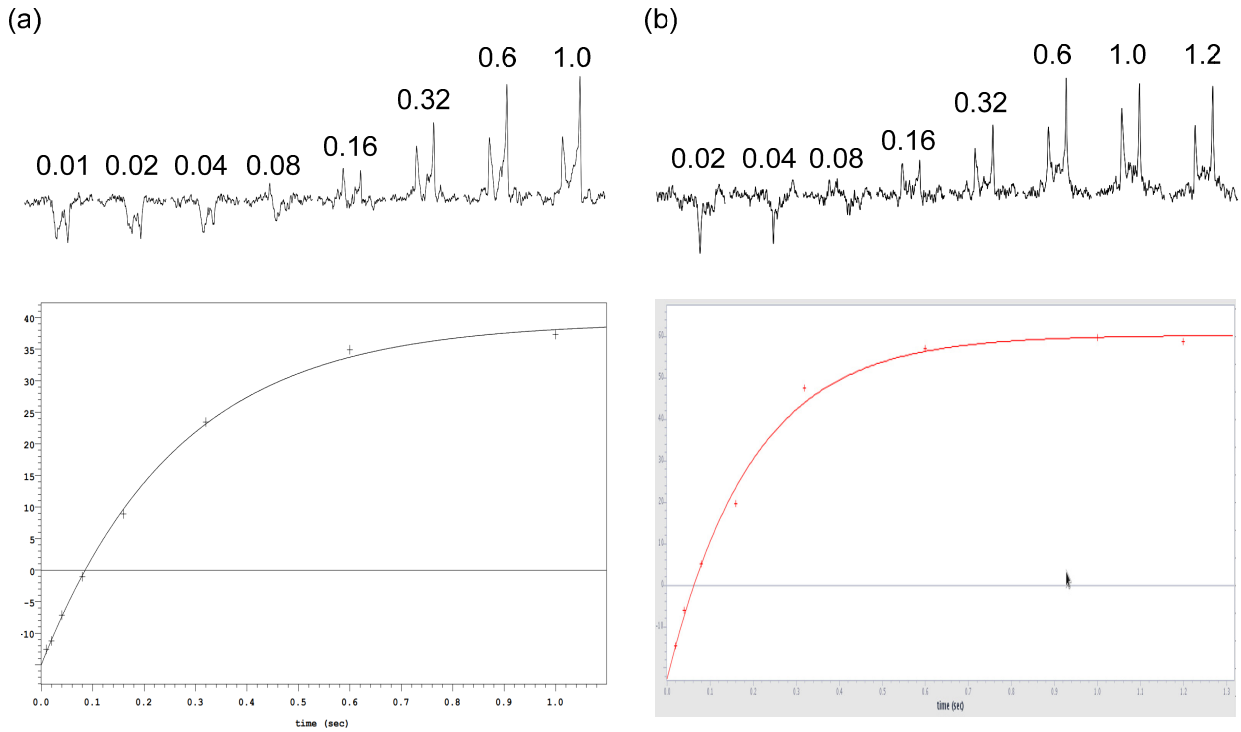

Figure S43 Inversion-recovery ^{2}H NMR spectroscopy data (300 K) and single exponential fit of (a) **C18-d_3** and (b) **C22-d_3**.