f-Block complexes of a *m*-terphenyl dithiocarboxylate ligand

Michael A. Boreen, Bernard F. Parker, Stephan Hohloch, Brighton Skeel, and John Arnold*

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, United States

E-mail: arnold@berkeley.edu

Supporting Information

NMR Spectra

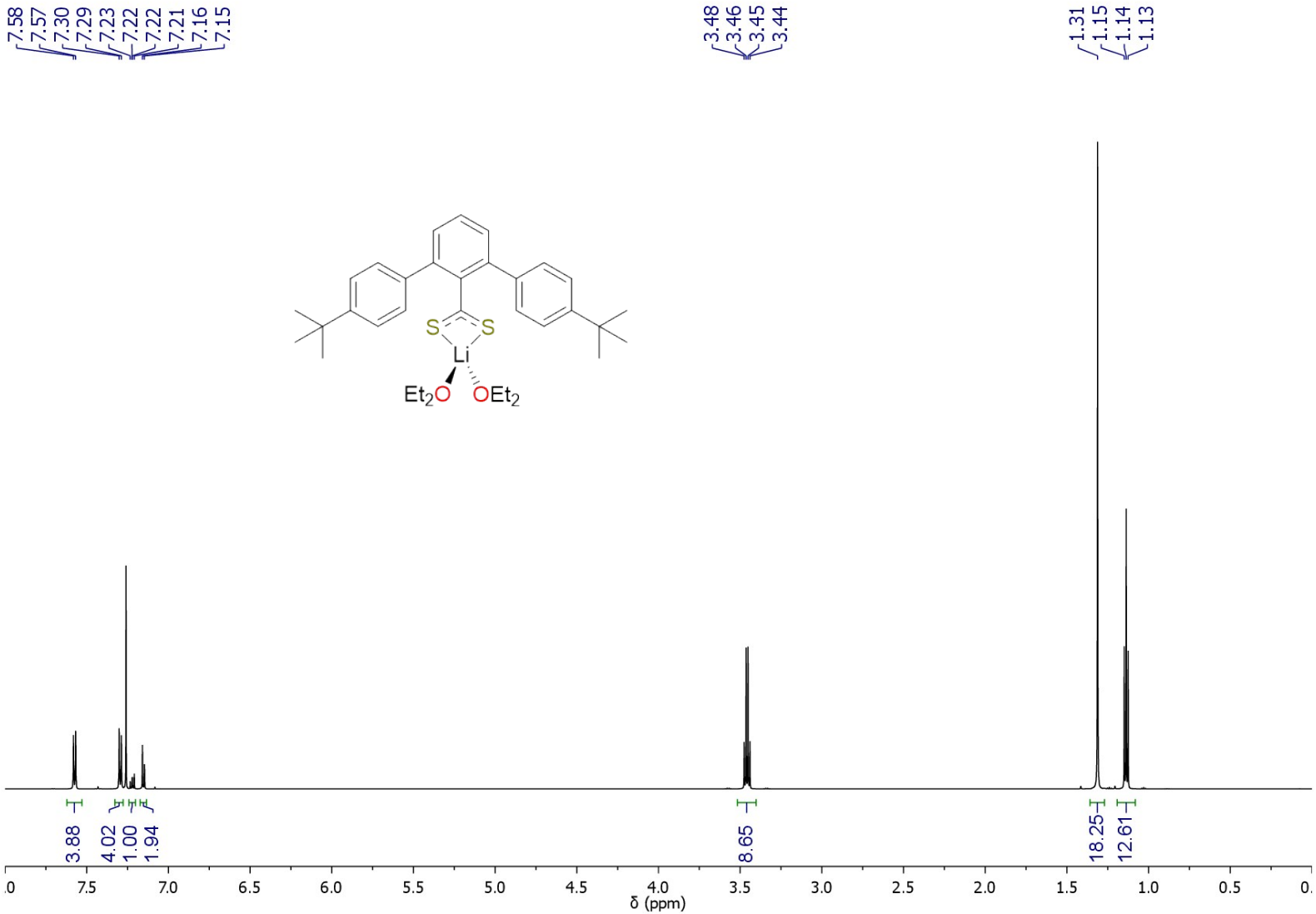

Figure S1. ^{1}H NMR spectrum of **1·Et$_2$O** in $CDCl_3$

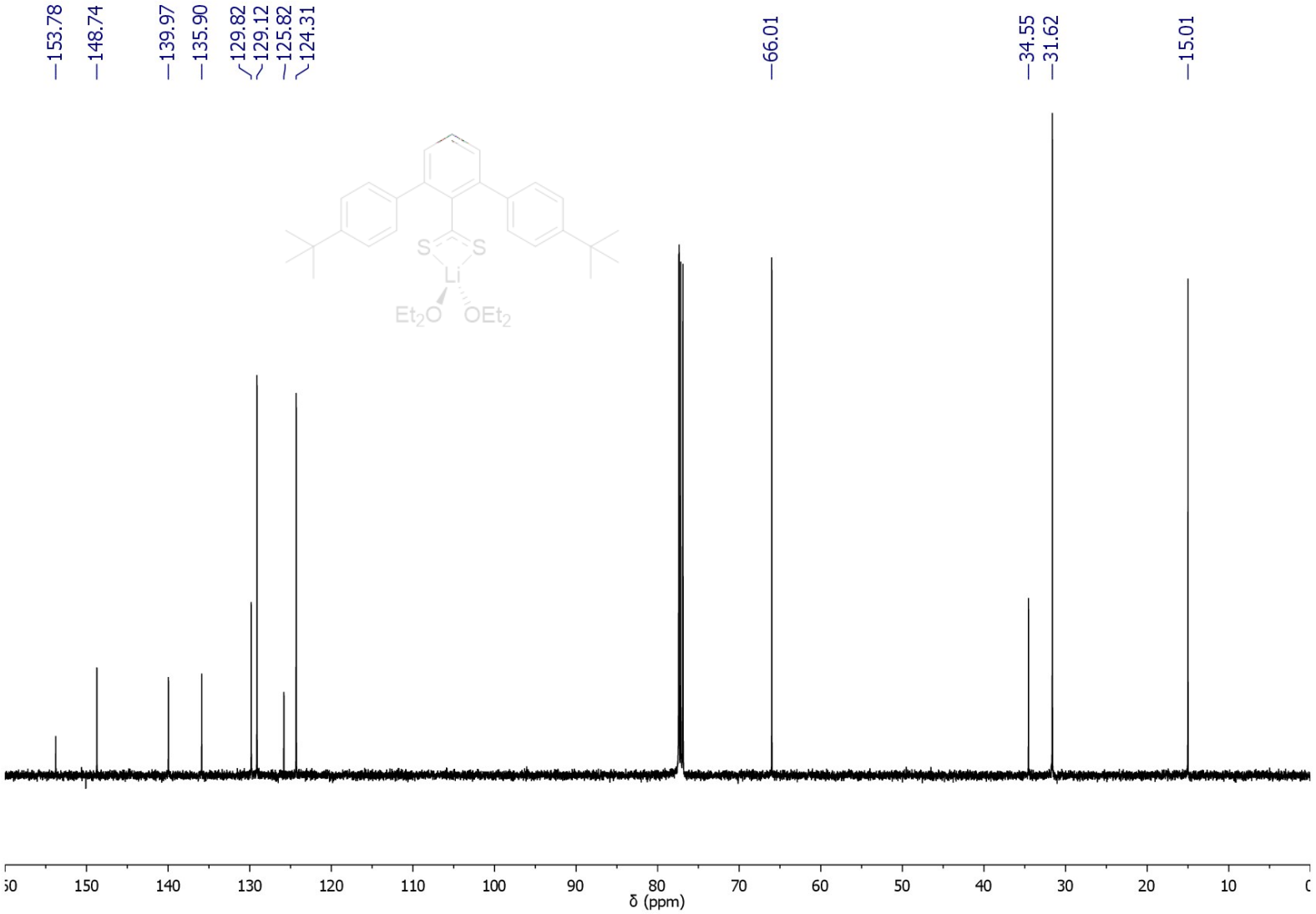

Figure S2. ^{13}C NMR spectrum of **1·Et$_2$O** in $CDCl_3$

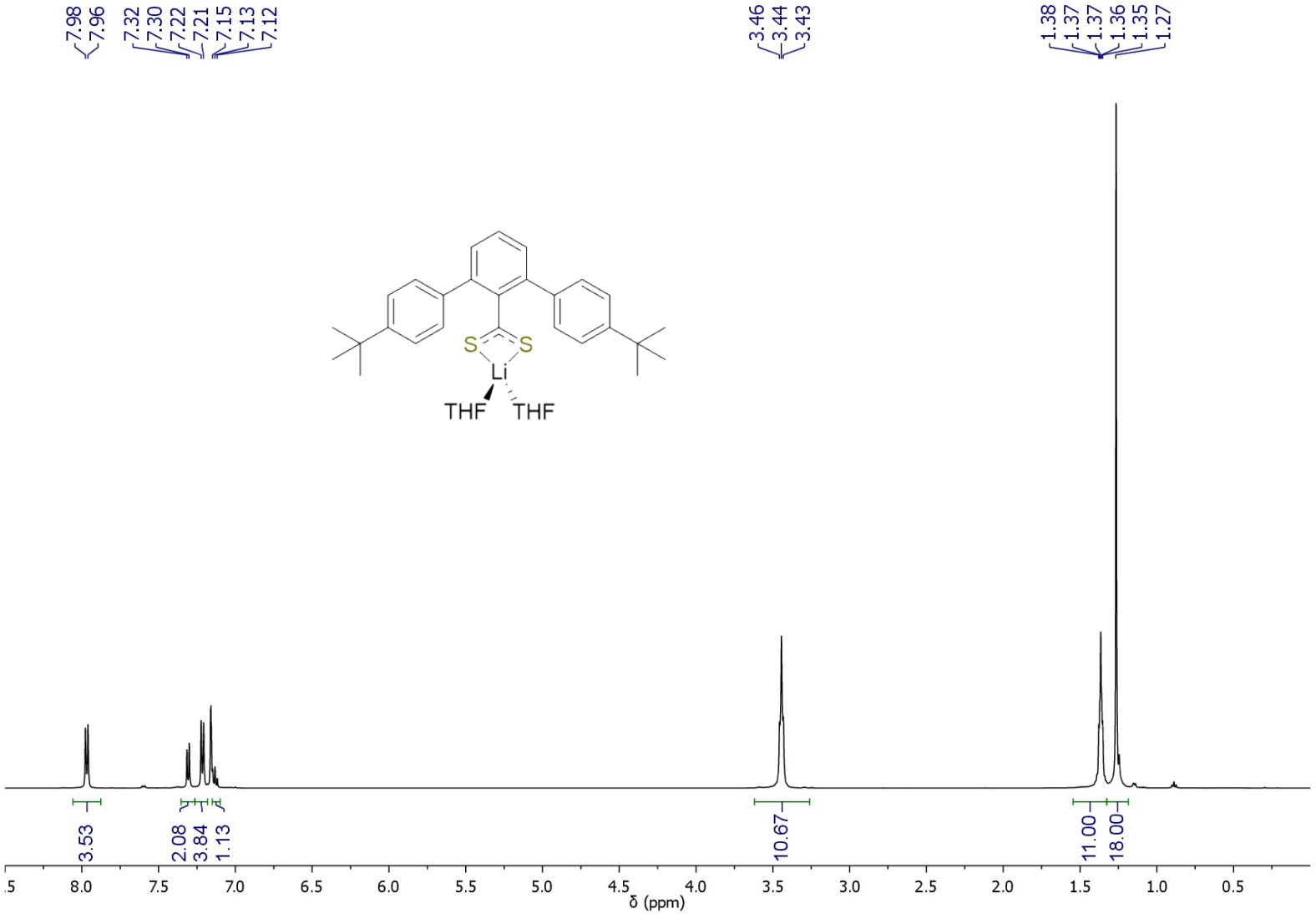

Figure S3. ^{1}H NMR spectrum of **1·THF** in C_6D_6

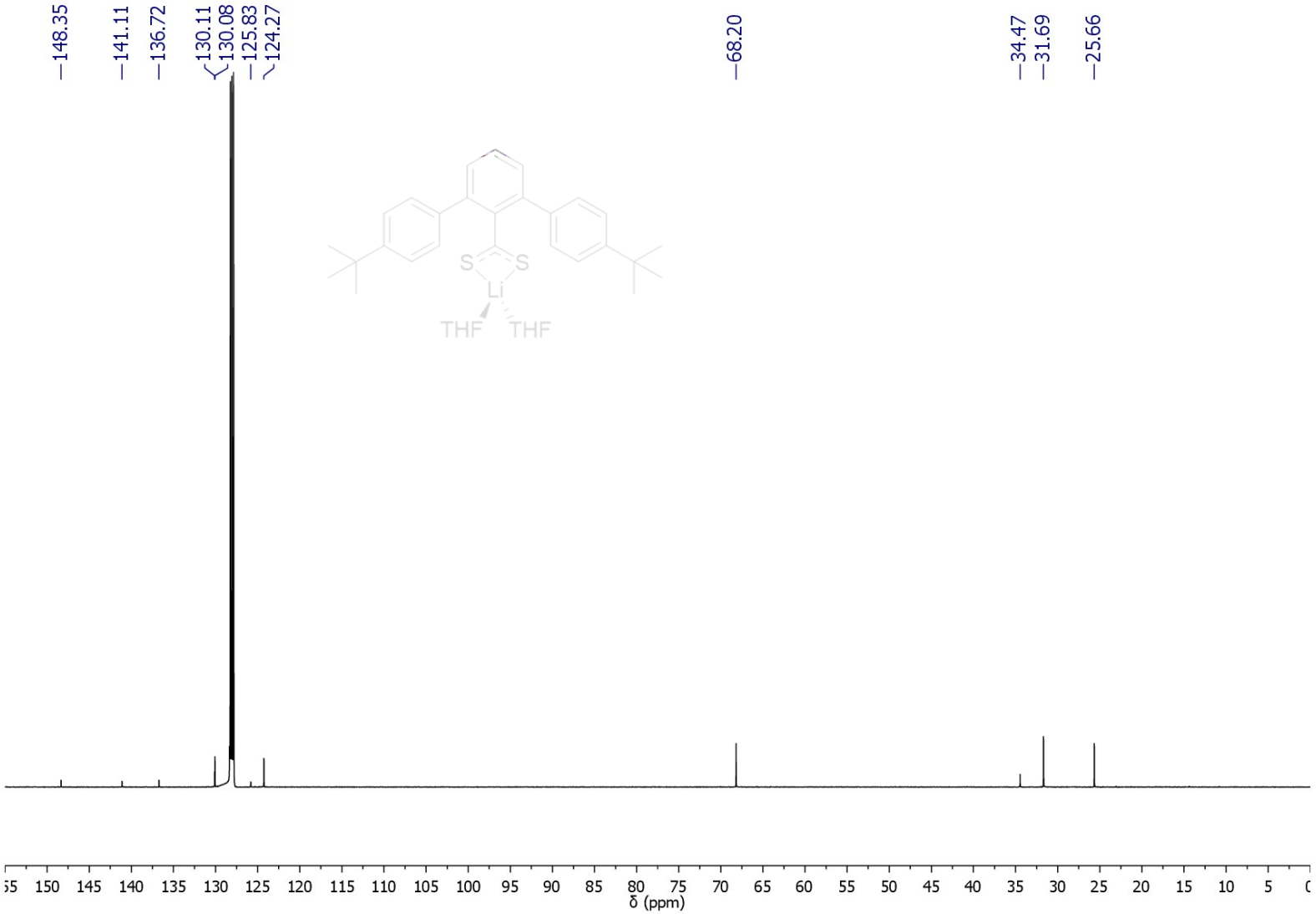

Figure S4. ^{13}C NMR spectrum of **1·THF** in C_6D_6

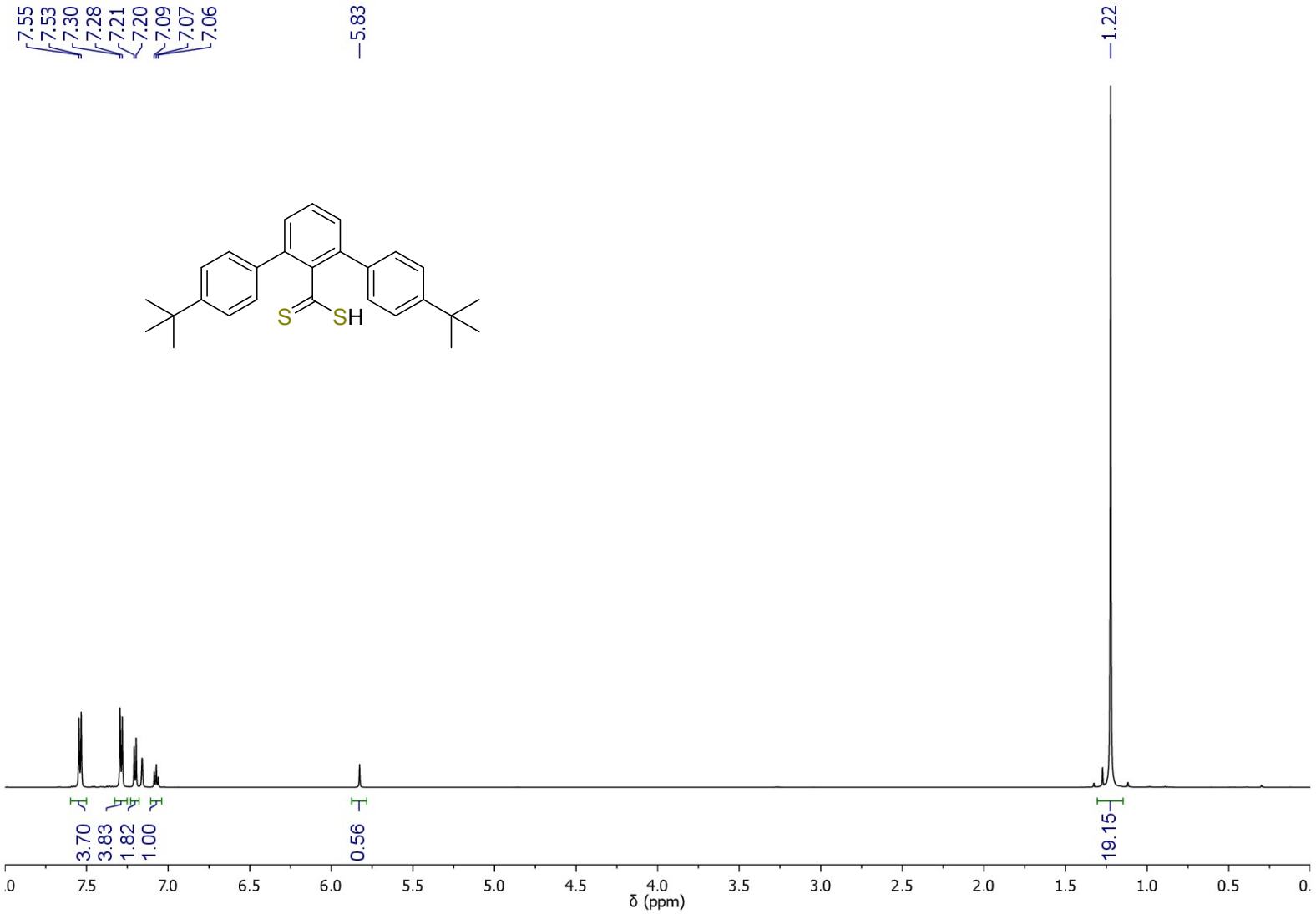

Figure S5. ^{1}H NMR spectrum of **2** in C_6D_6

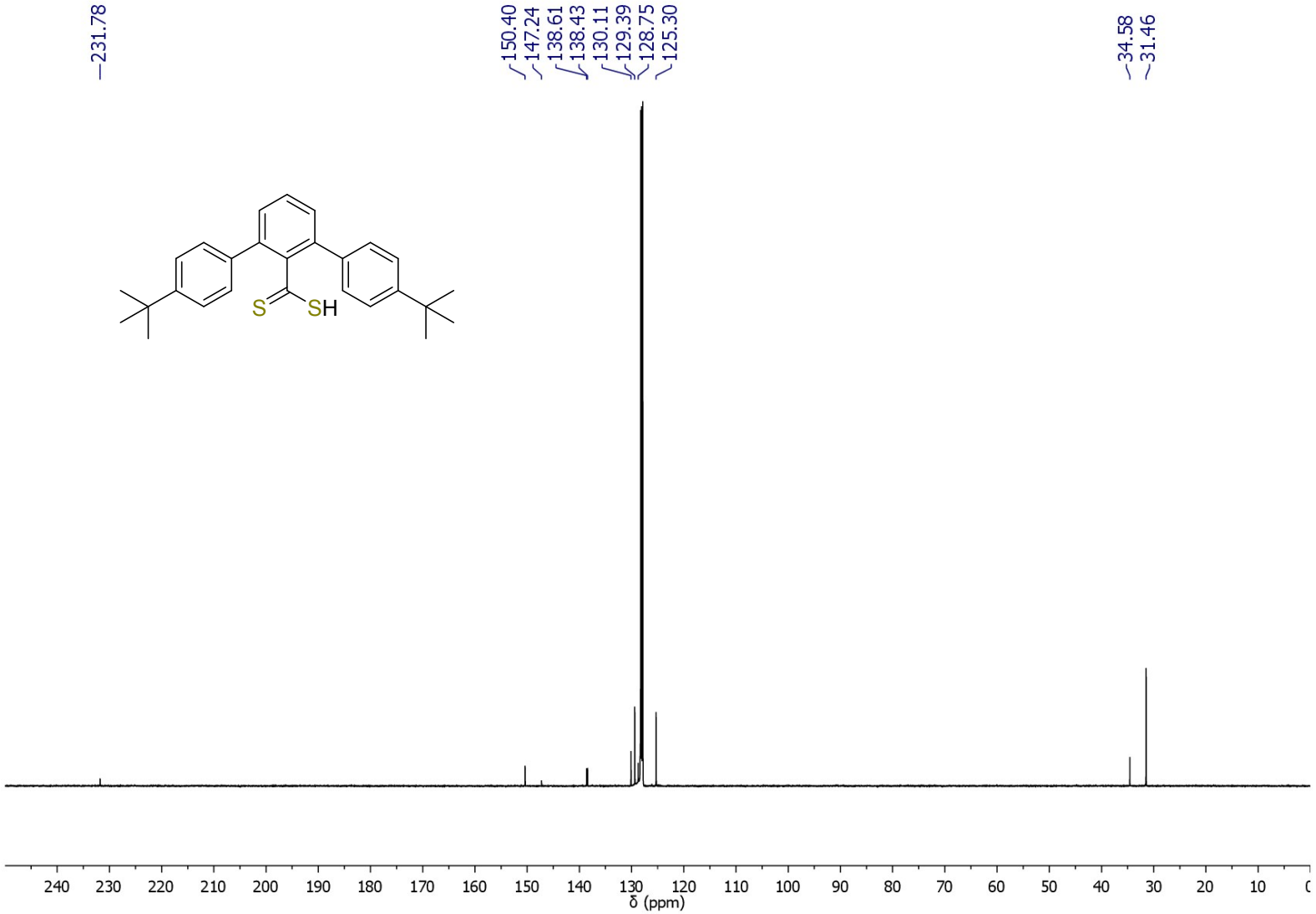

Figure S6. ^{13}C NMR spectrum of **2** in C_6D_6

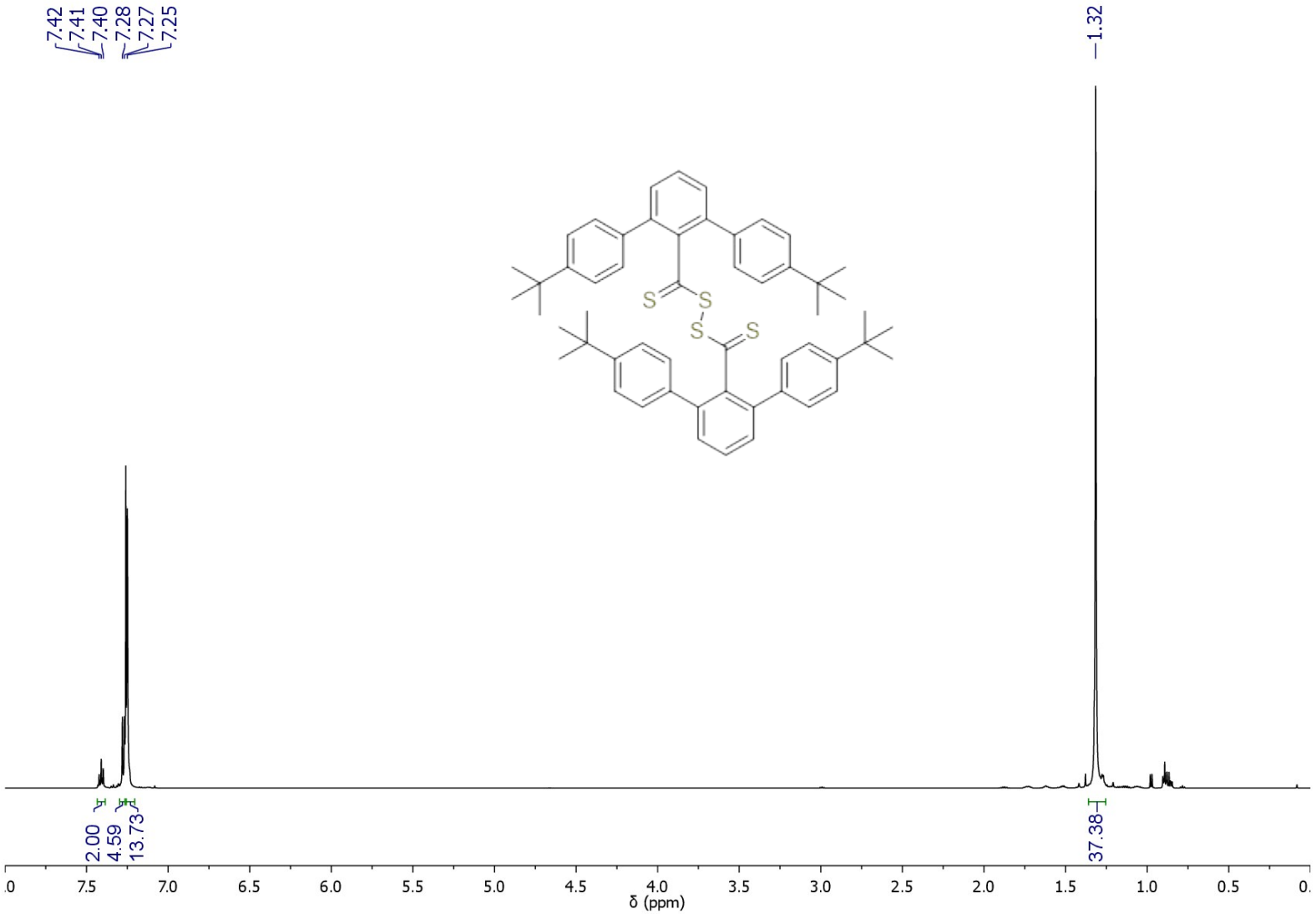

Figure S7. ^{1}H NMR spectrum of **3** in $CDCl_3$

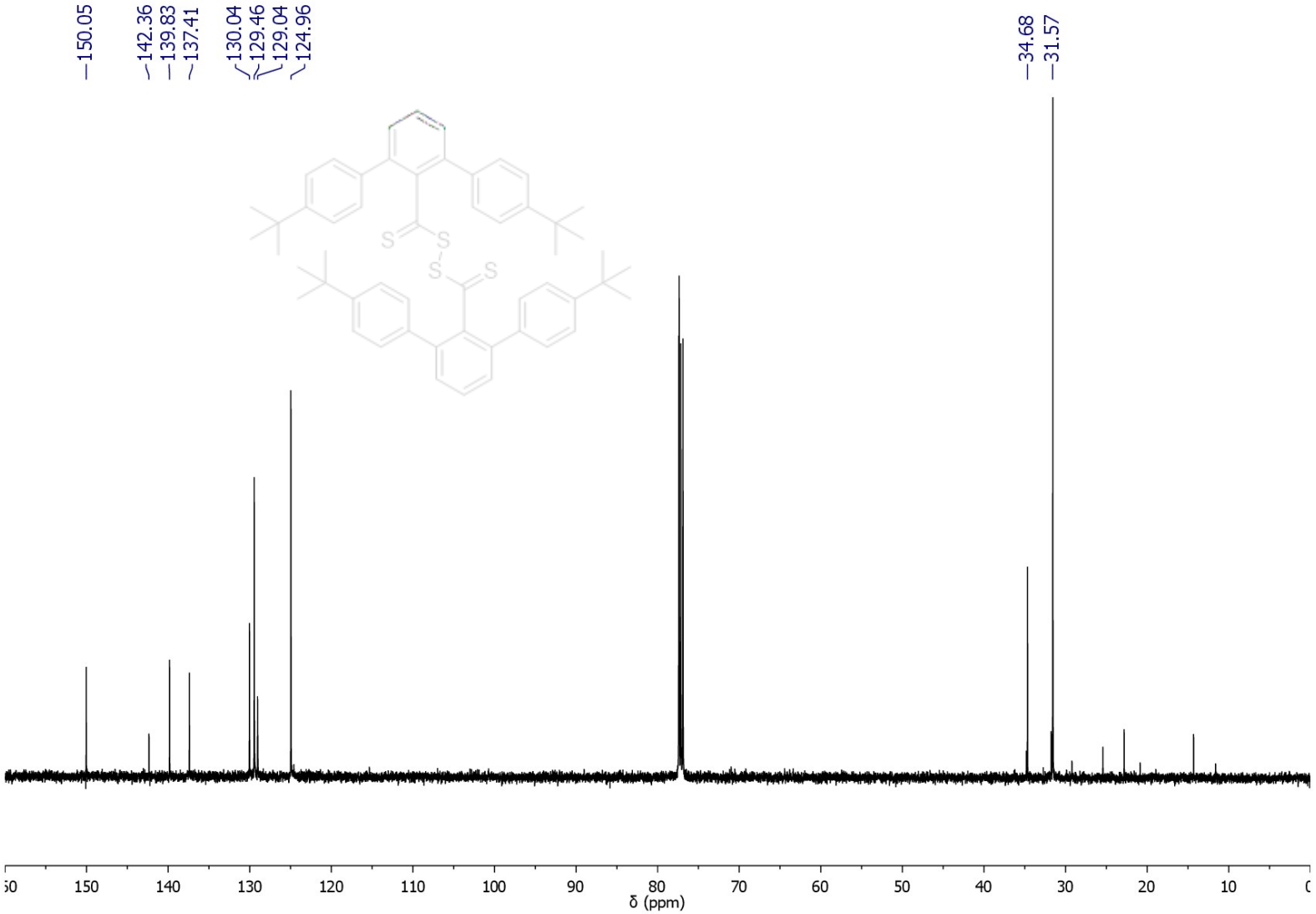

Figure S8. ^{13}C NMR spectrum of **3** in $CDCl_3$

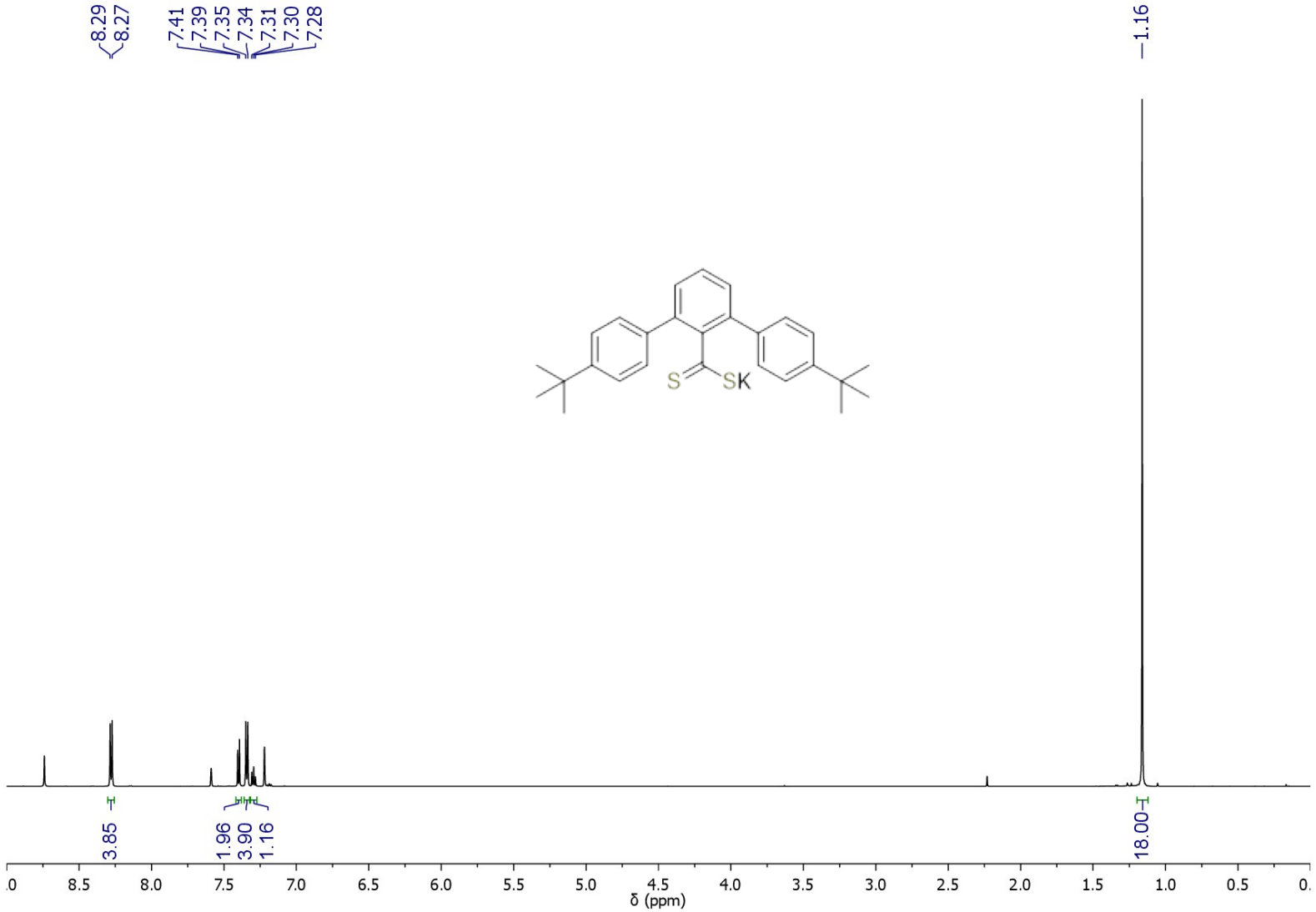

Figure S9. ^{1}H NMR spectrum of **4** in pyridine-d_5

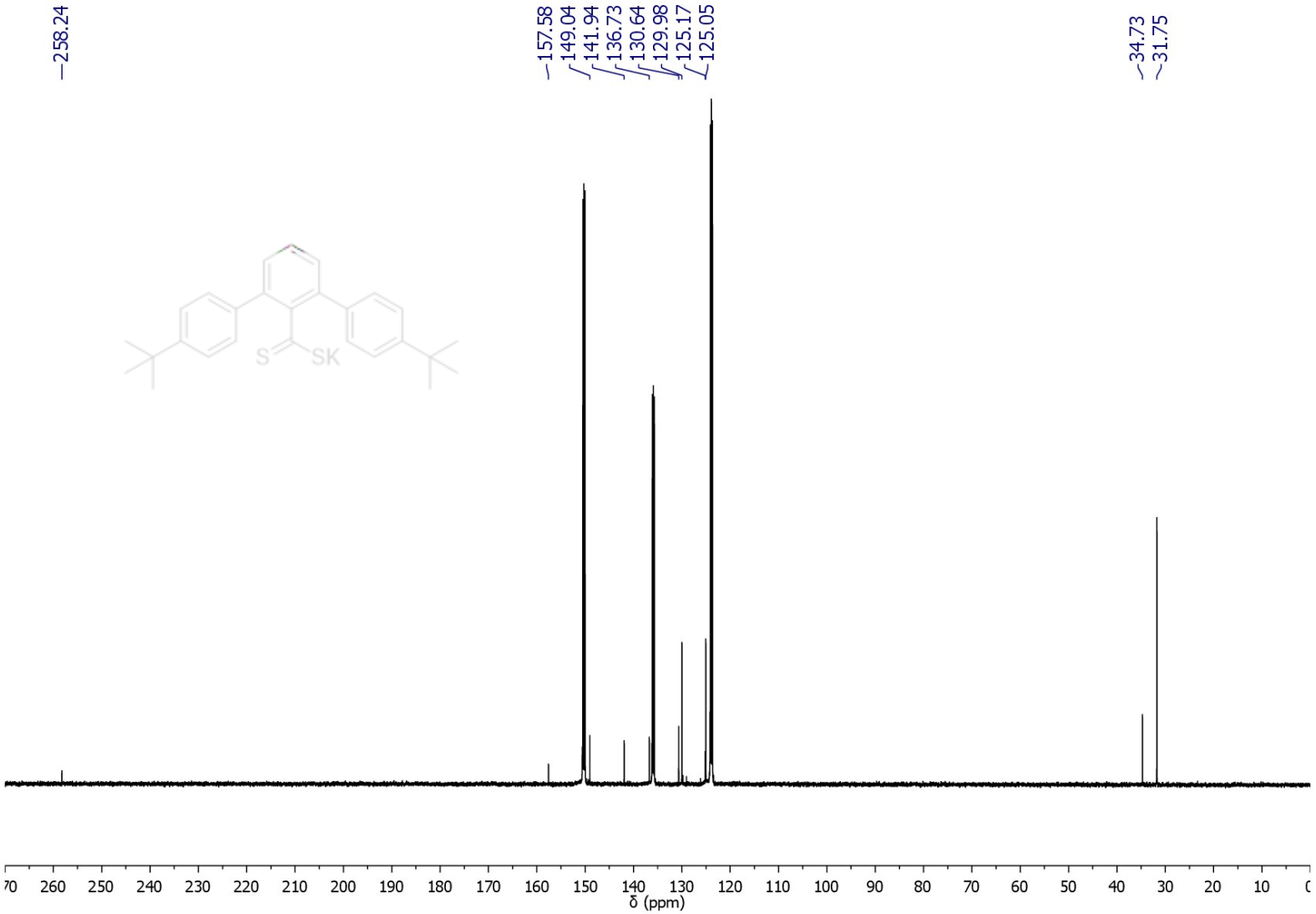

Figure S10. ^{13}C NMR spectrum of **4** in pyridine-d_5

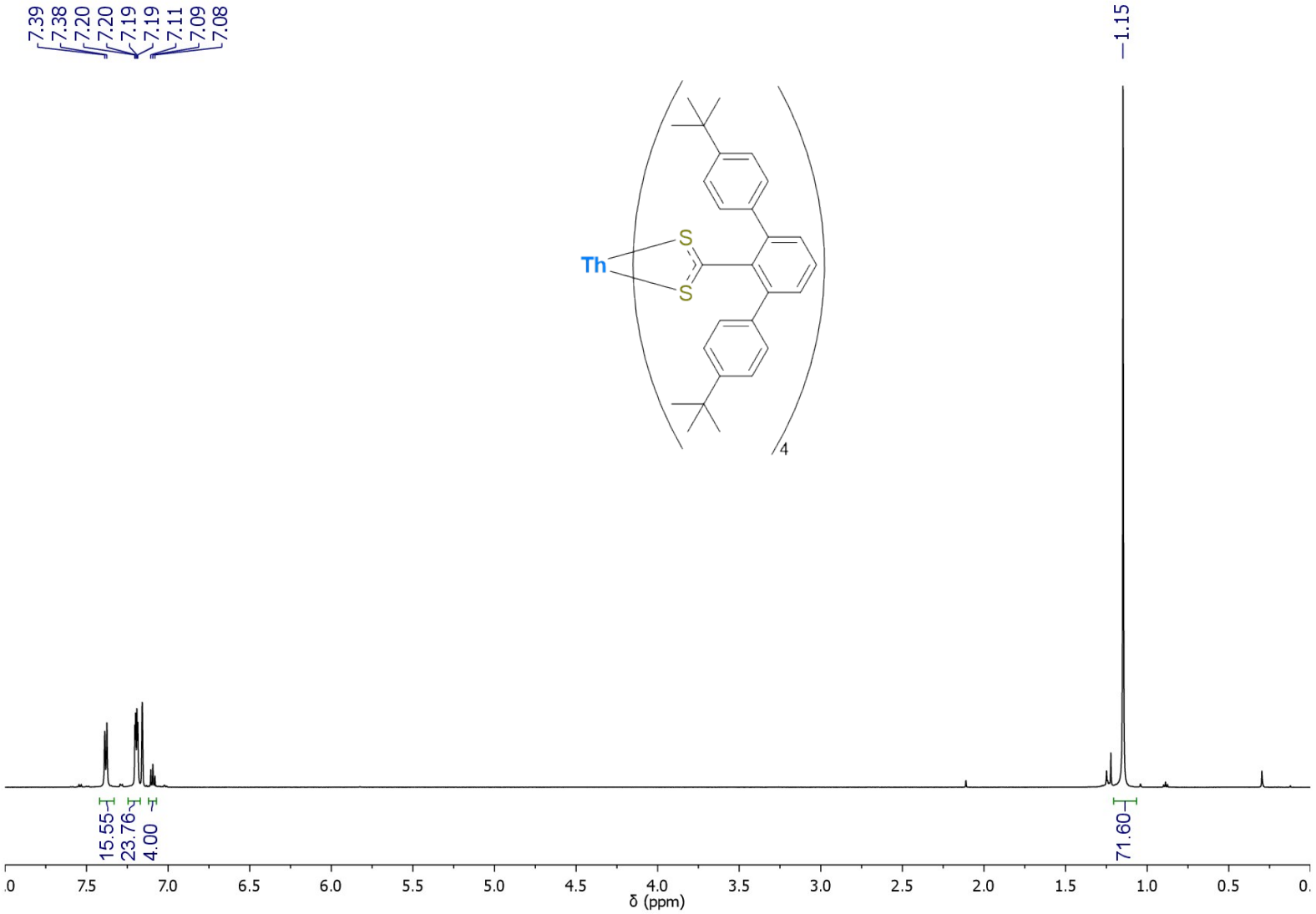

Figure S11. ^{1}H NMR spectrum of **5** in C_6D_6

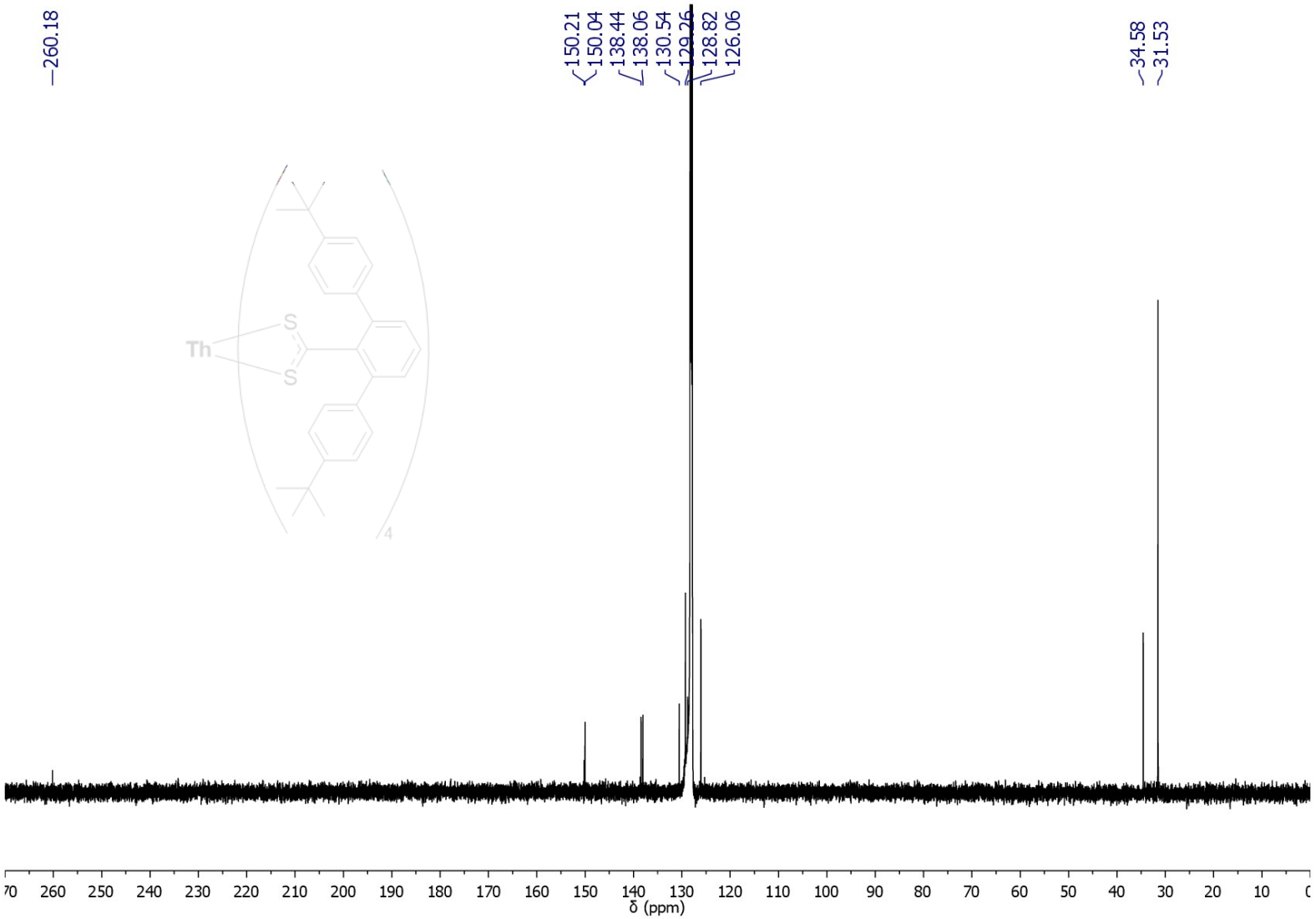

Figure S12. ^{13}C NMR spectrum of **5** in C_6D_6

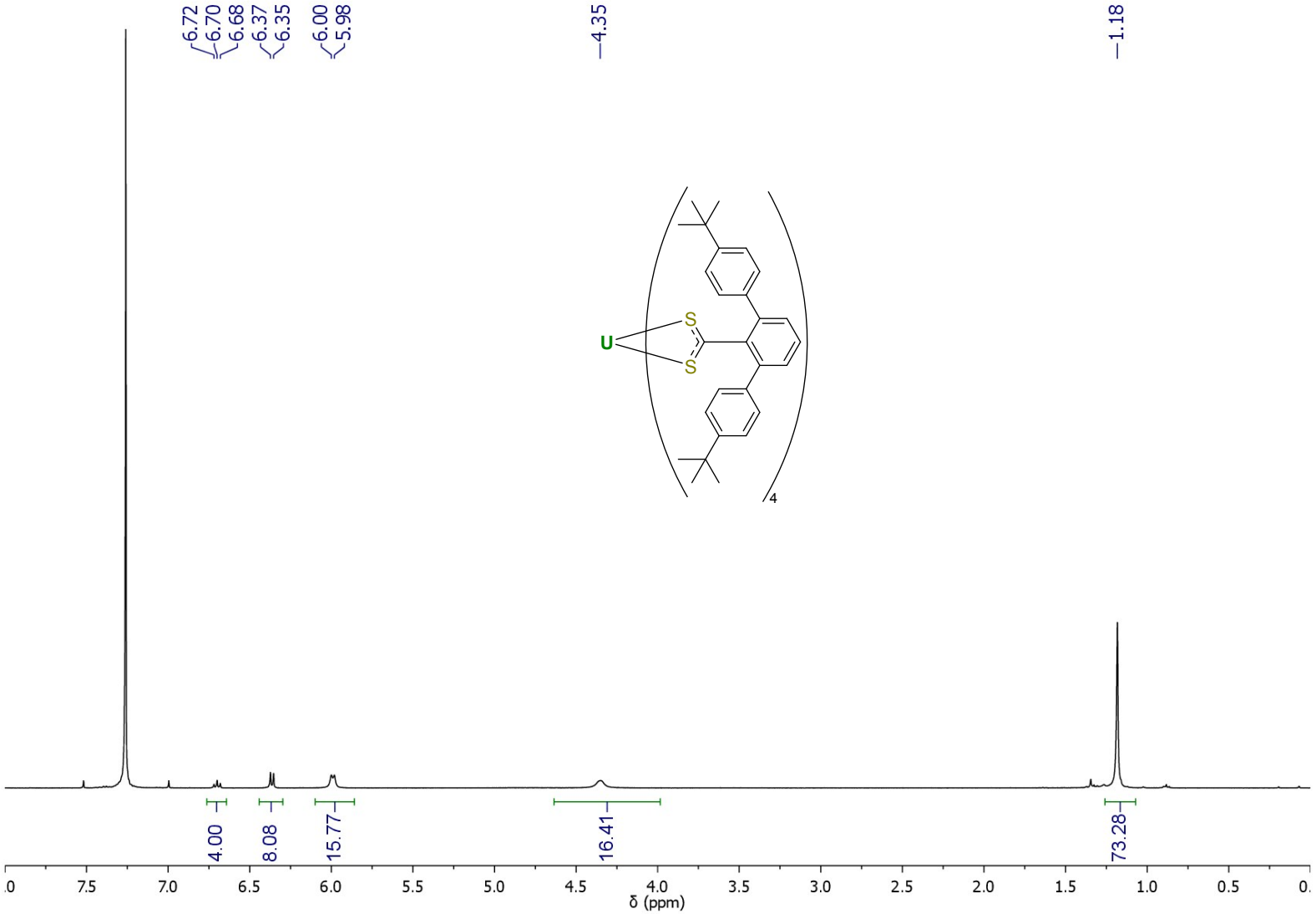

Figure S13. ^{1}H NMR spectrum of **6** in $CDCl_3$

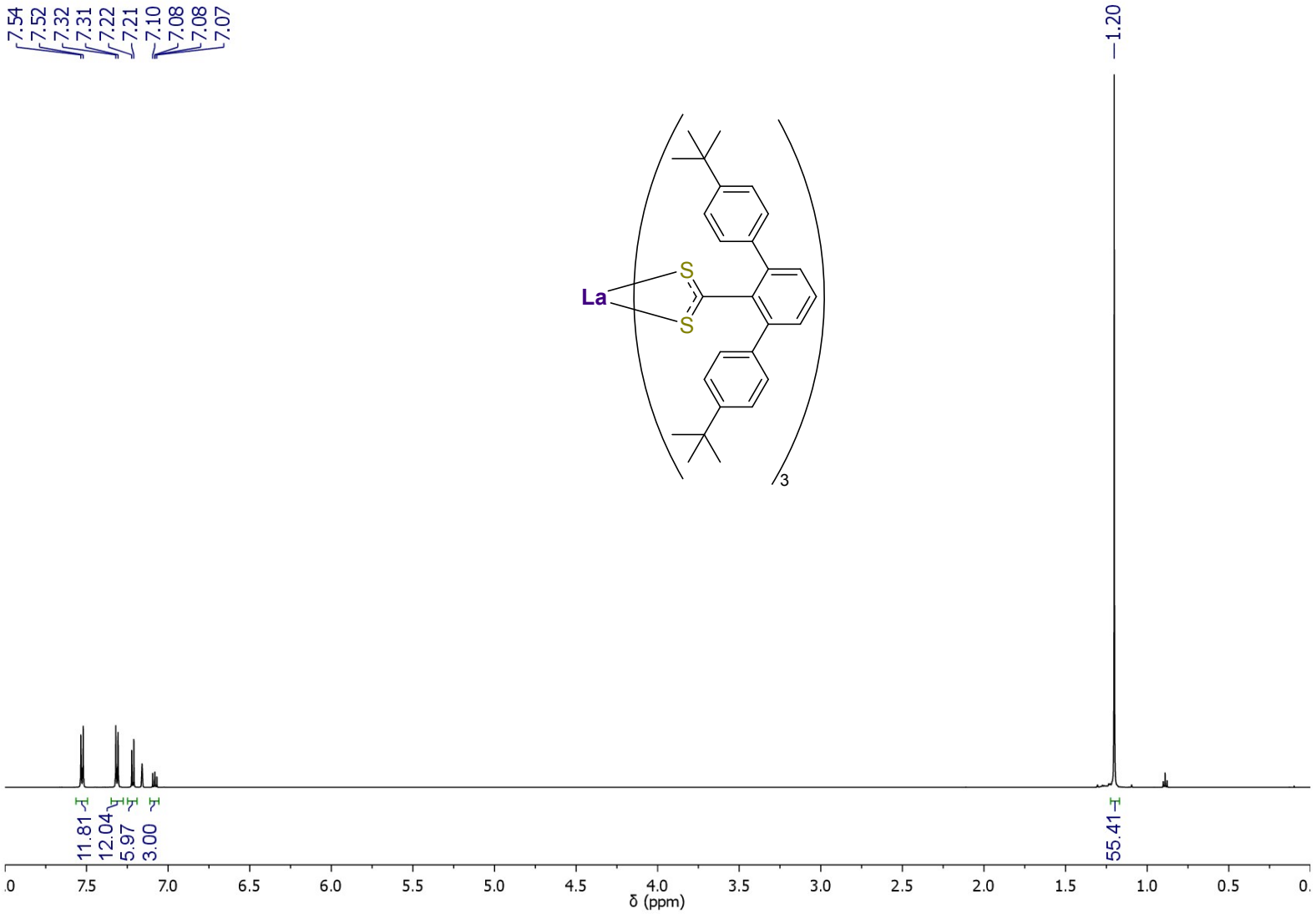

Figure S14. ^{1}H NMR spectrum of **7** in C_6D_6

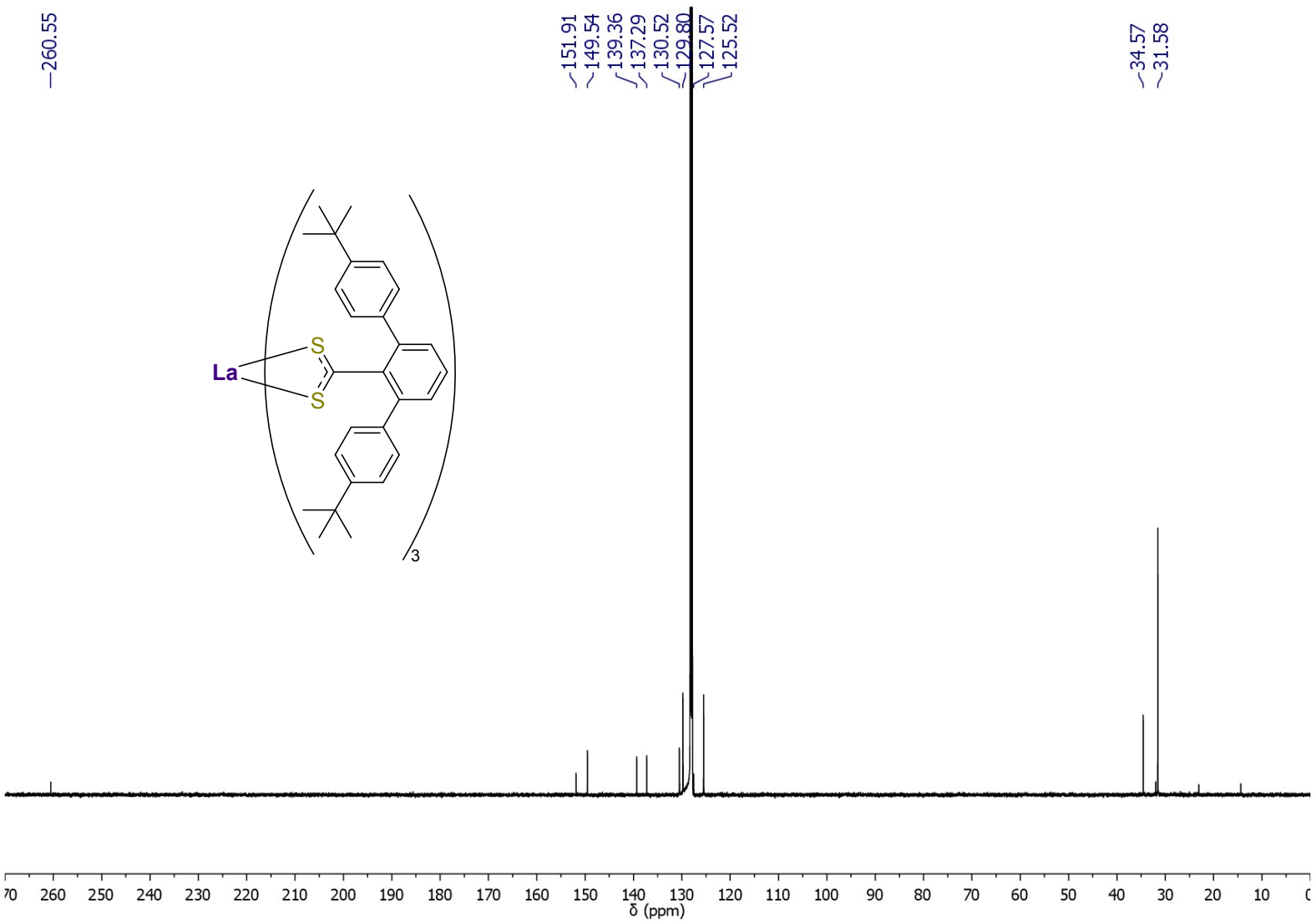

Figure S15. ^{13}C NMR spectrum of **7** in C_6D_6

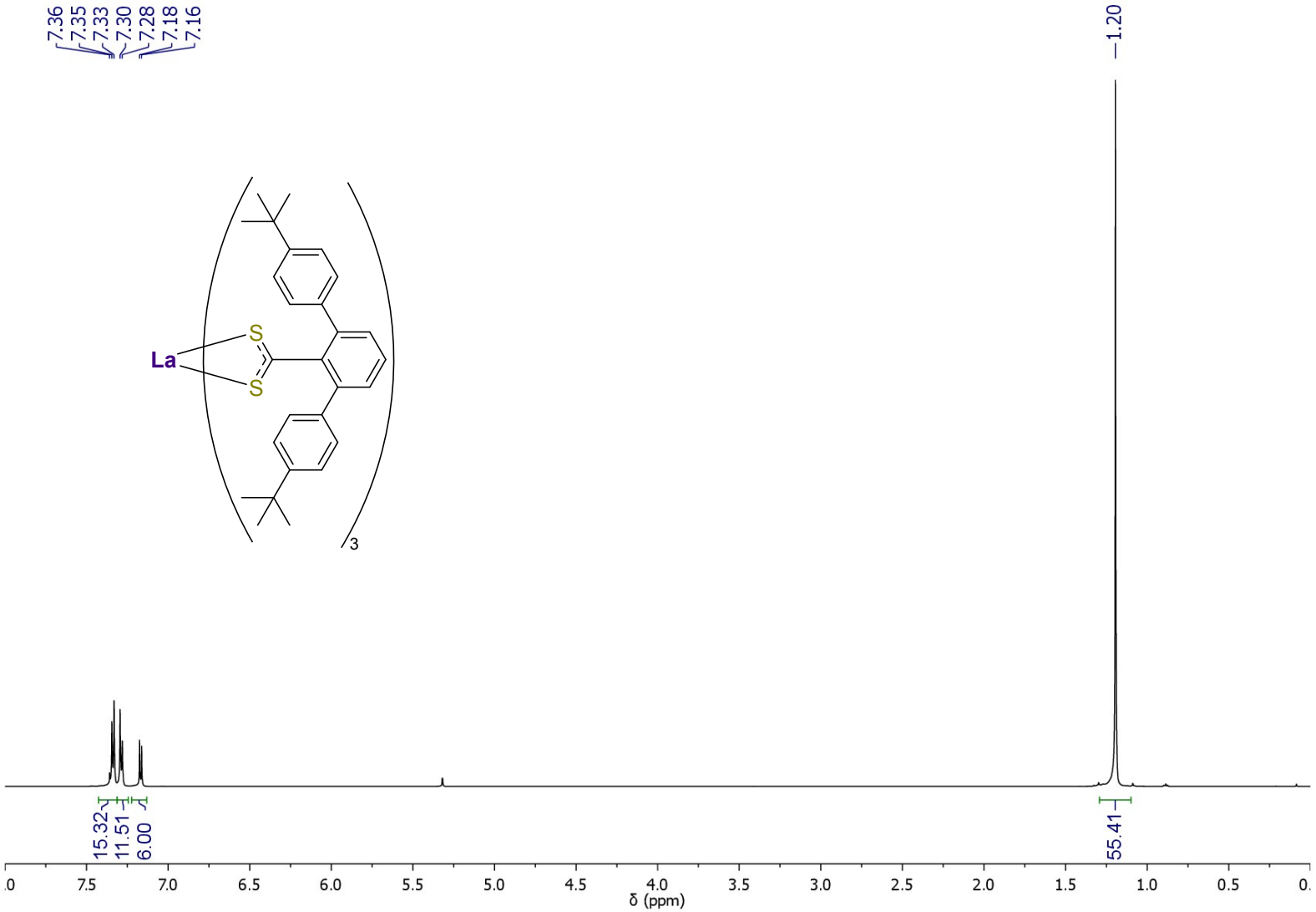

Figure S16. ^{1}H NMR spectrum of **7** in CD_2Cl_2

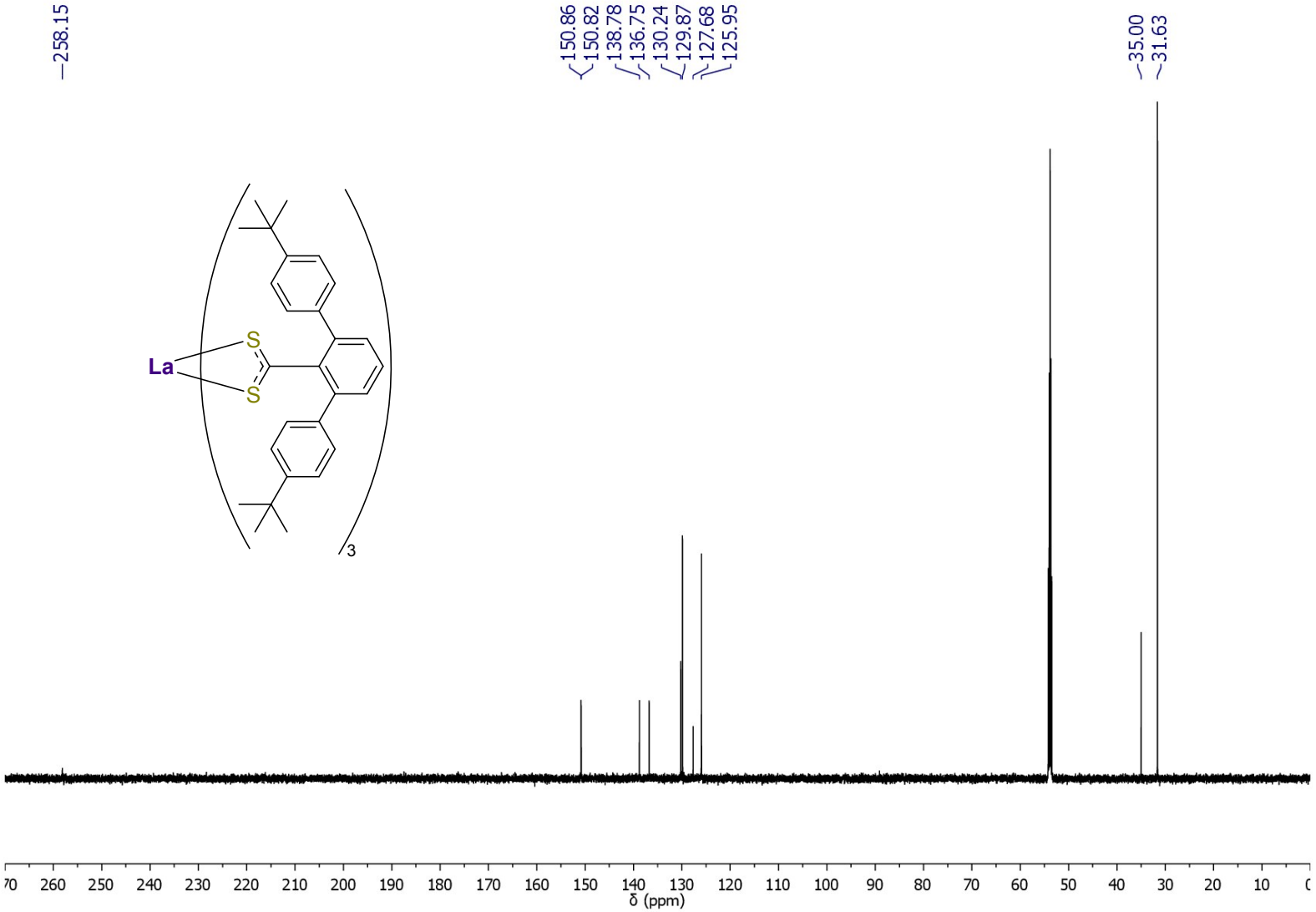

Figure S17. ^{13}C NMR spectrum of **7** in CD_2Cl_2

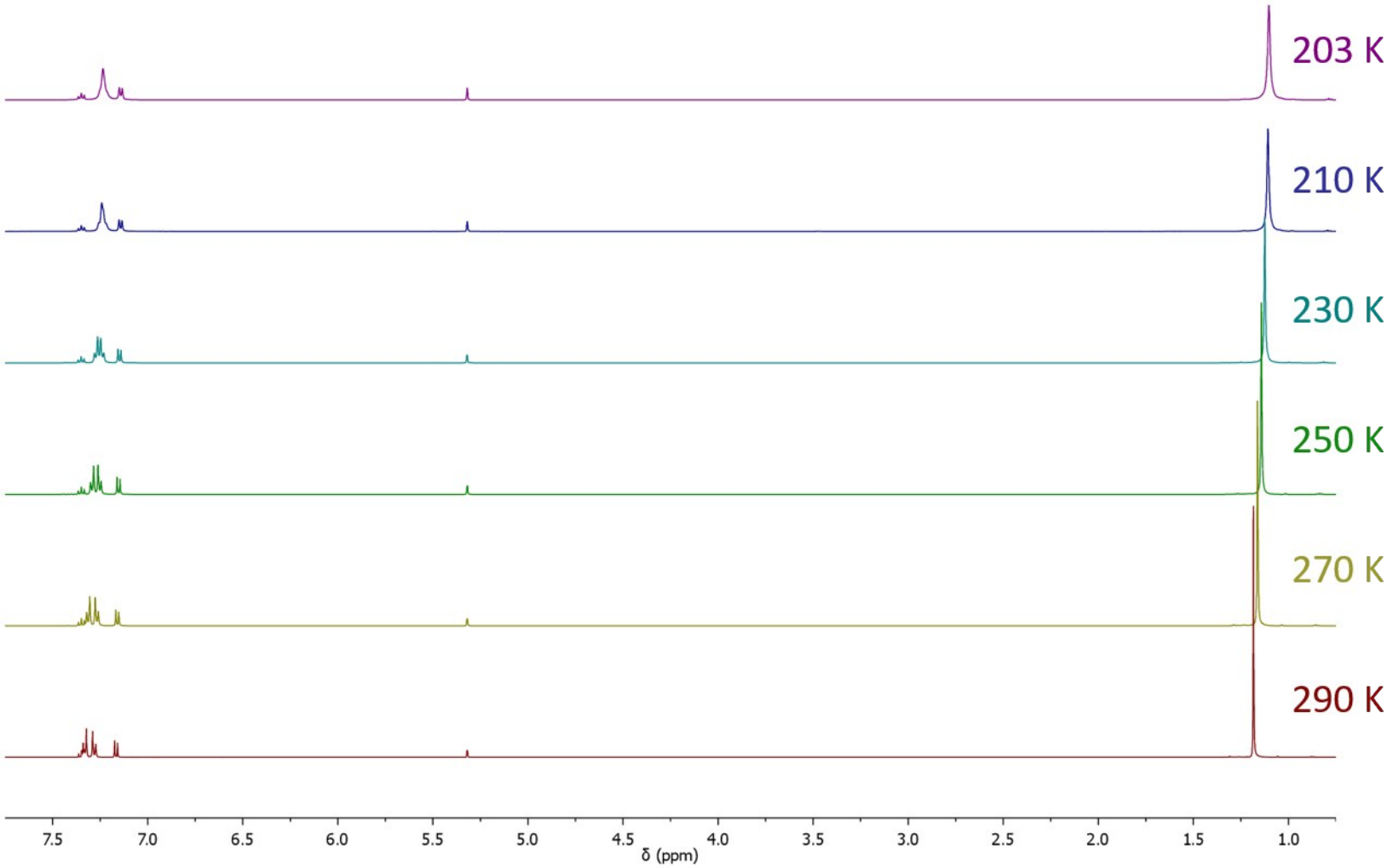

Figure S18. ^{1}H VT-NMR spectra for **7** in CD_2Cl_2 between 203 and 290 K

Electrochemistry Data

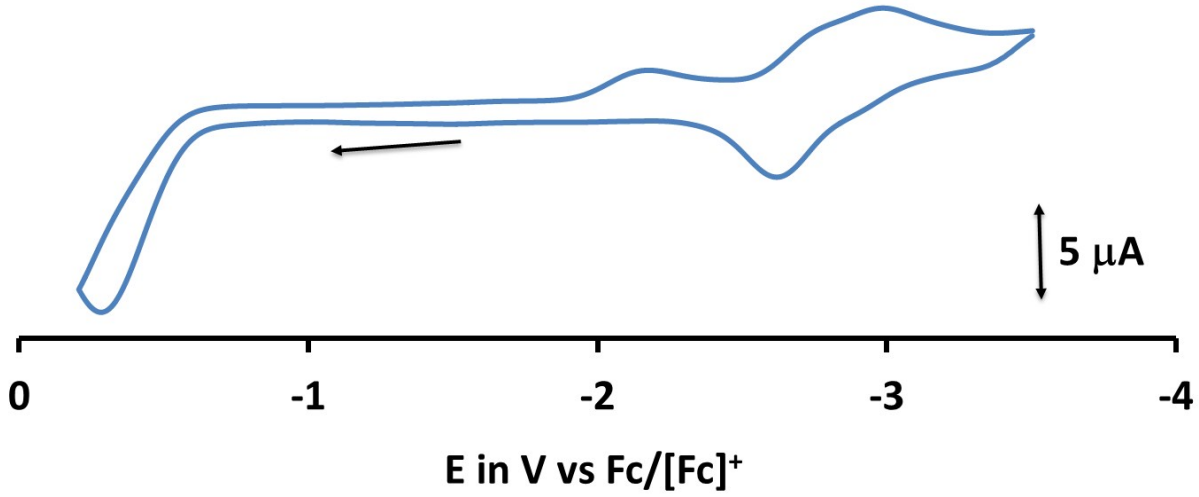

Figure S19. Cyclic voltammogram of TerphCS$_2$K (**4**). Scan rate: 100 mV/s. Analyte concentration: 1 mM.

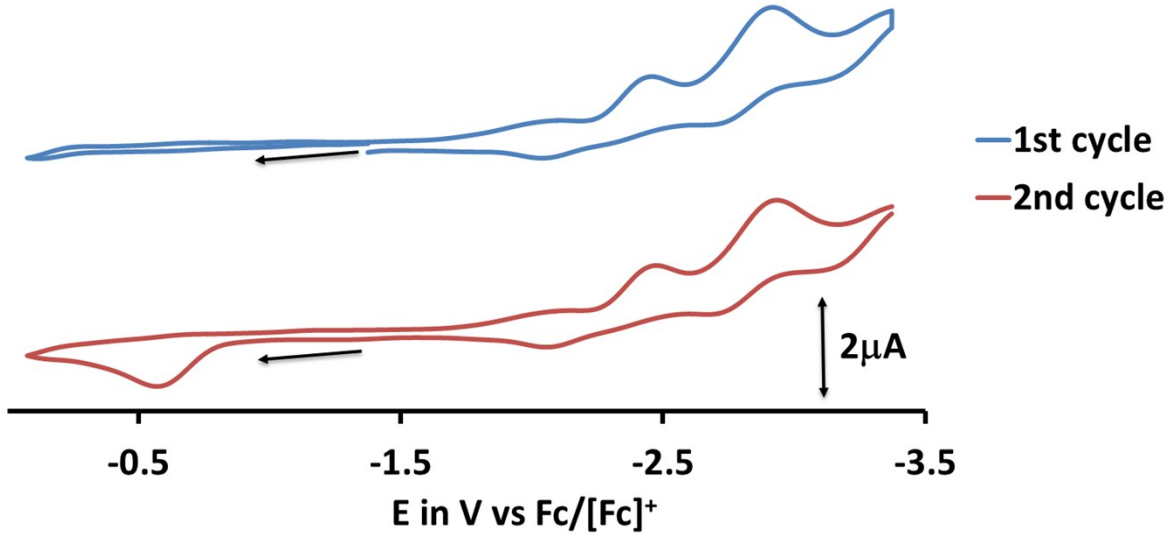

Figure S20. Cyclic voltammogram of (TerphCS$_2$)$_4$Th (**5**). Scan rate: 100 mV/s. Analyte concentration: 1 mM. The first scan is shown in blue on top, and the second scan is shown in red on the bottom. As observed with for **6**, the oxidation process for **5** occurs from a decay product after the first reduction (see Figs. S21 and S22).

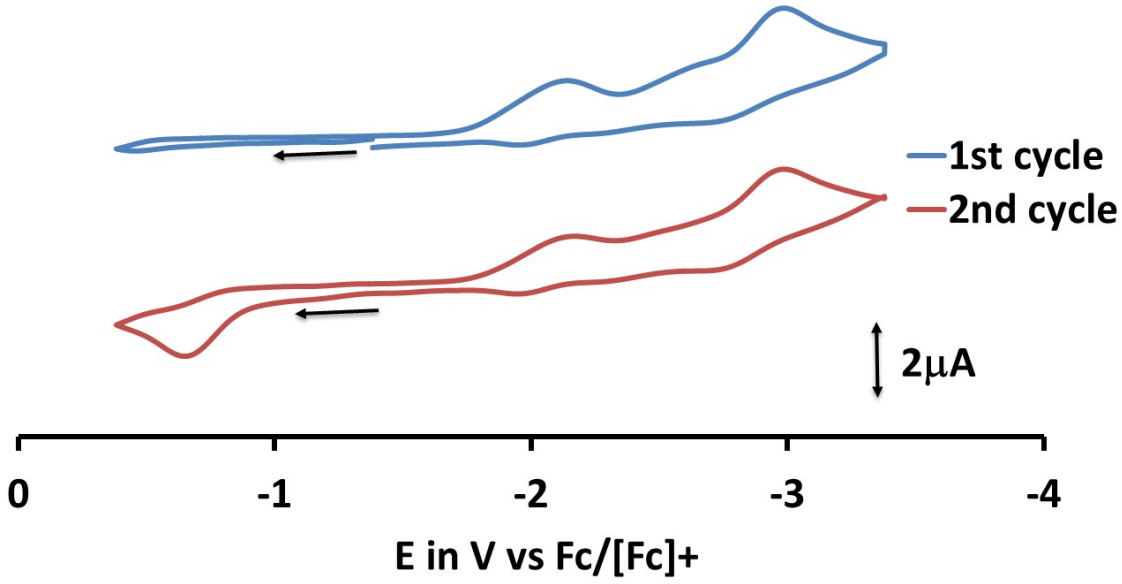

Figure S21. Cyclic voltammogram of $(TerphCS_2)_4U$ (**6**). Scan rate: 100 mV/s. Analyte concentration: 1 mM. The first scan is shown in blue on top, and the second scan is shown in red on the bottom.

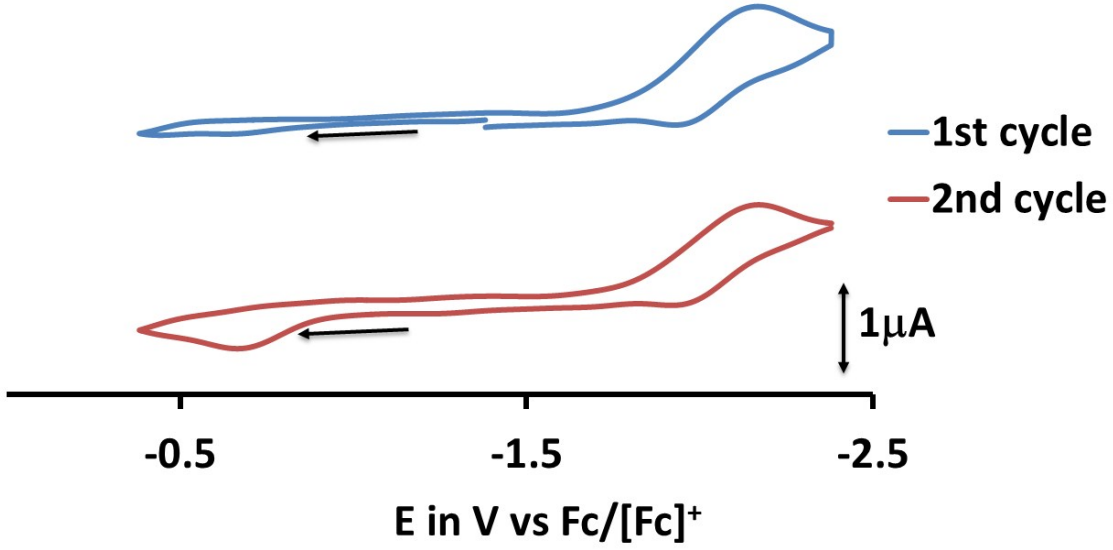

Figure S22. Cyclic voltammogram of **6** if only the first reduction is measured showing the oxidation process to occur from a new product forming after the first reduction.

Table S1. Observed potentials (in V vs Fc) for the compounds **4**, **5**, and **6**.

Analyte	1st oxidation, E_{pa}	1st reduction, E_{pc}	2nd reduction, E_{pc}	3rd reduction, E_{pc}
4	–0.30	–2.17	–2.73	–2.99
5	–0.68*	–2.16	–2.62	–2.99
6	–0.59*	–2.08	–2.44	–2.94

*only observed in the second cycle

X-ray Crystallographic Table

Table S2. Crystallographic data for $(TerphCS_2)_2$ (**3**)

Identification code	3	
Empirical formula	C54 H58 S4	
Formula weight	835.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.8864(6) Å	α= 79.6690(10)°.
	b = 13.5332(7) Å	β= 74.6710(10)°.
	c = 17.2923(9) Å	γ = 86.6720(10)°.
Volume	2639.0(2) $Å^3$	
Z	2	
Density (calculated)	1.051 Mg/m^3	
Absorption coefficient	0.211 mm^{-1}	
F(000)	892	
Crystal size	0.160 × 0.100 × 0.100 mm^3	
Theta range for data collection	1.530 to 25.376°.	
Index ranges	-14≤h≤14, -16≤k≤15, -20≤l≤20	
Reflections collected	69116	
Independent reflections	9663 [R(int) = 0.0729]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9663 / 0 / 535	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0592, wR2 = 0.1423	
R indices (all data)	R1 = 0.0909, wR2 = 0.1616	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.824 and -0.322 $e·Å^{-3}$	

Table S3. Crystallographic data for $(TerphCS_2)_4Th(THF)$ (**5·THF**)

Identification code	5THF	
Empirical formula	C116 H132 O2 S8 Th	
Formula weight	2046.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 18.3098(10) Å	α= 74.181(3)°.
	b = 18.5236(11) Å	β= 74.607(3)°.
	c = 19.3377(11) Å	γ = 63.541(3)°.
Volume	5569.8(6) $Å^3$	
Z	2	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	1.535 mm^{-1}	
F(000)	2124	
Crystal size	0.200 × 0.200 × 0.100 mm^3	
Theta range for data collection	1.110 to 25.474°.	
Index ranges	-22≤h≤22, -22≤k≤22, -23≤l≤21	
Reflections collected	158735	
Independent reflections	20500 [R(int) = 0.0441]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5619 and 0.4756	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20500 / 0 / 1168	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0935	
R indices (all data)	R1 = 0.0434, wR2 = 0.0966	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.810 and -1.133 $e·Å^{-3}$	

Table S4. Crystallographic data for $(TerphCS_2)_4U$ (**6**)

Identification code	6	
Empirical formula	C216 H232 S16 U2	
Formula weight	3817.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 17.6450(7) Å	α= 82.843(2)°.
	b = 20.5248(8) Å	β= 88.847(2)°.
	c = 28.1239(10) Å	γ = 70.436(2)°.
Volume	9520.0(6) $Å^3$	
Z	2	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	1.927 mm^{-1}	
F(000)	3936	
Crystal size	0.100 × 0.050 × 0.020 mm^3	
Theta range for data collection	1.061 to 25.432°.	
Index ranges	-20≤h≤21, -24≤k≤24, -33≤l≤33	
Reflections collected	152007	
Independent reflections	35027 [R(int) = 0.0590]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6154	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	35027 / 48 / 2185	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0682, wR2 = 0.1683	
R indices (all data)	R1 = 0.1089, wR2 = 0.1958	
Extinction coefficient	n/a	
Largest diff. peak and hole	6.928 and -2.147 $e·Å^{-3}$	

Table S5. Crystallographic data for $(TerphCS_2)_3La$ (**7**)

Identification code	7	
Empirical formula	C83 H91 Cl4 La S6	
Formula weight	1561.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 20.1124(13) Å	α= 90°.
	b = 25.4125(16) Å	β= 120.118(3)°.
	c = 17.7928(11) Å	γ = 90°.
Volume	7866.3(9) $Å^3$	
Z	4	
Density (calculated)	1.319 Mg/m^3	
Absorption coefficient	0.880 mm^{-1}	
F(000)	3240	
Crystal size	0.130 × 0.040 × 0.030 mm^3	
Theta range for data collection	1.418 to 28.375°.	
Index ranges	-26≤h≤26, -33≤k≤33, -23≤l≤23	
Reflections collected	131732	
Independent reflections	9834 [R(int) = 0.0467]	
Completeness to theta = 28.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6471 and 0.5543	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9834 / 0 / 435	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.0976	
R indices (all data)	R1 = 0.0503, wR2 = 0.1031	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.672 and -0.936 $e·Å^{-3}$	

Table S6. Crystallographic data for $(TerphCS_2)_3La$ (**7·tol**)

Identification code	7tol	
Empirical formula	C95 H103 La S6	
Formula weight	1576.04	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.1644(8) Å	α= 77.987(3)°.
	b = 15.2313(8) Å	β= 70.849(3)°.
	c = 21.2845(12) Å	γ = 75.738(2)°.
Volume	4163.3(4) $Å^3$	
Z	2	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.709 mm^{-1}	
F(000)	1652	
Crystal size	0.120 × 0.080 × 0.070 mm^3	
Theta range for data collection	1.393 to 25.441°.	
Index ranges	-17≤h≤17, -18≤k≤18, -25≤l≤25	
Reflections collected	66065	
Independent reflections	15364 [R(int) = 0.0347]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.7022	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15364 / 0 / 939	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.1037	
R indices (all data)	R1 = 0.0437, wR2 = 0.1062	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.734 and -0.796 e·$Å^{-3}$	