Cover Page for Supporting Information

Well-Defined Styryl and Biphenyl Calcium Complexes from Dilithio Compounds and Calcium Iodide: Synthesis, Structure and Reactivity toward Nitrous Oxide

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1) ^{1}H NMR and ^{13}C NMR Spectra of Compounds

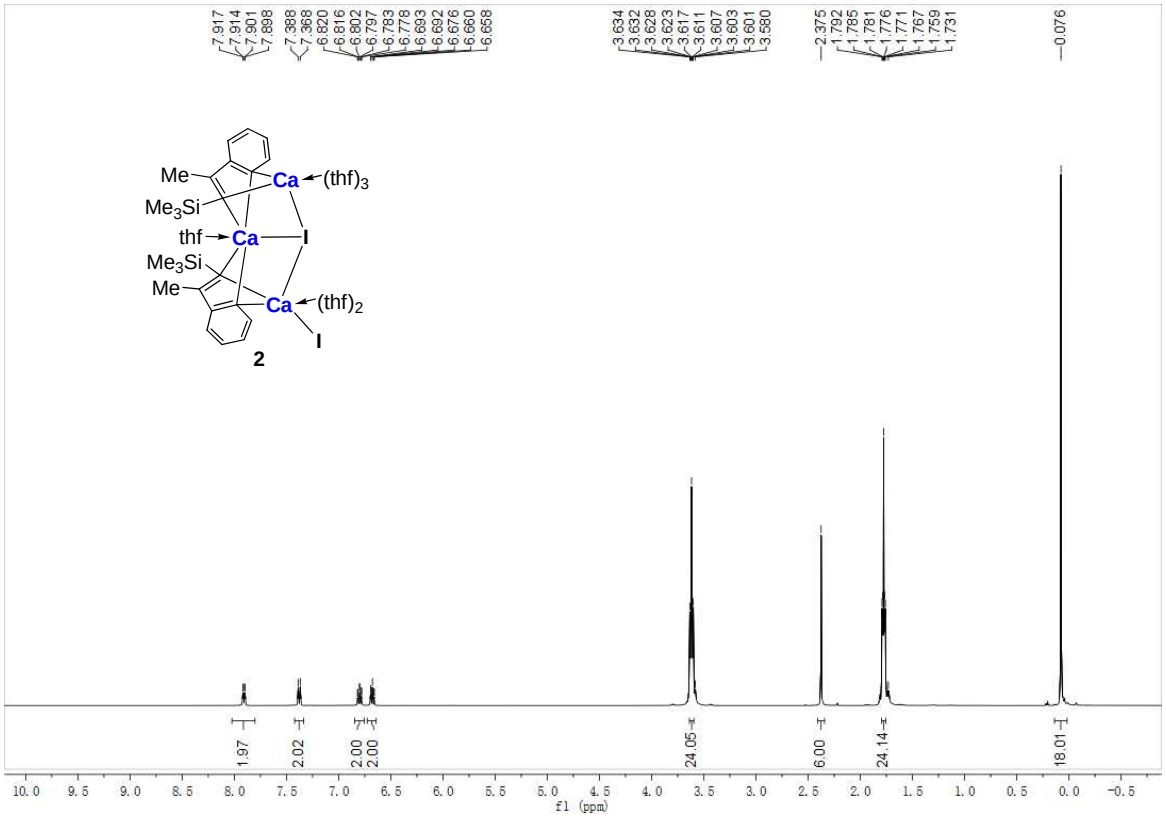

Figure S1. ^{1}H NMR Spectrum (400 MHz, d^{8}-THF) of Complex **2**

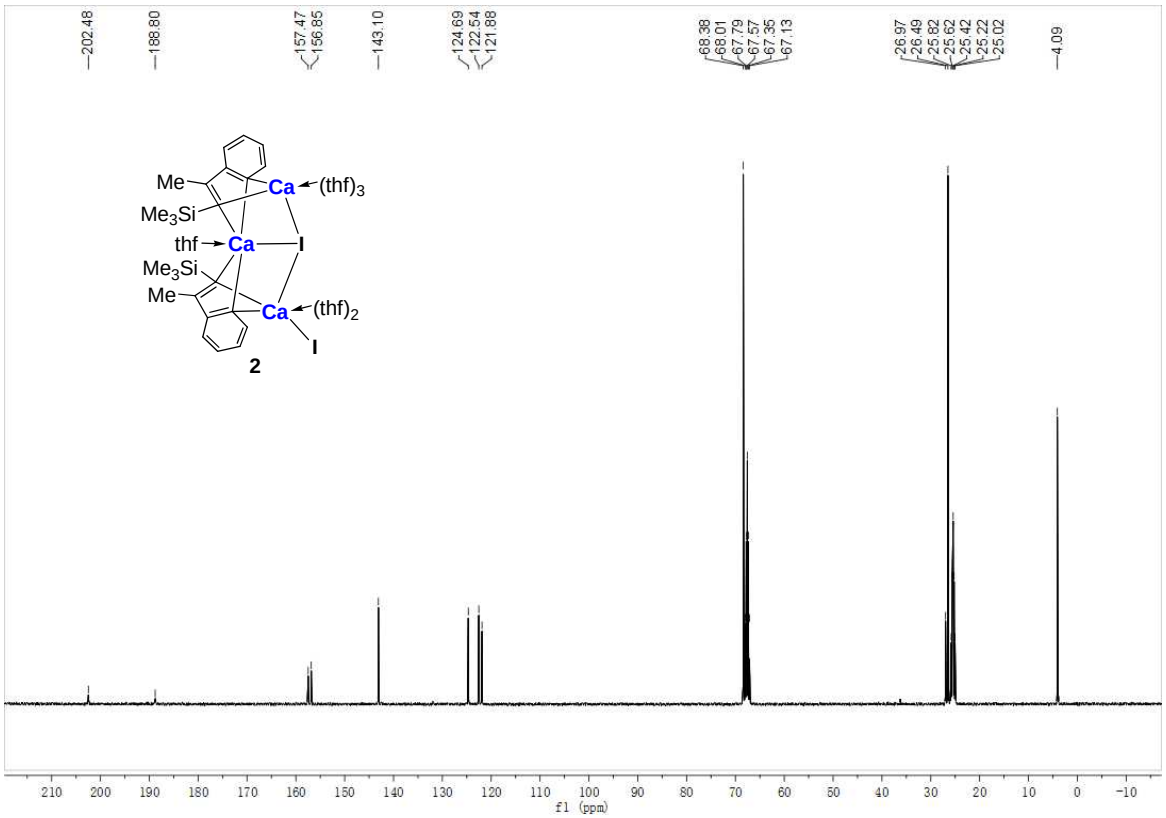

Figure S2. ^{13}C NMR Spectrum (100 MHz, d^{8}-THF) of Complex **2**

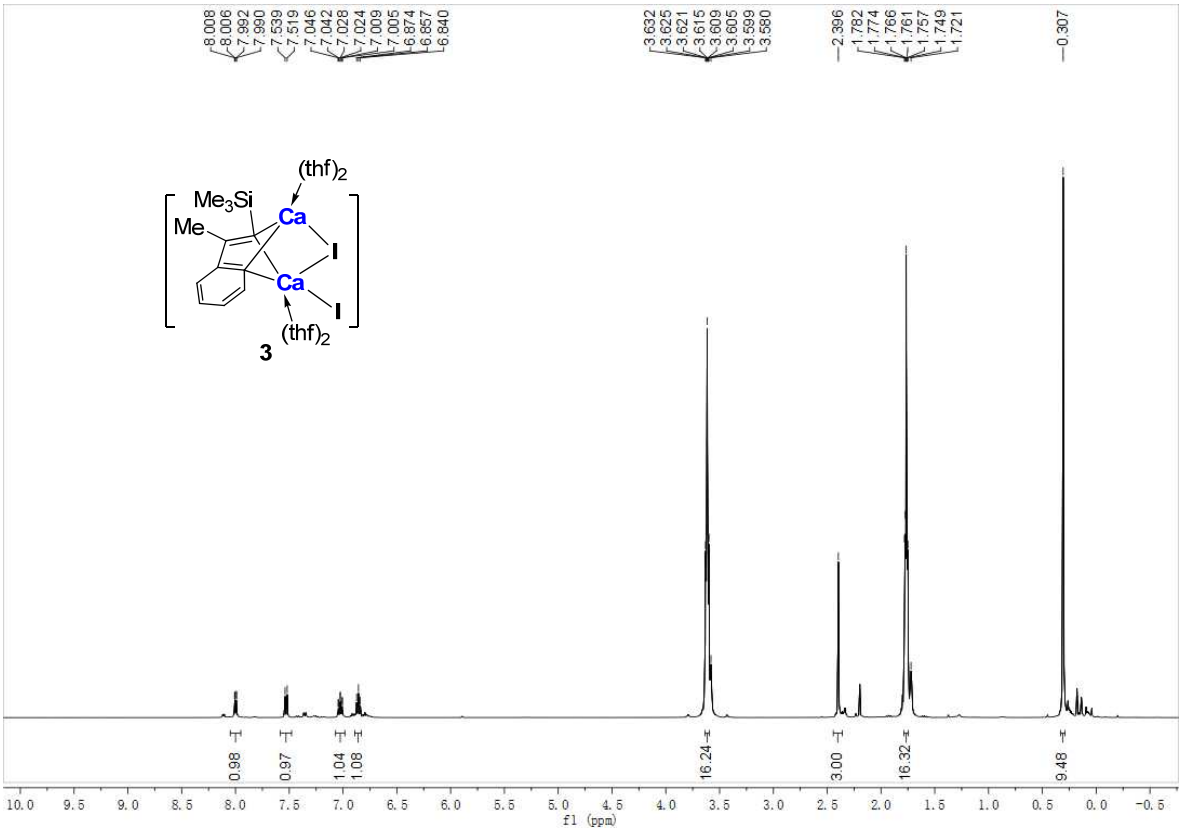

Figure S3. ^{1}H NMR Spectrum (400 MHz, d^{8}-THF) of Intermediate **3**

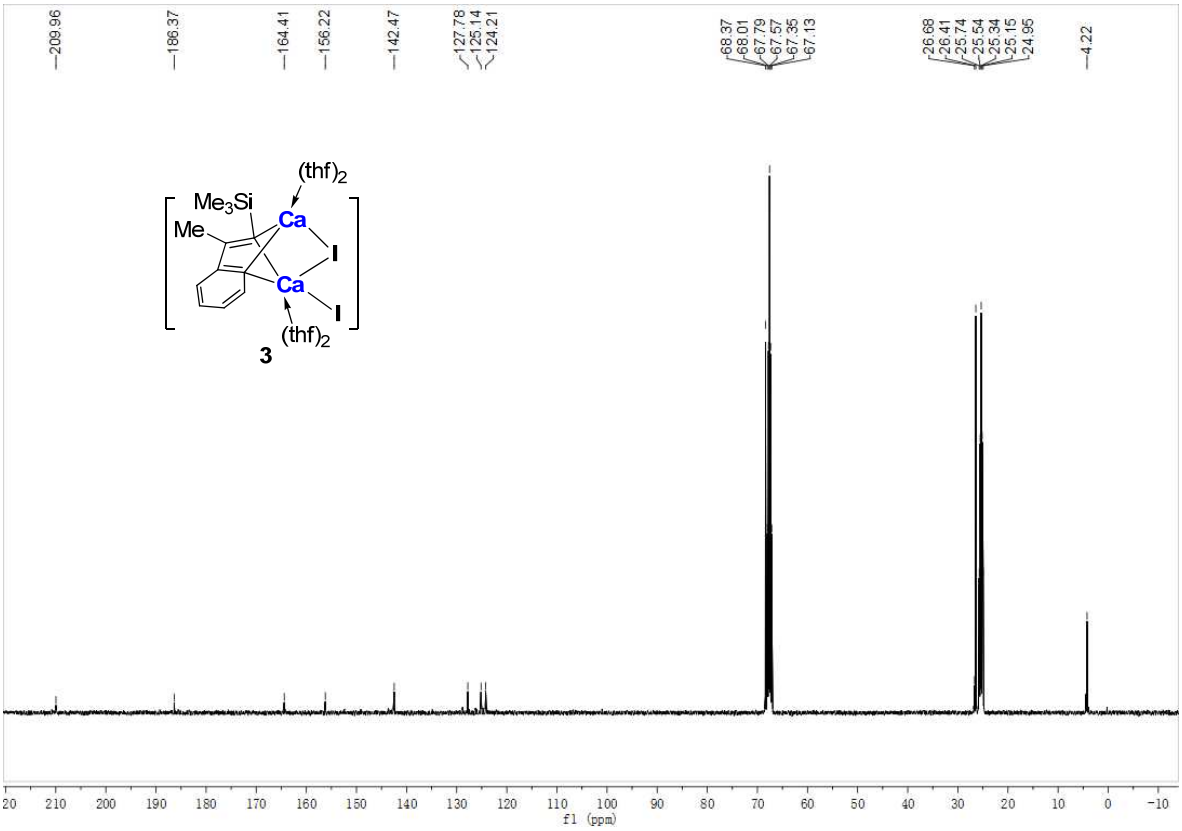

Figure S4. ^{13}C NMR Spectrum (100 MHz, d^{8}-THF) of Intermediate **3**

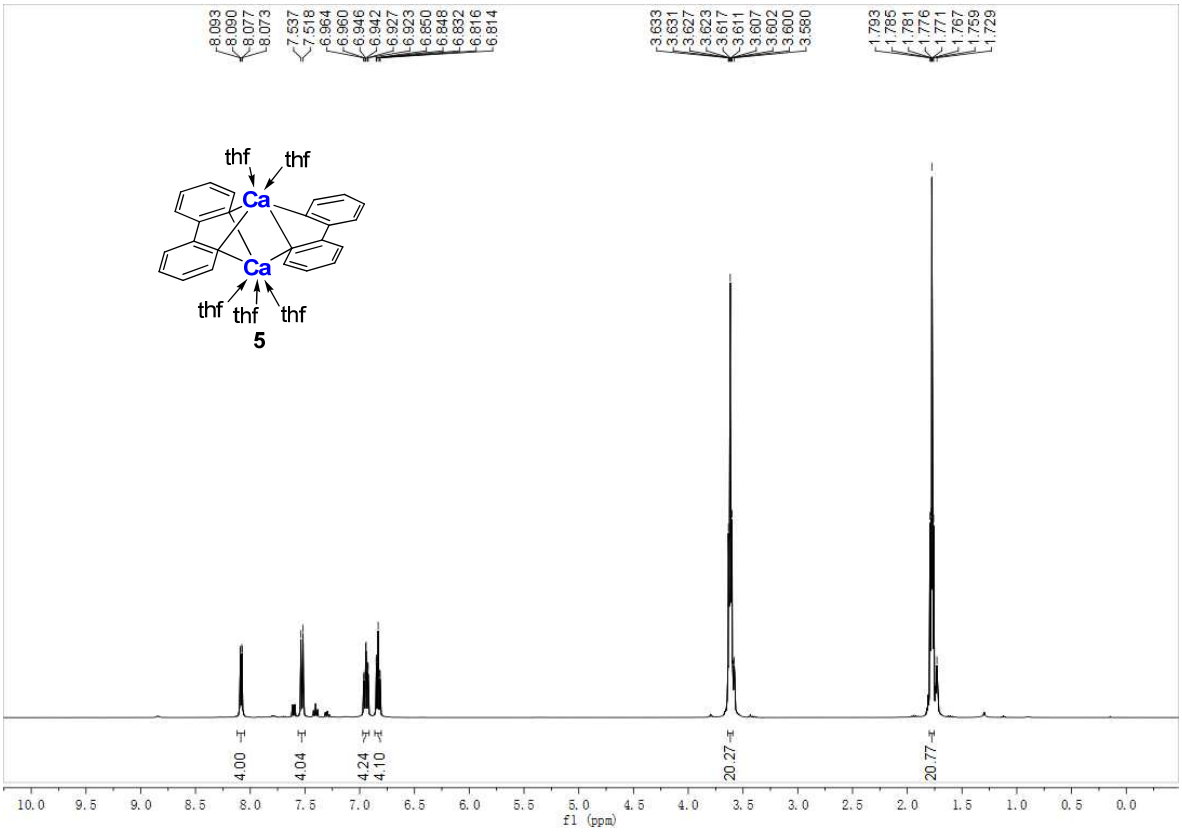

Figure S5. ^{1}H NMR Spectrum (400 MHz, d^{8}-THF) of Complex **5**

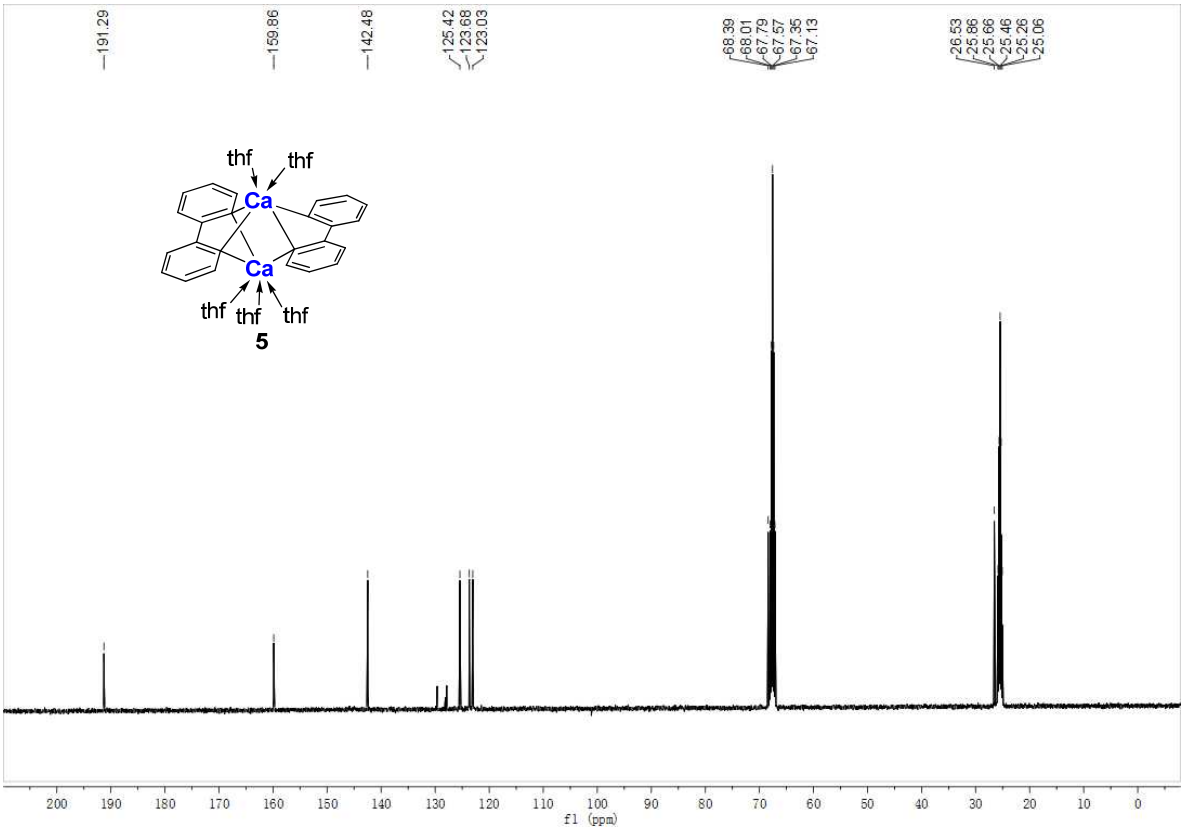

Figure S6. ^{13}C NMR Spectrum (100 MHz, d^{8}-THF) of Complex **5**

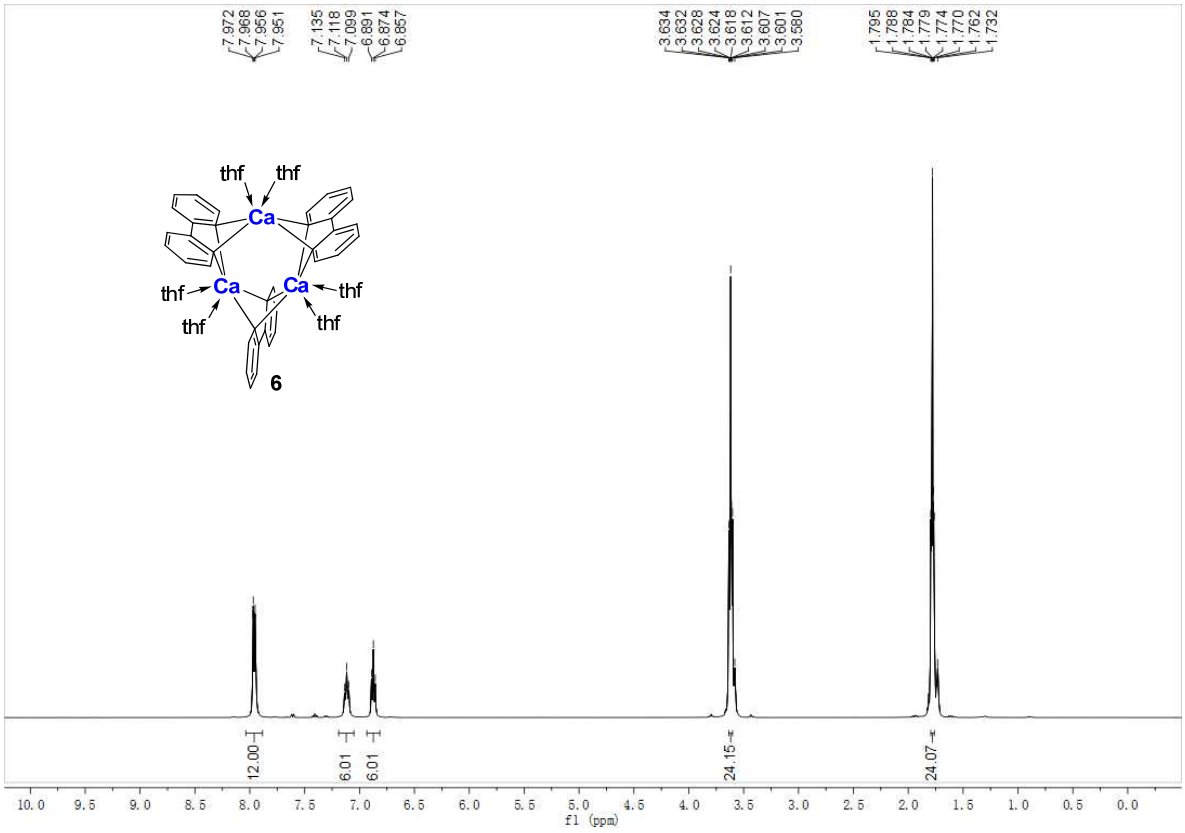

Figure S7. ^{1}H NMR Spectrum (400 MHz, d^{8}-THF) of Complex **6**

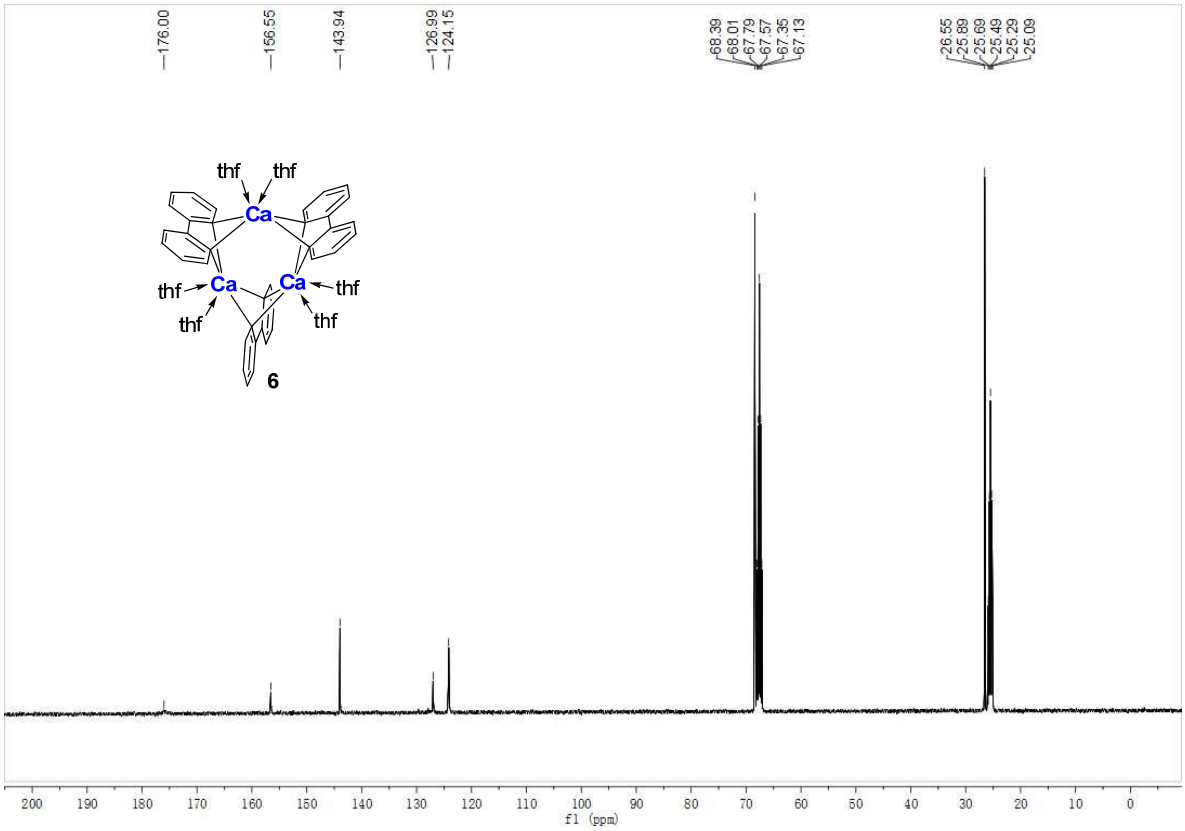

Figure S8. ^{13}C NMR Spectrum (100 MHz, d^{8}-THF) of Complex **6**

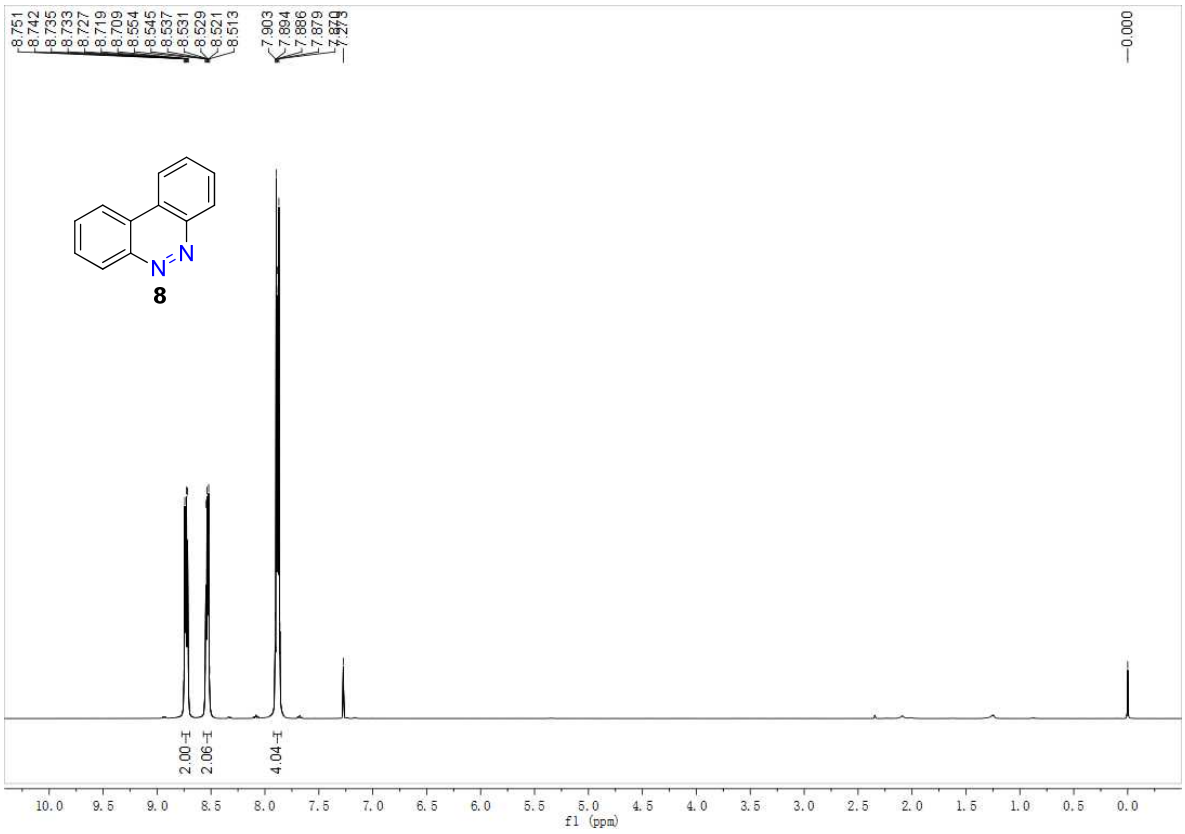

Figure S9. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **8**

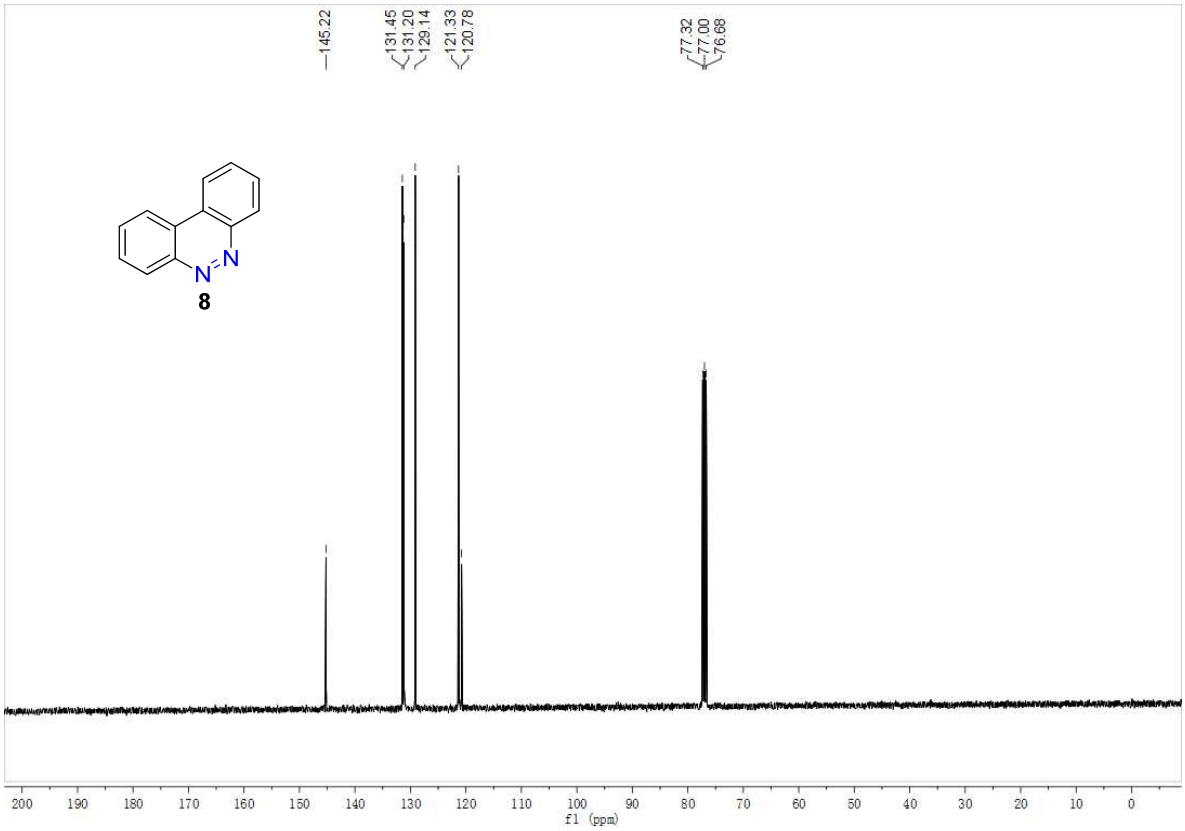

Figure S10. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **8**

2) X-ray Crystallographic Study

Single crystals of **2** suitable for X-ray analysis were grown in mixed Et_2O/THF (20:1) solvent at -28°C for 3 days. Single crystals of **5** suitable for X-ray analysis were grown in THF at -28°C with exposure to hexane vapor for 3 days. Single crystals of **6** suitable for X-ray analysis were grown in toluene/THF (10:1) at -28°C with exposure to hexane vapor for 3 days. Data collections for them were performed at 180 K or 130 K on a XtaLAB Pro: Kappa single diffractometer using Mo Kα radiation (λ = 0.71073 Å). Using Olex2, the structures were solved with Superflip solution program using Charge Flipping or ShelXS-97 solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. A very large solvent accessible void in **2** was squeezed by using Platon. In all of the structures, the commands DELU, SIMU and ISOR were applied to mostly restrain the disorders of coordinated THF molecules. In the structure of **6**, the command AFIX 66 was applied to constrain one benzene ring. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1823281 (**2**), CCDC-1823282 (**5**), CCDC-1823283 (**6**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

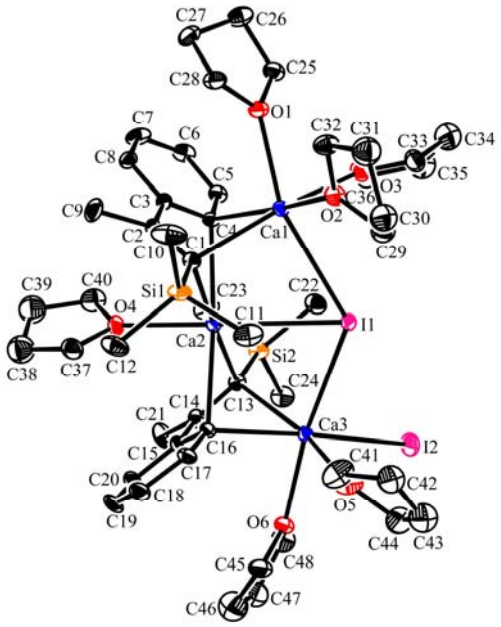

Figure S11. ORTEP drawing of **2** with 20% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S1 Crystal data and structure refinement for 2.

Identification code	**2**
Empirical formula	$C_{48}H_{80}Ca_3I_2O_6Si_2$
Formula weight	1183.34
Temperature/K	180.0(3)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.3201(2)
b/Å	17.4852(4)
c/Å	34.1897(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7365.1(2)
Z	4
ρ_{calc}g/cm^3	1.067
μ/mm^{-1}	1.127
F(000)	2440.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.014 to 52.042
Index ranges	$-15 \le h \le 15$, $-21 \le k \le 21$, $-42 \le l \le 42$
Reflections collected	141676
Independent reflections	14478 [R_{int} = 0.0362, R_{sigma} = 0.0170]
Data/restraints/parameters	14478/160/558
Goodness-of-fit on F^2	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1492
Final R indexes [all data]	R_1 = 0.0538, wR_2 = 0.1520
Largest diff. peak/hole / e Å^{-3}	1.33/-0.78

Flack parameter	0.191(4)

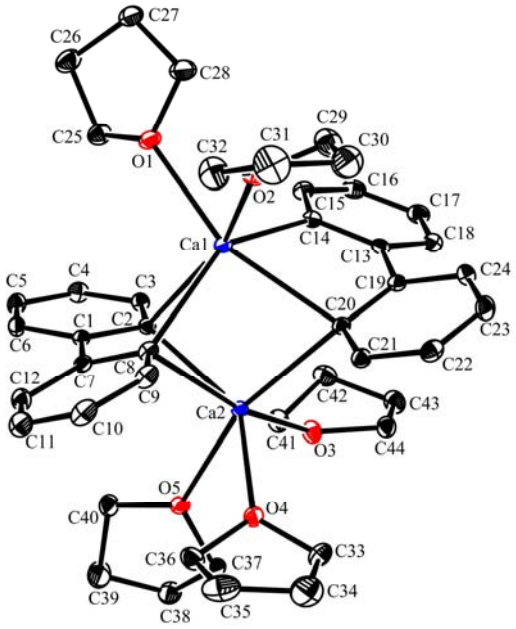

Figure S12. ORTEP drawing of **5** with 20% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S2 Crystal data and structure refinement for 5.

Identification code	**5**
Empirical formula	$C_{44}H_{56}Ca_2O_5$
Formula weight	745.04
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.1464(3)
b/Å	14.7588(2)
c/Å	20.6595(5)
α/°	90
β/°	126.1900(10)
γ/°	90
Volume/Å^3	3973.32(14)

Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.331
F(000)	1600.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.79 to 52.044
Index ranges	-17 ≤ h ≤ 19, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	47278
Independent reflections	7796 [R_{int} = 0.0382, R_{sigma} = 0.0258]
Data/restraints/parameters	7796/52/460
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1043
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.72/-0.56

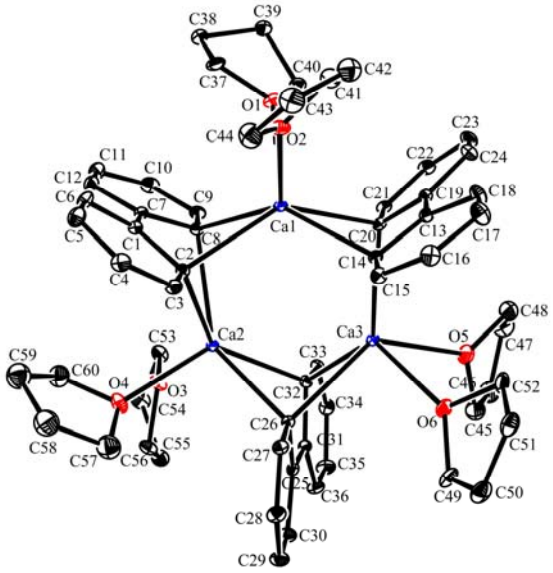

Figure S13. ORTEP drawing of **6** with 20% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S3 Crystal data and structure refinement for 6.

Identification code	**6**
Empirical formula	$C_{60}H_{72}Ca_3O_6$
Formula weight	1009.41
Temperature/K	130.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.2714(2)
b/Å	21.1518(5)
c/Å	37.3847(5)
α/°	88.6660(10)
β/°	85.4240(10)
γ/°	80.768(2)
Volume/Å^3	7990.9(3)
Z	6
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	0.360
F(000)	3240.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.71 to 52.044
Index ranges	$-12 \leq h \leq 12$, $-26 \leq k \leq 26$, $-46 \leq l \leq 46$
Reflections collected	191741
Independent reflections	31373 [R_{int} = 0.0557, R_{sigma} = 0.0353]
Data/restraints/parameters	31373/761/1852
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0986, wR_2 = 0.2379
Final R indexes [all data]	R_1 = 0.1137, wR_2 = 0.2495
Largest diff. peak/hole / e Å^{-3}	1.82/-1.67