Synthesis of Highly Soluble and Oxidatively Stable Tetraceno[2,3-*b*]thiophenes and Pentacenes

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Supplementary Information

Contents

Synthesis.

6,11-Dihydroxy-5,12-tetracenequinone[2,3-*b*]thiophene (13). Compound **9** (1.72 g, 7 mmol) was mixed with 2,3-thiophenedicarboxaldehyde (1g, 7 mmol) in ethanol (250 ml). While stirring 5% KOH (10 ml) was added and the mixture refluxed for about 12 hours. After the completion of the reaction, the reaction mixture was cooled. Dark brown precipitate was collected by vacuum filtration. This precipitate was washed several times with EtOH. Dichloromethane was used as the eluent for the column chromatography. Yield: 75 %; ^{1}H NMR (300 MHz $CDCl_3$) δ = 9.05 (s, 1H), 8.95 (s, 1H), 8.55 (m, 2H), 7.85 (m, 3H), 7.65 (d, 1H), 3.60 (broad, 2H). HRMS *m/z* $[M]^+$ calcd for $C_{20}H_{10}O_4S$ 346.0299, found 346.0294.

6,11-Dimethoxy-5,12-tetracenequinone[2,3-*b*]thiophene (11) & 5,12-dimethoxy-6,11-tetracenequinone[2,3-*b*]thiophene (14) (isomeric products). Compound **13** (500 mg, 1.4 mmol) was added to a 500 ml oven dried round-bottom flask equipped with a stir bar and acetone (100 ml) and dioxane (50 ml) were added. While stirring dimethyl sulfate (2.38 ml, 14.3 mmol) and anhydrous potassium carbonate (2.39 g, 18.8 mmol) were also added. The whole mixture was stirred under argon and then refluxed for 36 hours whereupon an orange yellow precipitate formed. This reaction mixture was poured into ice cold water bath to complete the precipitation and filtered. This solid product was washed with cold water several times and then dried in vacuum oven. The solid product turned out to be an isomeric mixture of **11** and **14**, which were separated by an extremely long hour column using dichloromethane as the eluent. **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.84 (s, 1H), 8.75 (s, 1H), 8.45 (m, 2H), 7.77 (m, 3H), 7.60 (d, 1H), 4.18 (s, 6H). **14**: ^{1}H

NMR (300 MHz, $CDCl_3$) δ = 9.00 (s, 1H), 8.92 (s, 1H), 8.32 (m, 2H), 7.75 (m, 3H), 7.61 (d, 1H), 4.21 (s, 6H).

Figure S1. Thin film absorption spectra of 1-6

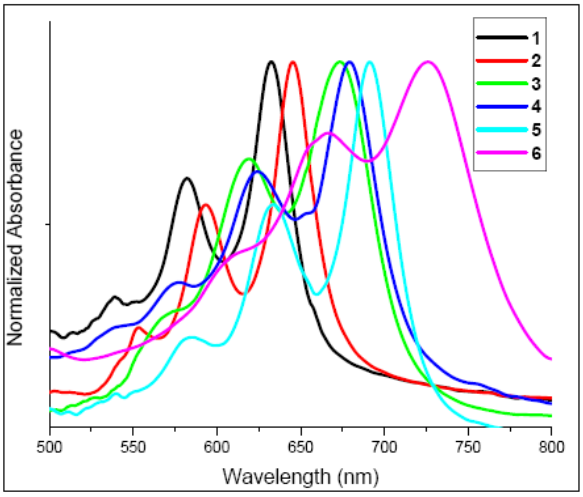

Figure S2. Cyclic Voltammograms of 1-6

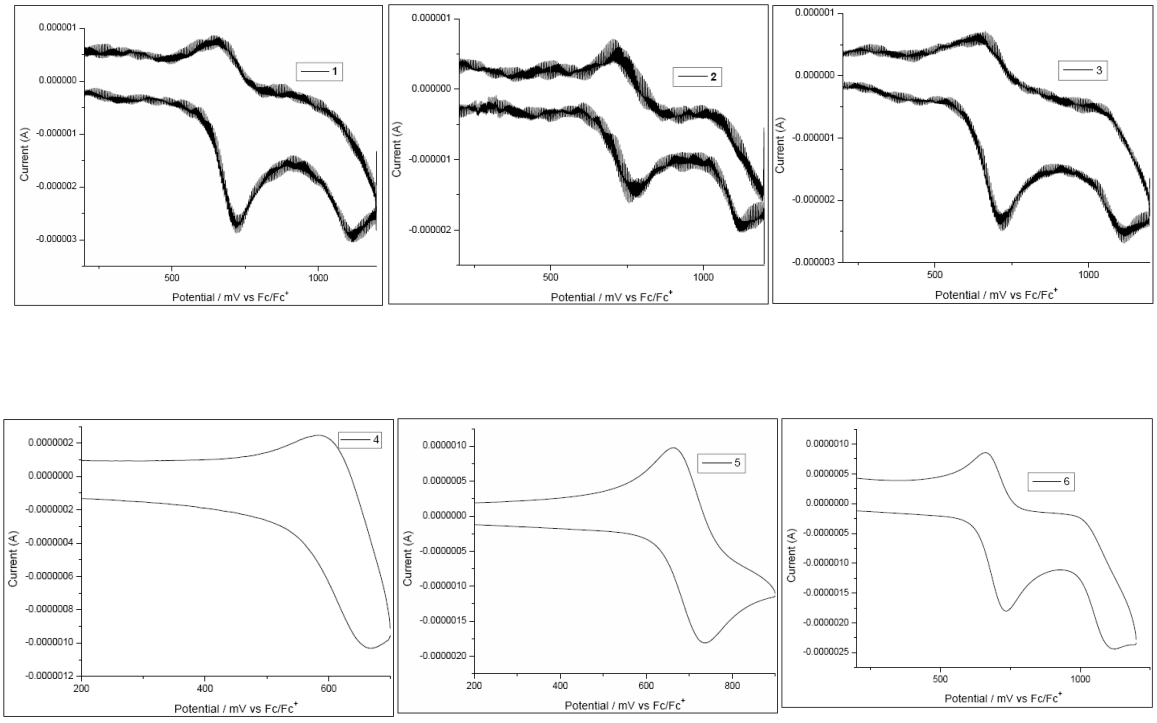

Figure S3. Fluorescence spectra of 1-6 in different solvents

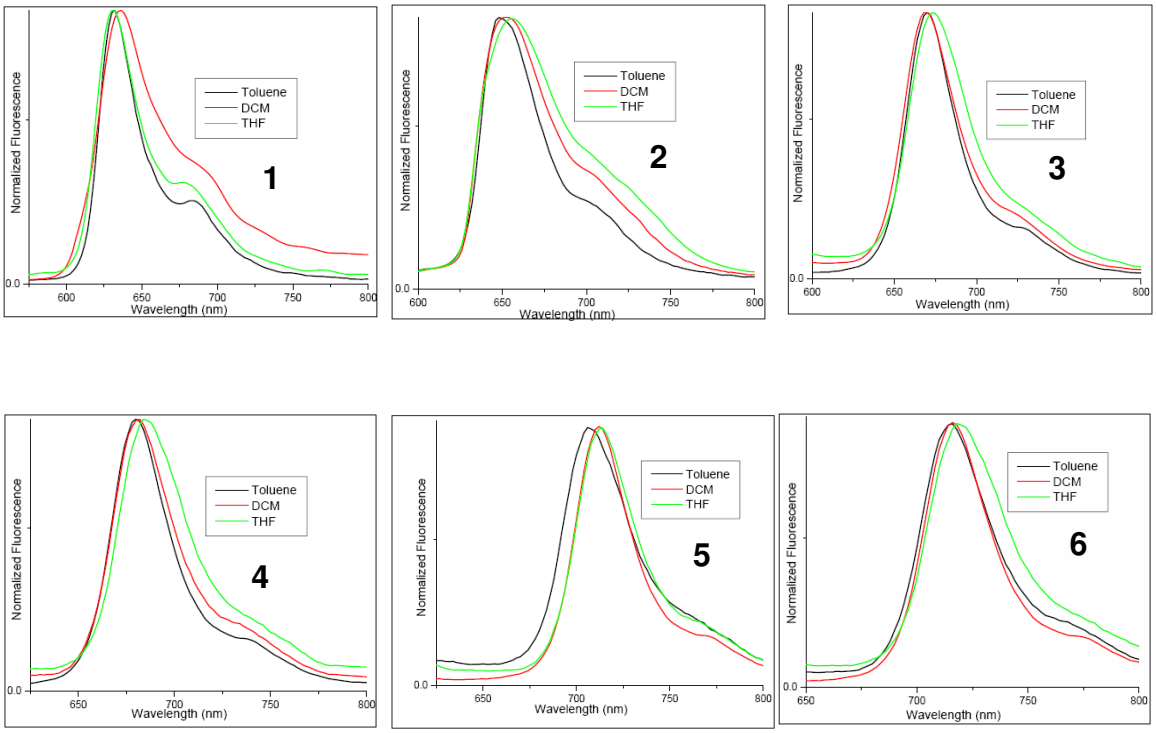

Table S1. Quantum yield of fluorescence (Φ_F) values of 1-6 recorded in different solvents

Compound	Φ_F		
	Toluene	CH_2Cl_2	THF
1	0.14	0.08	0.10
2	0.10	0.09	0.09
3	0.10	0.11	0.13
4	0.10	0.09	0.11
5	0.13	0.12	0.08
6	0.11	0.11	0.12

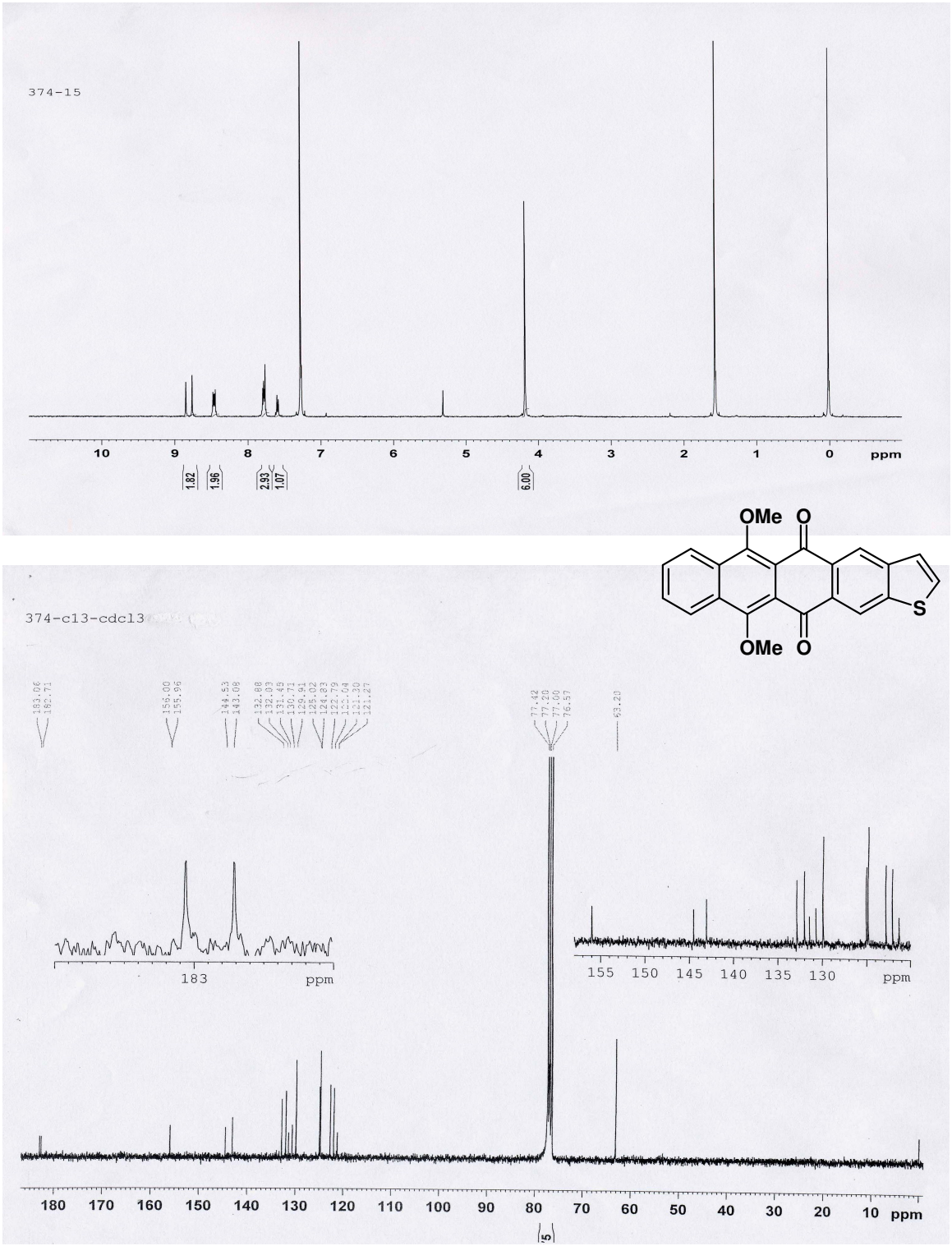

Figure S4. ^{1}H and ^{13}C NMR spectra of **11**.

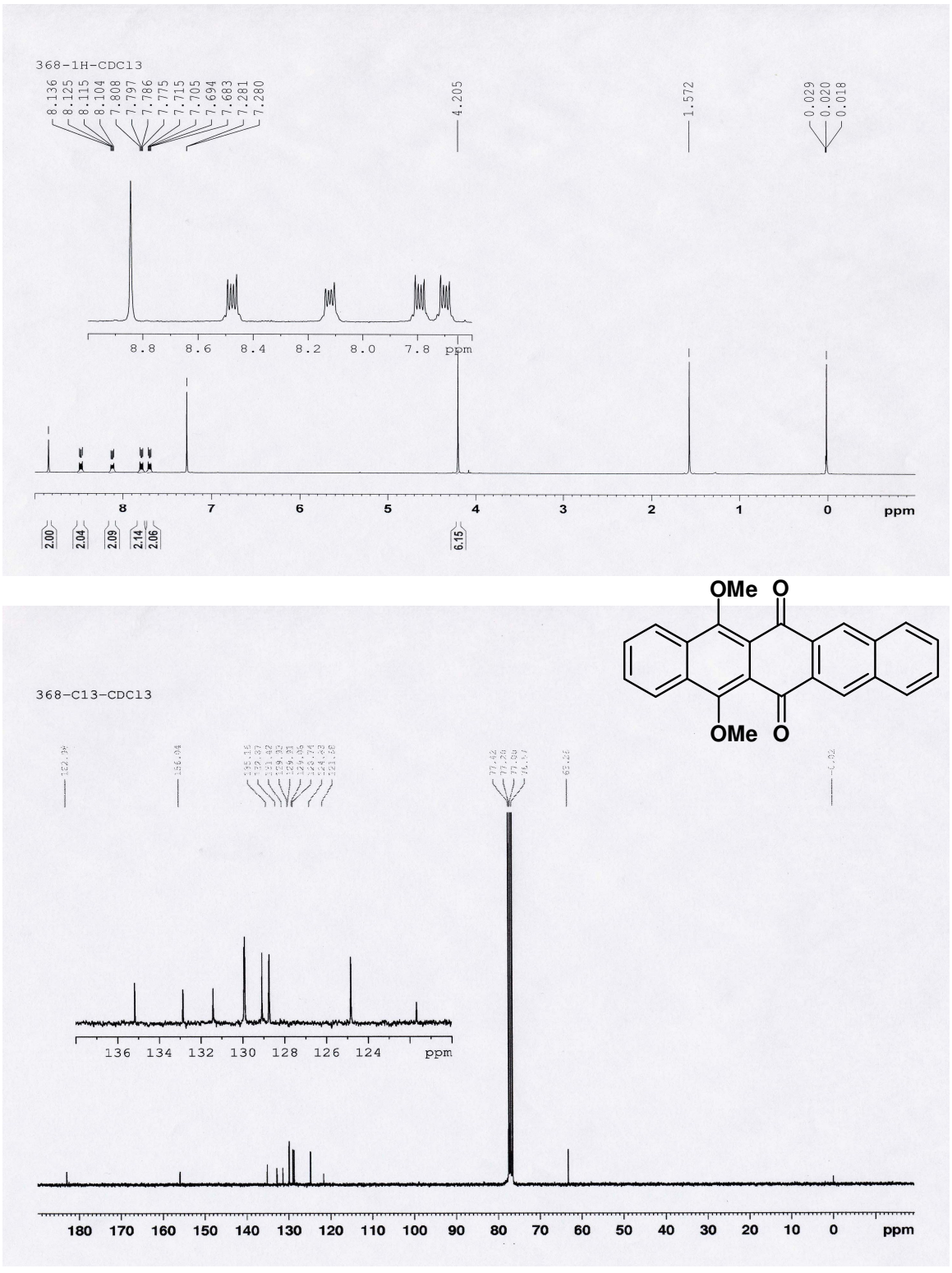

Figure S5. ^{1}H and ^{13}C NMR spectra of **12**.

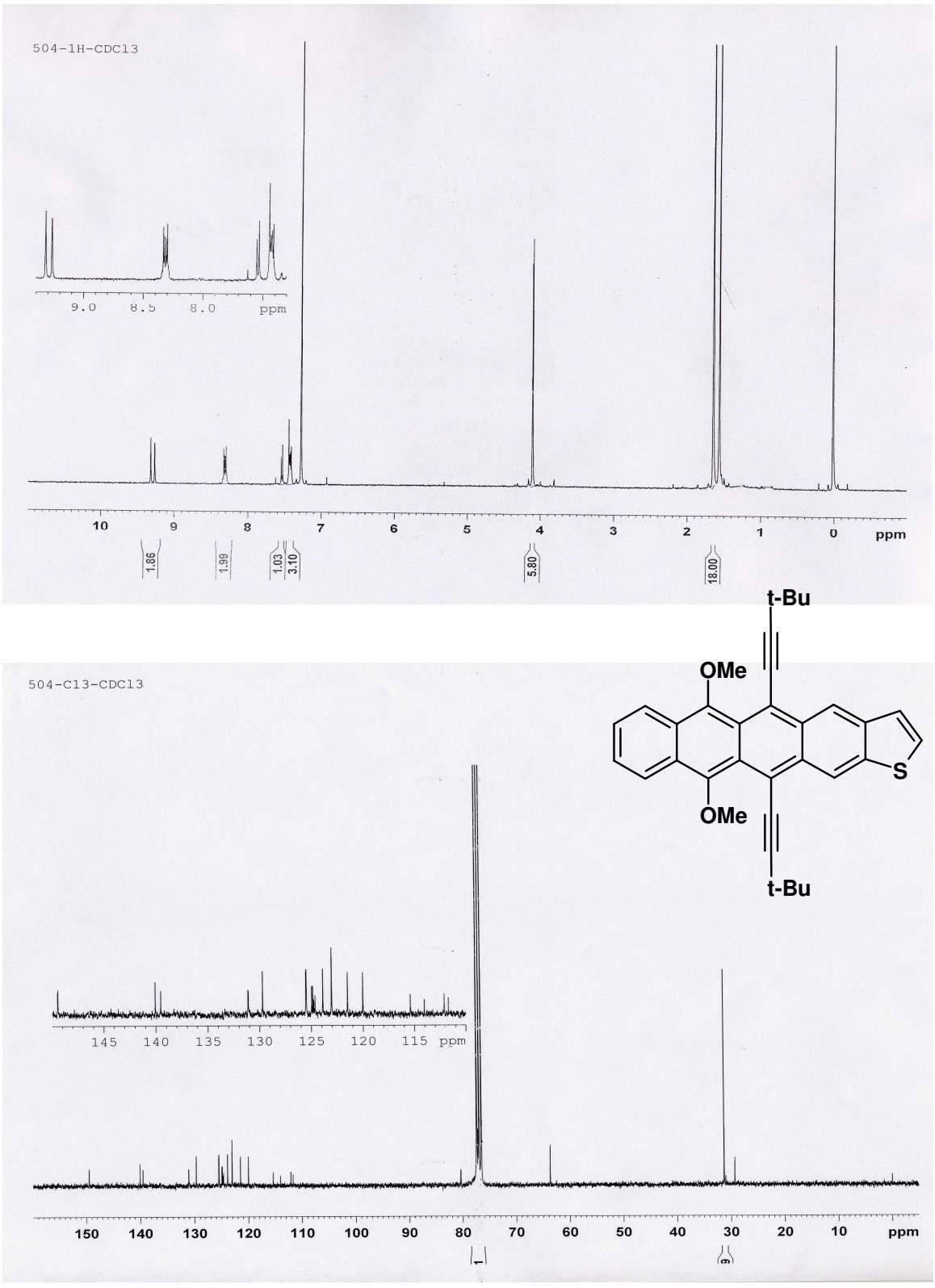

Figure S6. ^{1}H and ^{13}C NMR spectra of **1**.

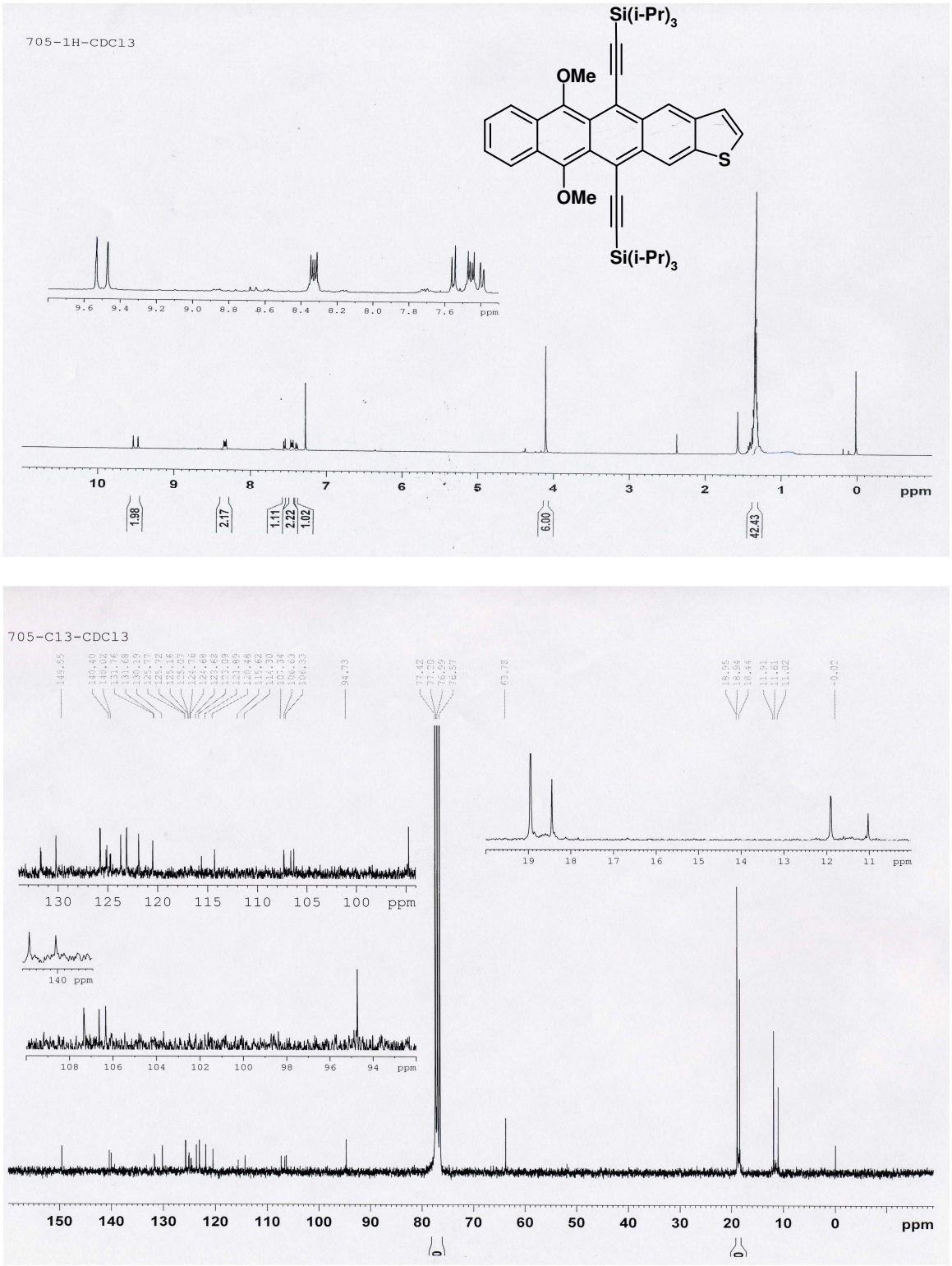

Figure S7. ^{1}H and ^{13}C NMR spectra of **2**.

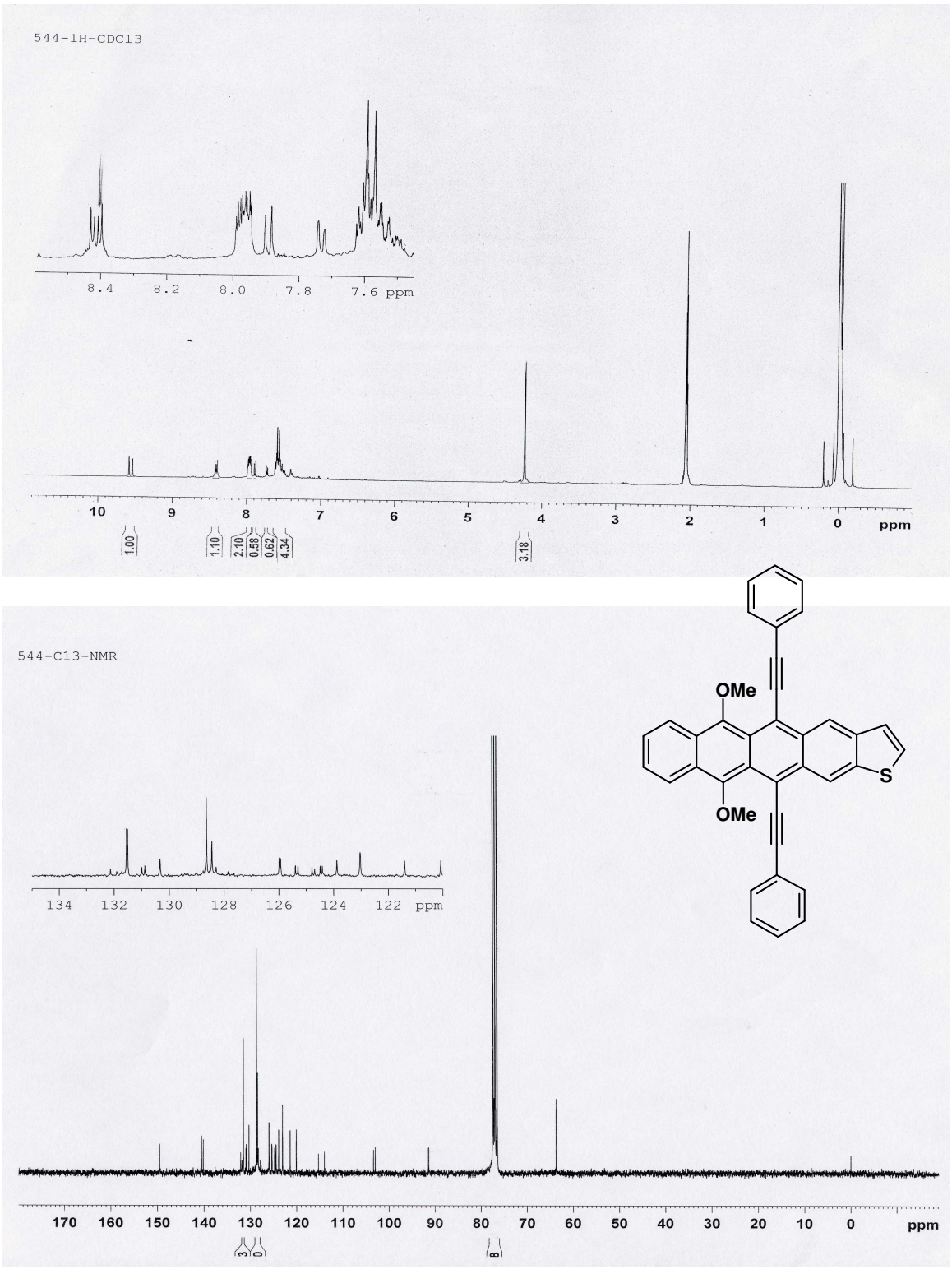

Figure S8. ^{1}H and ^{13}C NMR spectra of **3**.

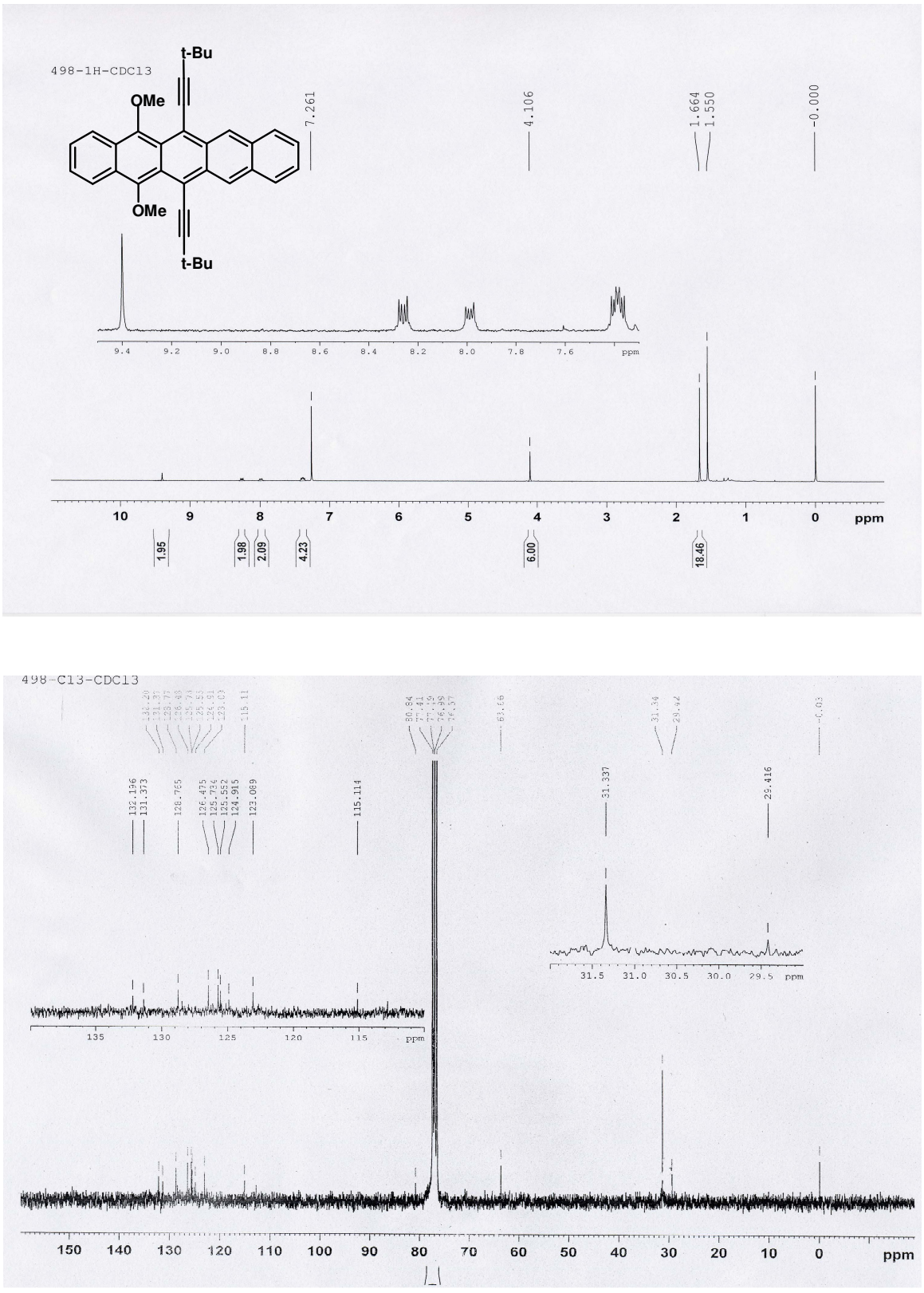

Figure S9. ^{1}H and ^{13}C NMR spectra of **4**.

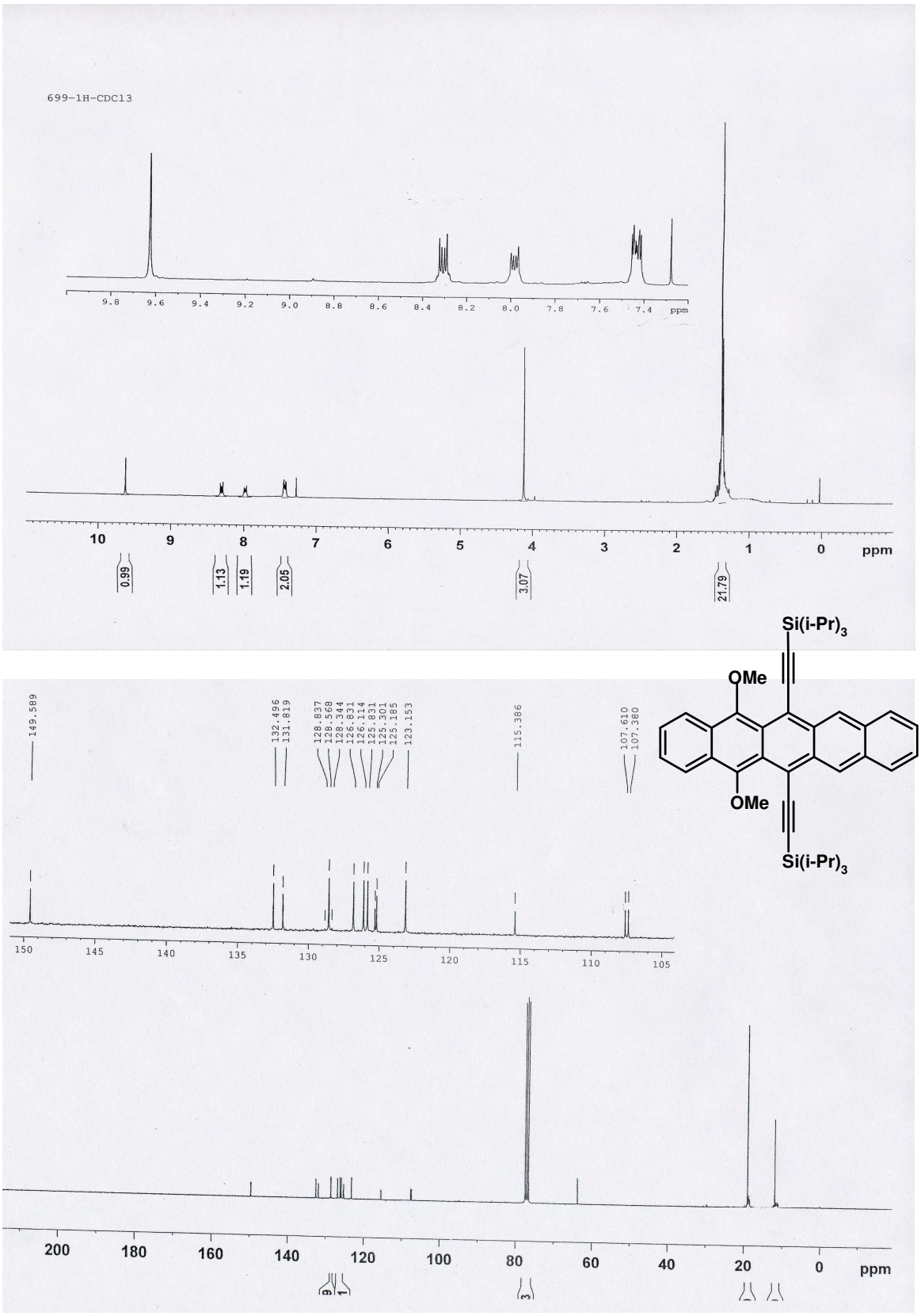

Figure S10. ^{1}H and ^{13}C NMR spectra of **5**.

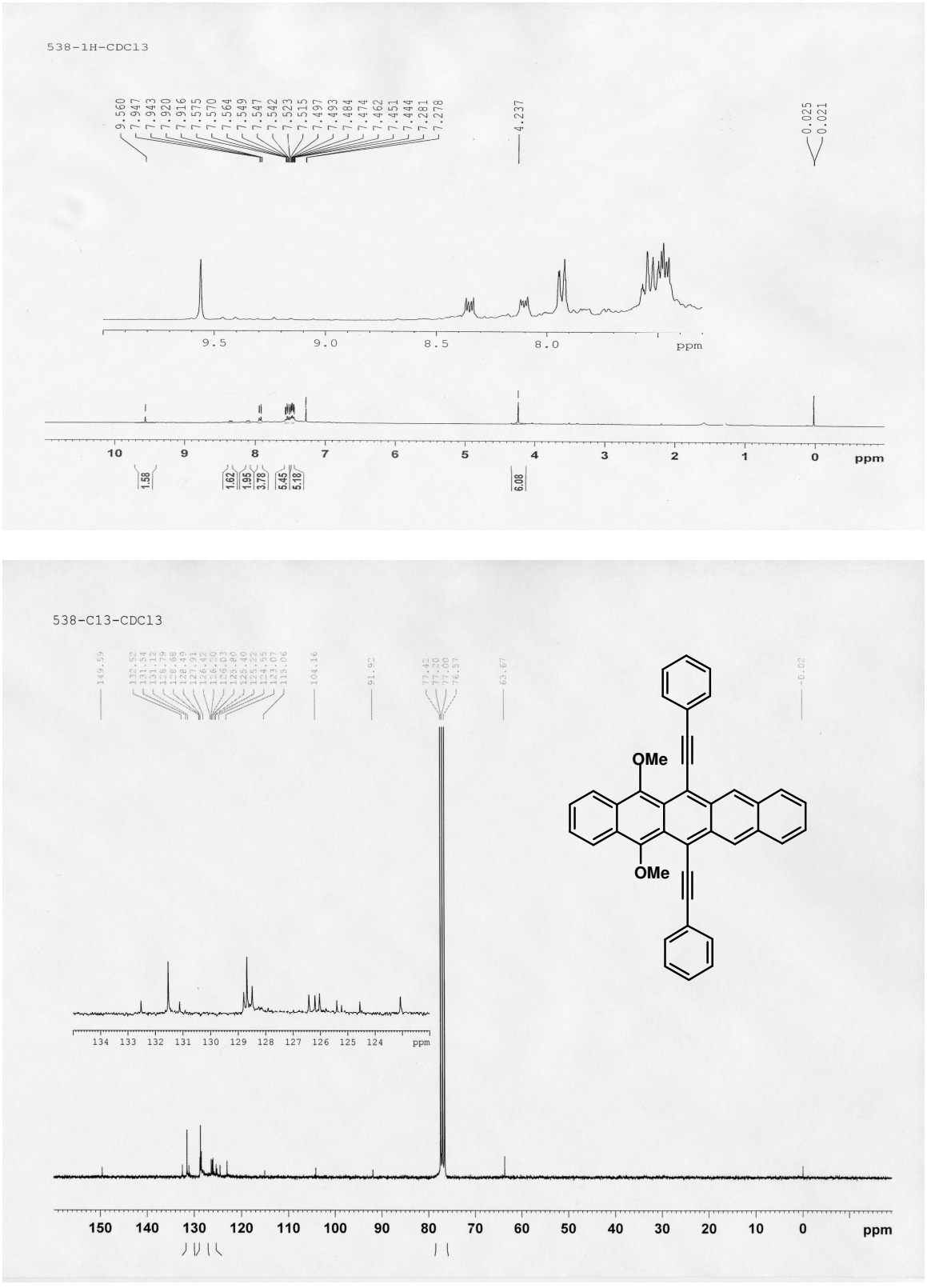

Figure S11. ^{1}H and ^{13}C NMR spectra of **6**.

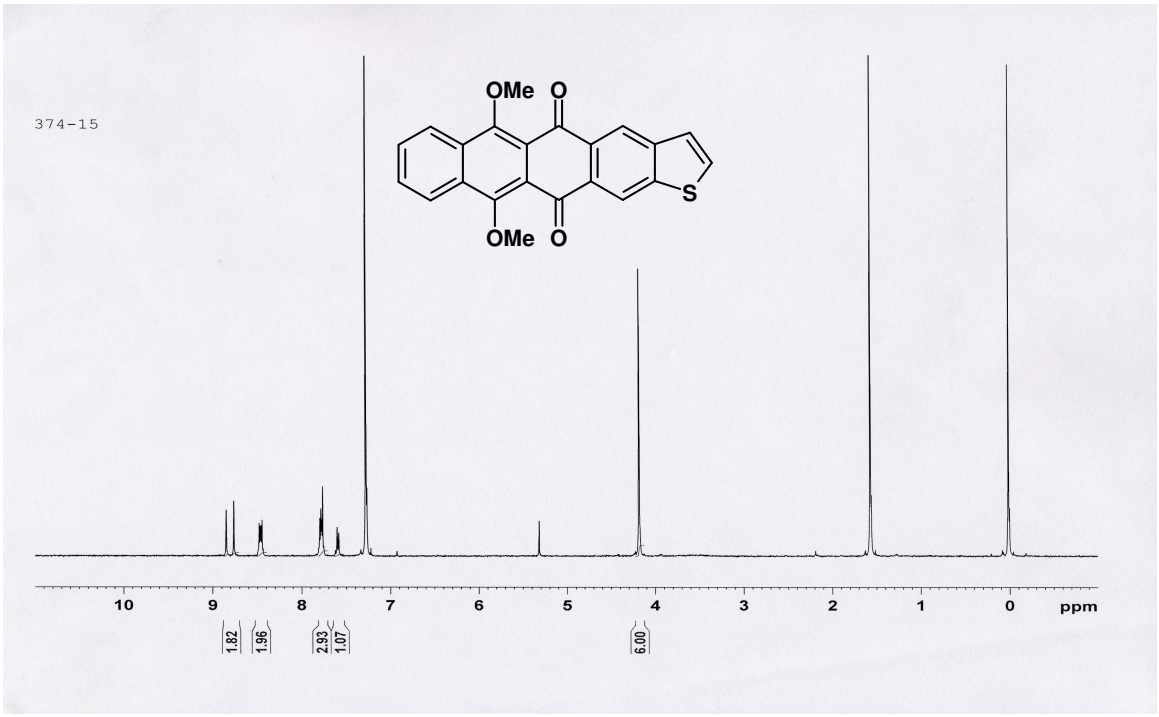

Figure S12. ^{1}H NMR spectrum of **11**.

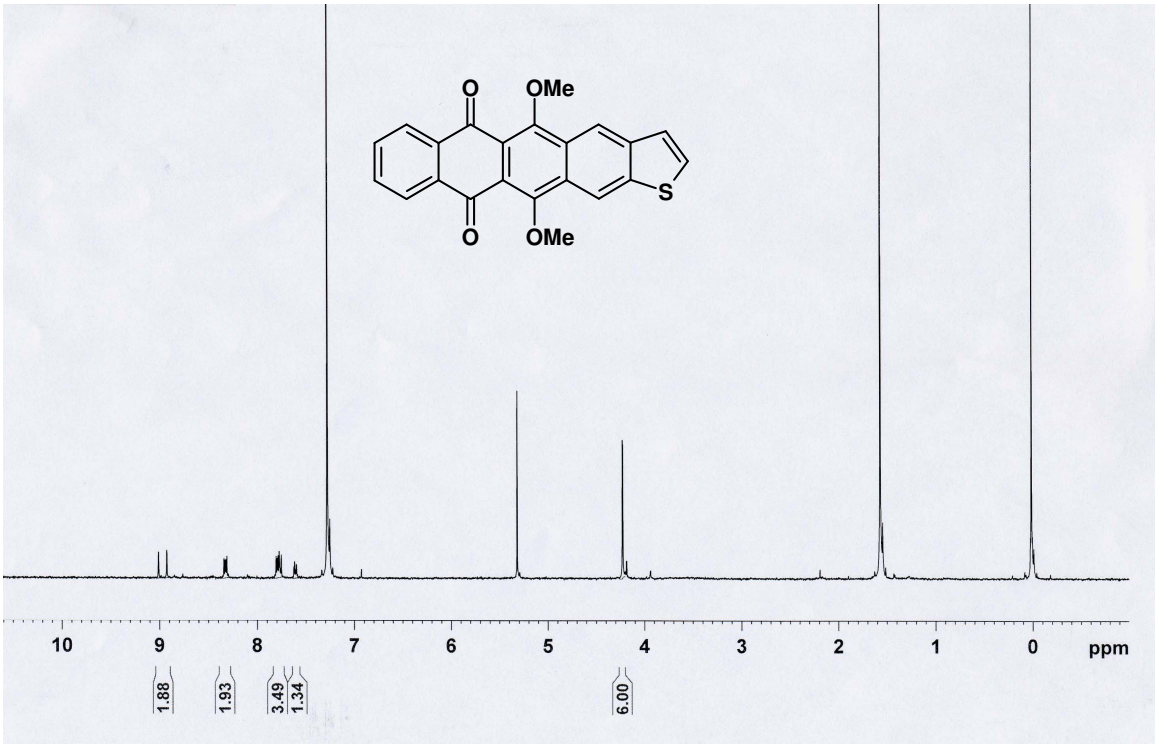

Figure S13. ^{1}H NMR spectrum of **14**.

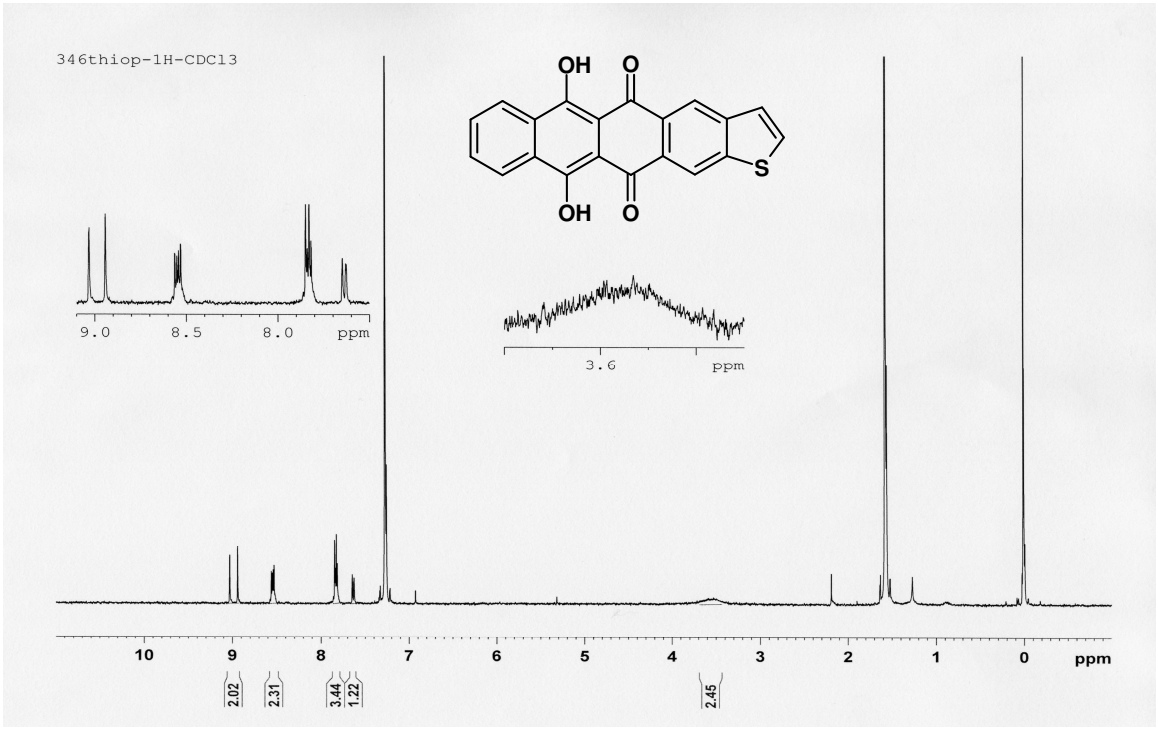

Figure S14. ^{1}H NMR spectrum of **13**.