Supporting Information

Regioselective Copper-Catalyzed Direct Arylation of Benzodithiophene-*S,S*-Tetraoxide

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CONTENTS

General methods:

All the reactions were performed under Ar atmosphere. Tetrabutylammonium bromide (TBAB), n-BuLi (2.5M in hexanes), CuI, K_3PO_4, Cs_2CO_3 and Ag_2CO_3 were purchased from Sigma-Aldrich. Thiophene-3-carboxylic acid, oxalyl chloride, formic acid and aryl iodides were purchased from Oakwood Chemicals. Diethylamine was purchased from Alfa-Aesar. Zinc powder was purchased from Acros Organics. Na_2CO_3 was purchased from Fischer Scientific. All the chemicals were used as purchased. Column chromatography was performed with Silica (60 Å, 230 x 400 mash, Sorbent Technology). Solvents used were from Solvent Purification System (Innovative Technology) for the reactions. All glassware for the reactions was oven dried. Melting points were uncorrected. MBraun UNIlab pro glove box workstation was used for the reactions. NMR experiments were performed with I-400 Bruker NMR instrument. $CDCl_3$ was used as solvent for NMR samples. All the spectra were referenced to δ 7.26 the residual chloroform solvent peak. HRMS analysis was performed at Biochemistry and Molecular Biology Recombinant DNA and Protein Core Facility. All the HRMS data were calculated for compound [Na^+]. 4,8-Didodecyloxybenzo[1,2-b;3,4-b]dithiophene-1,1,5,5-dioxide **1** was synthesized according to the literature.[1, 2]

Experimental section:

General procedure for regioselective direct arylation: 4,8-didodecyloxybenzo[1,2-b;3,4-b]dithiophene-1,1,5,5-tetraoxide (50 mg, 0.080 mmol) was added in a glovebox to a 10 mL reaction vessel, followed by aryl iodide (0.800 mmol), CuI (4.6 mg, 0.024 mmol), 1,10-phenanthroline (8.7 mg, 0.048 mmol), Ag_2CO_3(22.1 mg, 0.080 mmol), K_3PO_4 (34.9 mg, 0.161 mmol), and dry DMF (2 mL). The reaction color was dark brownish green. The reaction vessel was sealed, removed from glovebox, and stirred at 115-120 °C for 20 h. The reaction mixture was allowed to cool to room temperature, poured into water and extracted with diethyl ether:hexanes mixture (1:1, 2 X 5 mL). The organic layer was passed through a celite plug to remove the solid impurities. The resulting solution was washed with deionized water (5 x 15 mL), brine (2 x 15 mL), dried over anhydrous $MgSO_4$, filtered and solvents removed. The crude was recrystallized in dichloromethane/ethanol (1:1) and subsequent rotary evaporation to precipitate the product. The suspension were filtered, and washed with cold ethanol to obtain the pure product.

4,8-Didodecyloxy-2,6-diphenylbenzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (3): orange color solid, yield 69%, mp 163-167°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.80 (m, 4H), 7.49 (dd, J = 5.2, 2.0 Hz, 6H), 7.45 (s, 2H), 4.51 (t, J = 6.5 Hz, 4H), 1.93 (p, J = 6.5 Hz, 4H), 1.57–1.52 (m, 4H), 1.43–1.22 (m, 32H), 0.88 (t, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.10, 142.74, 131.76, 130.80, 129.35, 127.59, 126.83, 126.76, 118.35, 31.93, 30.01, 29.69, 29.66, 29.62, 29.58, 29.37, 29.35, 25.82, 22.70, 14.13. HRMS (m/z): calcd. 797.3877; found, 797.3825

4,8-Bis(dodecyloxy)-2,6-di-*p*-tolylbenzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (4): orange color solid, yield 72%, mp 185-189°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 4H), 7.38 (s, 2H), 7.30 (d, *J* = 7.9 Hz, 4H), 4.49 (t, *J* = 6.6 Hz, 4H), 2.42 (s, 6H), 1.92 (p, *J* = 6.8 Hz, 4H), 1.53 (m, 4H), 1.46–1.17 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.02, 142.74, 141.35, 131.74, 130.05, 127.58, 126.63, 124.01, 117.27, 31.94, 30.02, 29.70, 29.67, 29.63, 29.59, 29.38, 29.36, 25.82, 22.71, 21.61, 14.14. HRMS (m/z): calcd. 825.4193; found, 825.4165

4,8-Bis(dodecyloxy)-2,6-bis(4-methoxyphenyl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (5): Orange color solid, 65%, mp 174-178°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 4H), 7.28 (s, 2H), 6.99 (d, *J* = 8.4 Hz, 4H), 4.47 (t, *J* = 6.7 Hz, 4H), 3.87 (s, 6H), 1.92 (p, *J* = 6.7 Hz, 4H), 1.55 (m, 4H), 1.42–1.25 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 M Hz, $CDCl_3$) δ 161.59, 144.94, 142.37, 131.60, 128.36, 127.54, 119.35, 115.90, 114.87, 55.50, 31.94, 30.03, 29.70, 29.67, 29.64, 29.60, 29.38, 25.83, 22.71, 14.14. HRMS (m/z): calcd. 857.4092; found, 857.4026.

2,6-Bis(4-bromophenyl)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (6): bright orange color solid, yield 81%, mp 157-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 4H), 7.65–7.58 (m, 4H), 7.44 (s, 2H), 4.50 (t, *J* = 6.5 Hz, 4H), 1.97–1.86 (p, *J* = 6.7 Hz, 4H), 1.55–1.49 (m, 4H), 1.44–1.16 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.07, 141.53, 132.59, 131.42, 128.05, 127.45, 125.63, 125.40, 118.87, 31.94, 29.99, 29.71, 29.68, 29.64, 29.59, 29.39, 29.35, 25.79, 22.71, 14.15. HRMS (m/z): calcd. 955.207; found, 955.2041

2,6-Di([1,1'-biphenyl]-4-yl)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (7): orange color solid, yield 72%, mp 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.87 (m, 4H), 7.76–7.69 (m, 4H), 7.63 (dt, *J* = 6.4, 1.3 Hz, 4H), 7.52–7.45 (m, 6H), 7.43–7.38 (m, 2H), 4.54 (t, *J* = 6.5 Hz, 4H), 1.99–1.91 (m, 4H), 1.58 (d, *J* = 7.5 Hz, 4H), 1.47–1.21 (m, 34H), 0.86 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.10, 142.52, 141.38, 138.78, 130.68, 127.97, 127.12, 126.92, 126.63, 126.12, 126.08, 124.62, 116.93, 30.91, 29.01, 28.69, 28.65, 28.62, 28.58, 28.36, 28.34, 24.81, 21.67, 13.10. HRMS (m/z): calcd. 949.4506; found, 949.4489.

4,8-Bis(dodecyloxy)-2,6-bis(4-(trifluoromethyl)phenyl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (8): yellow-orange color solid, yield 66%, mp 177-181°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.54 (s, 2H), 4.51 (t, *J* = 6.5 Hz, 4H), 1.92 (t, *J* = 7.5 Hz, 4H), 1.52 (m, 4H), 1.38–1.25 (m, 32H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.27, 141.39, 131.48, 130.13, 127.56, 127.10, 127.10, 126.33, 126.30, 31.92, 29.98, 29.71, 29.69, 29.67, 29.62, 29.57, 29.37, 29.32, 25.79, 22.69, 14.11. HRMS (m/z): calcd. 933.3628; found, 933.3607

4,8-Bis(dodecyloxy)-2,6-bis(4-fluorophenyl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (9): orange color solid, yield 75%, mp 157-160°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.80 (m, 4H), 7.38 (s, 2H), 7.23–7.16 (m, 4H), 4.50 (t, *J* = 6.5 Hz, 4H), 1.96–1.88 (m, 4H), 1.53 (q, *J* = 7.5 Hz, 6H), 1.42–1.25 (m, 34H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10 (d, *J* = 253.0 Hz), 145.06, 141.64, 131.43, 128.93(d, *J* = 8.6 Hz), 127.47, 123.04 (d, *J* = 3.4 Hz), 118.17(d, *J* = 1.6 Hz), 116.70 (d, *J* = 22.2 Hz), 31.93, 30.00, 29.72, 29.69, 29.67, 29.63, 29.58, 29.38, 29.34, 25.80, 22.71, 14.14. HRMS (m/z): calcd. 833.3692; found, 833.3659

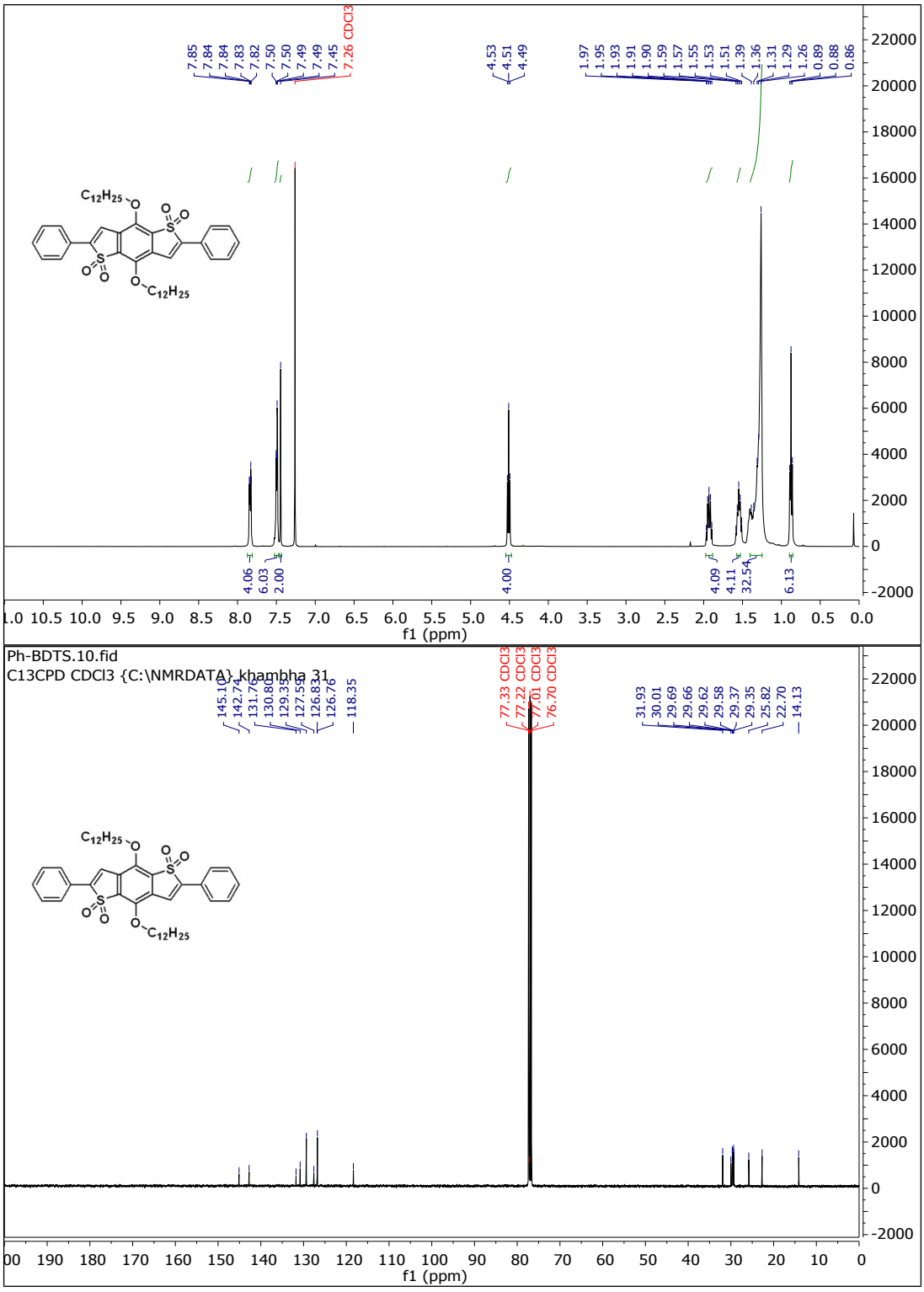
4,8-Bis(dodecyloxy)-2,6-bis(4-nitrophenyl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (10): dark red color solid, yield 79%, mp 175-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38–8.34 (m, 4H), 8.03–7.99 (m, 4H), 7.65 (s, 2H), 4.56 (t, J = 6.5 Hz, 4H), 1.98–1.91 (m, 4H), 1.57 (d, J = 2.5 Hz, 4H), 1.33–1.25 (m, 32H), 0.88 (d, J = 1.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59, 145.37, 140.55, 132.60, 131.22, 127.59, 124.54, 121.87, 31.94, 29.98, 29.72, 29.72, 29.70, 29.63, 29.58, 29.39, 29.33, 25.78, 22.71, 14.15. HRMS (m/z): calcd. 887.3582; found, 887.3566

Dimethyl-4,4'-(4,8-bis(dodecyloxy)-1,1,5,5-tetraoxidobenzo[1,2-b:4,5-b']-dithiophene-2,6-diyl)dibenzoate (11): dark green color solid, yield 60%, mp 186-190°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 4H), 7.65–7.58 (m, 4H), 7.44 (s, 2H), 4.50 (t, *J* = 6.5 Hz, 4H), 1.97–1.86 (p, *J* = 6.5 Hz, 4H), 1.55–1.49 (m, 4H), 1.44–1.16 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.11, 141.63, 132.63, 131.45, 128.09, 127.49, 125.65, 125.43, 118.81, 31.95, 29.99, 29.71, 29.68, 29.64, 29.59, 29.39, 29.35, 25.80, 22.72, 14.16. HRMS (m/z): calcd. 913.3990; found, 913.3963

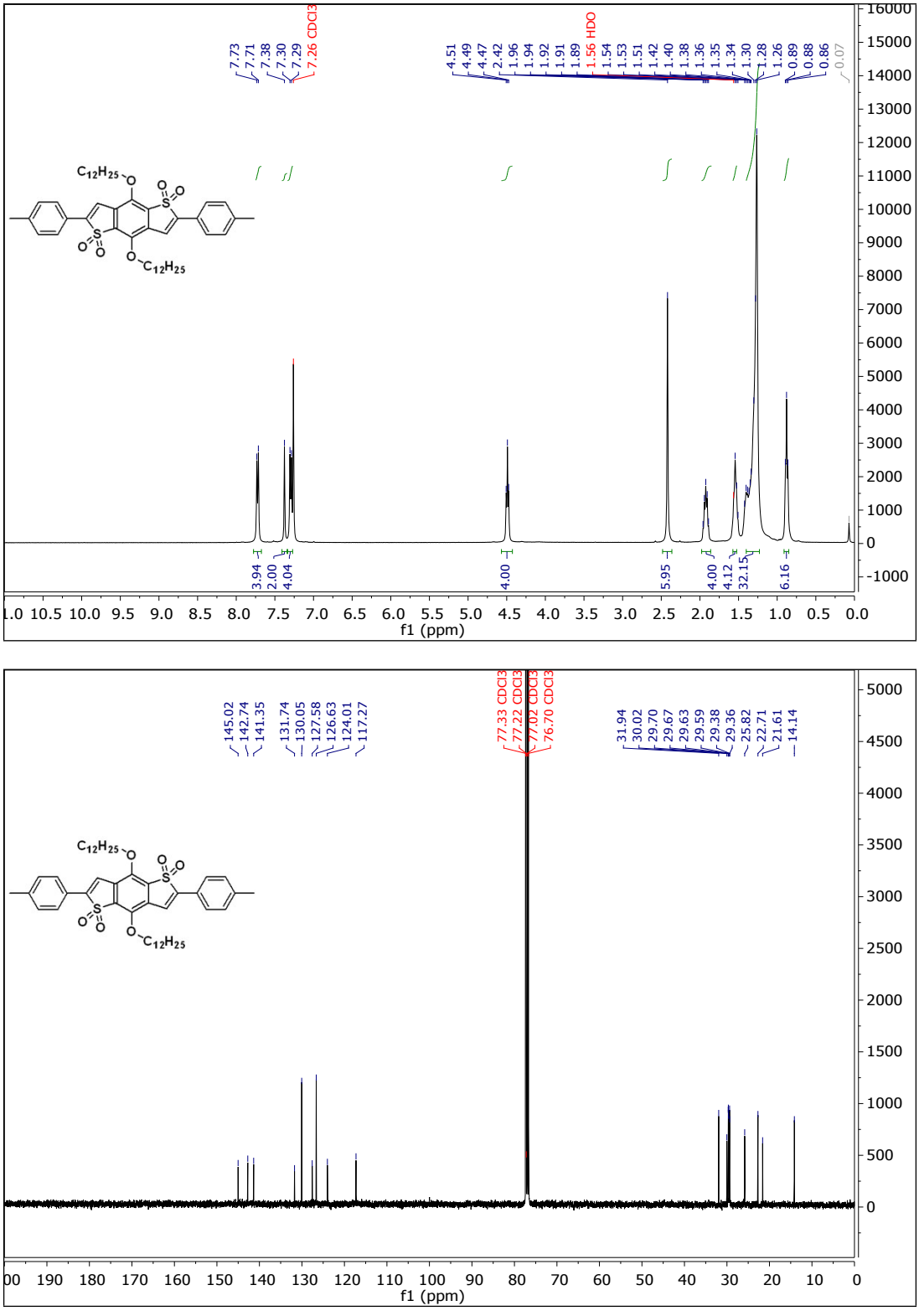
4,8-Bis(dodecyloxy)-2,6-di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (12): bright red color solid, yield 83%, mp 167-169°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.7, 1.0 Hz, 2H), 7.51 (dd, J = 5.1, 1.1 Hz, 2H), 7.22–7.15 (m, 4H), 4.48 (t, J = 6.5 Hz, 4H), 1.93 (p, J = 6.7 Hz, 4H), 1.58–1.52 (m, 4H), 1.43–1.24 (m, 32H), 0.88 (t, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.22, 137.85, 131.26, 129.09, 129.02, 128.80, 128.80, 127.66, 115.76, 31.94, 29.99, 29.69, 29.67, 29.61, 29.58, 29.38, 29.34, 25.82, 22.71, 14.14. HRMS (m/z): calcd. 809.3008; found, 809.2949

4,8-Bis(dodecyloxy)-2,6-di(pyridin-2-yl)benzo[1,2-b:4,5-b']dithiophene-1,1,5,5-tetraoxide (13): bright green color solid, yield 92%, mp 178-181°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.3 Hz, 2H), 7.93 (s, 2H), 7.77 (dt, *J* = 15.2, 7.9 Hz, 4H), 7.30 (t, *J* = 6.0 Hz, 2H), 4.47 (t, *J* = 6.6 Hz, 4H), 1.88 (p, *J* = 6.8 Hz, 4H), 1.53–1.44 (m, 4H), 1.39–1.10 (m, 36H), 0.81 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.74, 144.95, 144.70, 141.25, 136.02, 131.40, 126.72, 123.58, 121.11, 49.85, 30.90, 29.00, 28.66, 28.63, 28.59, 28.54, 28.34, 24.71, 21.67, 13.11. HRMS (m/z): calcd. 799.3785; found, 799.3716

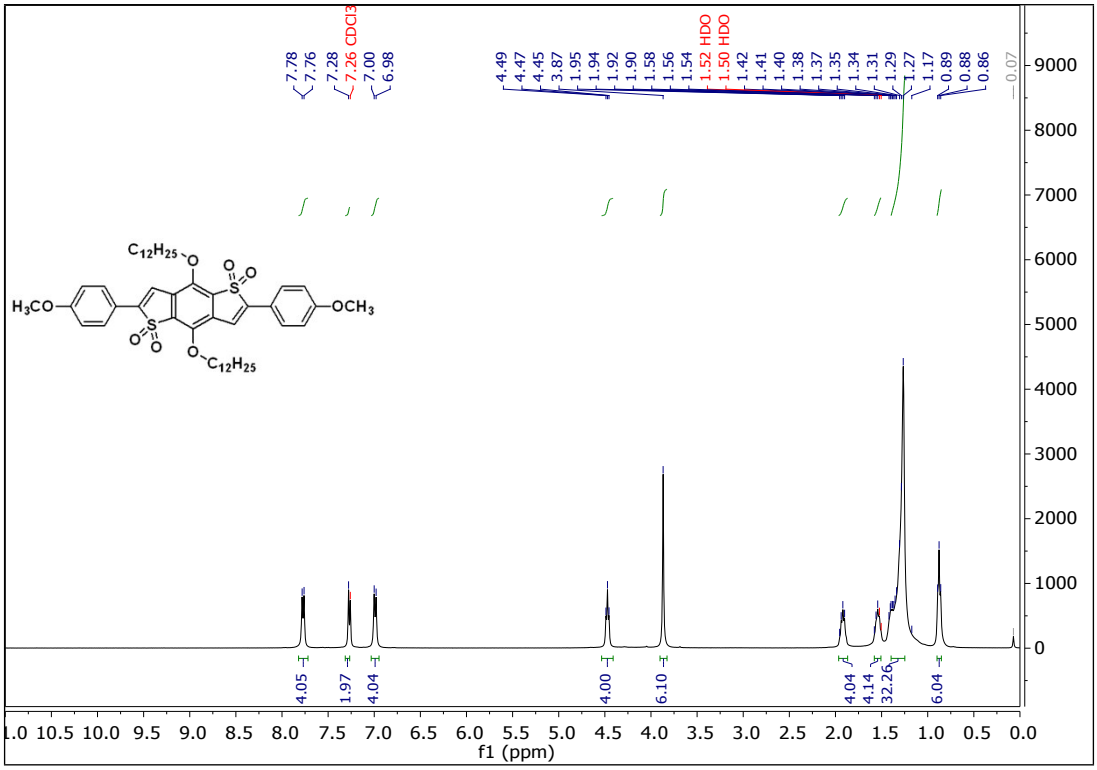
2,6-Bis(4-(9,9-dioctyl-9H-fluoren-2-yl)phenyl)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene 1,1,5,5-tetraoxide (14): 2,6-Bis(4-bromophenyl)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene 1,1,5,5-tetraoxide (50.0 mg, 0.054 mmol), 9,9-dioctylfluorene-2-boronic acid pinacol ester (56.7 mg, 0.109 mmol), $Pd(PPh_3)_4$ (1.8 mg, 3 mol %) and potassium carbonate (123.3 mg, 0.894 mmol) were added In a 10 mL Schlenk flask inside the glove box. A condenser with a septum on was connected at the top of the flask. Vacuum was applied to the reaction for 15 min and then it was filled with Ar. Dry THF (1.5 mL) and degassed distilled water (1.5 mL) was added in to the reaction. The reaction flask was heated to 110 °C for 20 h. After 20 h, distilled water (10 mL) was added to the reaction flask, and crude product was extracted in to ethyl acetate (15 mL x 3). The organic layer was washed with saturated sodium chloride (15 mL x 2) and dried over anhydrous Na_2SO_4. Then the solvent was evaporated. The resulting residue was purified by column chromatography with silica column using dichloromethane/hexane (2:3), followed by recrystallization with dichloromethane and methanol to afford an orange colored solid. Yield 43.0 mg, 52%; mp 102-104 °C; ^{1}H NMR (400 MHz, CDCl3) δ 7.93 (s, 4H), 7.84–7.56 (m, 12H), 7.49 (s, 2H), 7.36 (s, 6H), 4.55 (s, 4H), 1.99 (s, 12H), 1.57 (s, 9H), 1.17 (d, *J* = 85.6 Hz, 76H), 0.84 (d, *J* = 23.8 Hz, 19H), 0.68 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.84, 151.30, 145.33, 144.25, 142.68, 141.56, 140.65, 138.70, 131.94, 128.15, 127.89, 127.57, 127.35, 127.08, 126.20, 125.62, 123.16, 121.60, 120.34, 120.13, 117.98, 55.42, 40.55, 32.15, 31.99, 30.26, 30.22, 29.92, 29.89, 29.86, 29.83, 29.60, 29.43, 29.41, 26.07, 24.01, 22.92, 22.82, 14.36, 14.30. HRMS (m/z): calcd. 1574.0140; found, 1575.0169

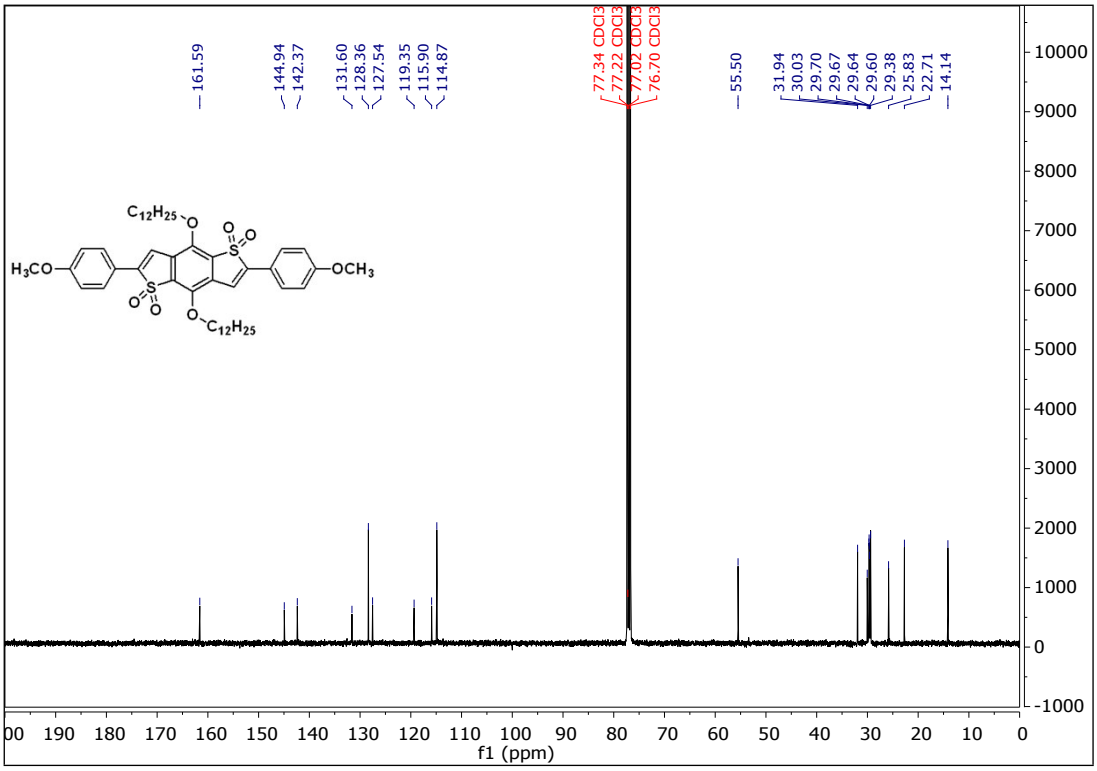


Compound (**3**): ^{1}H NMR (above) and ^{13}C NMR (below)

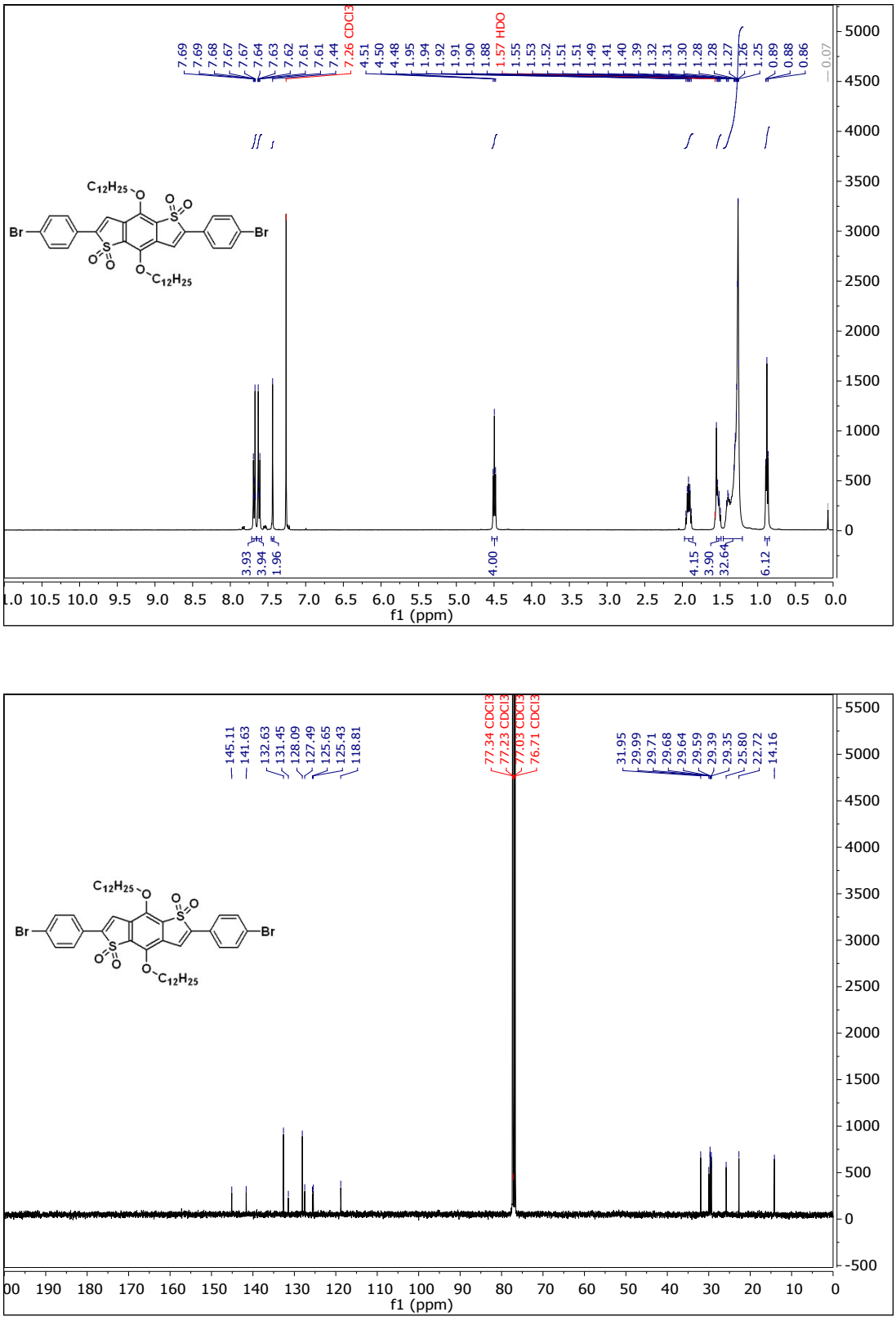


Compound (**4**): ^{1}H NMR (above) and ^{13}C NMR (below)

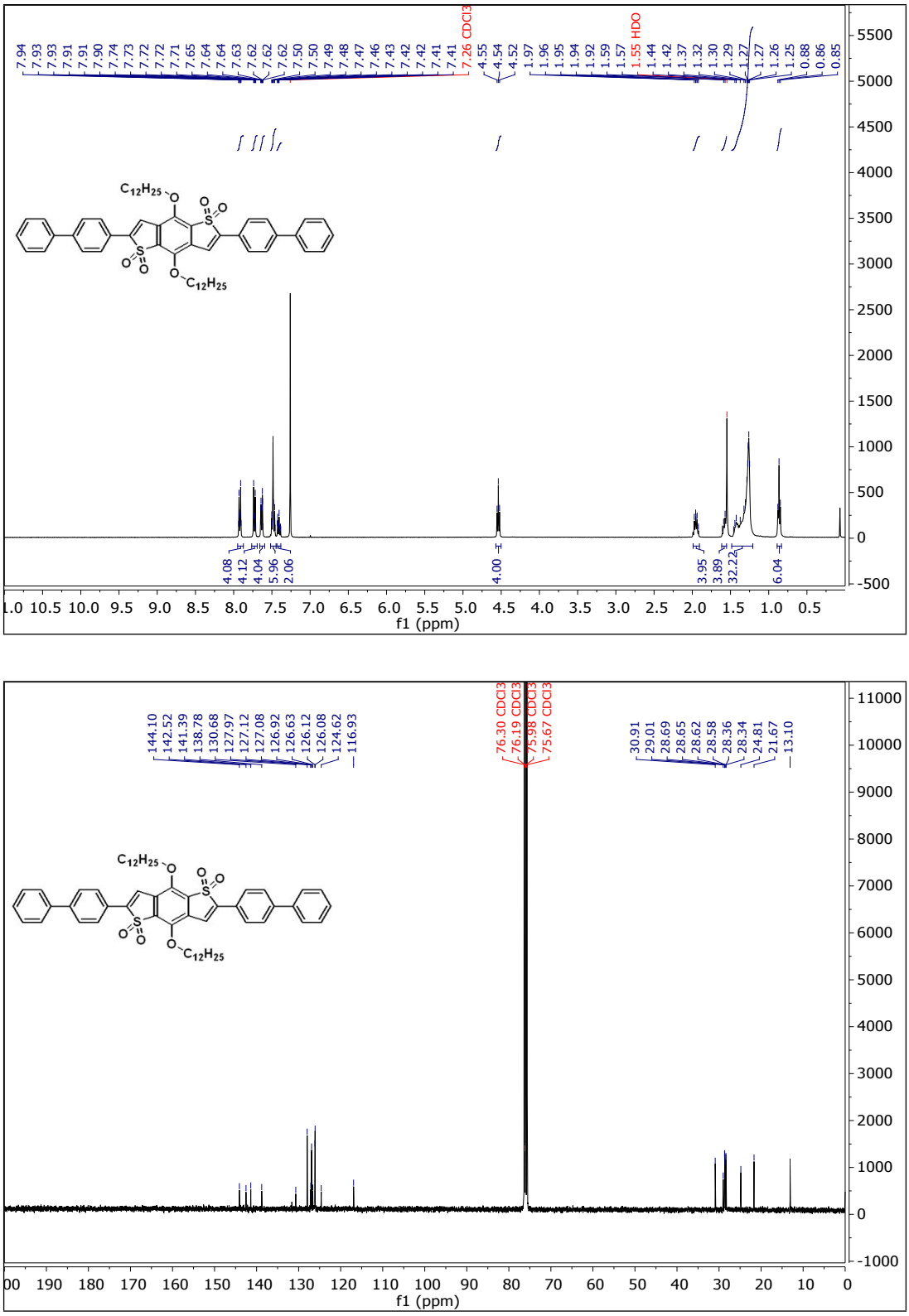




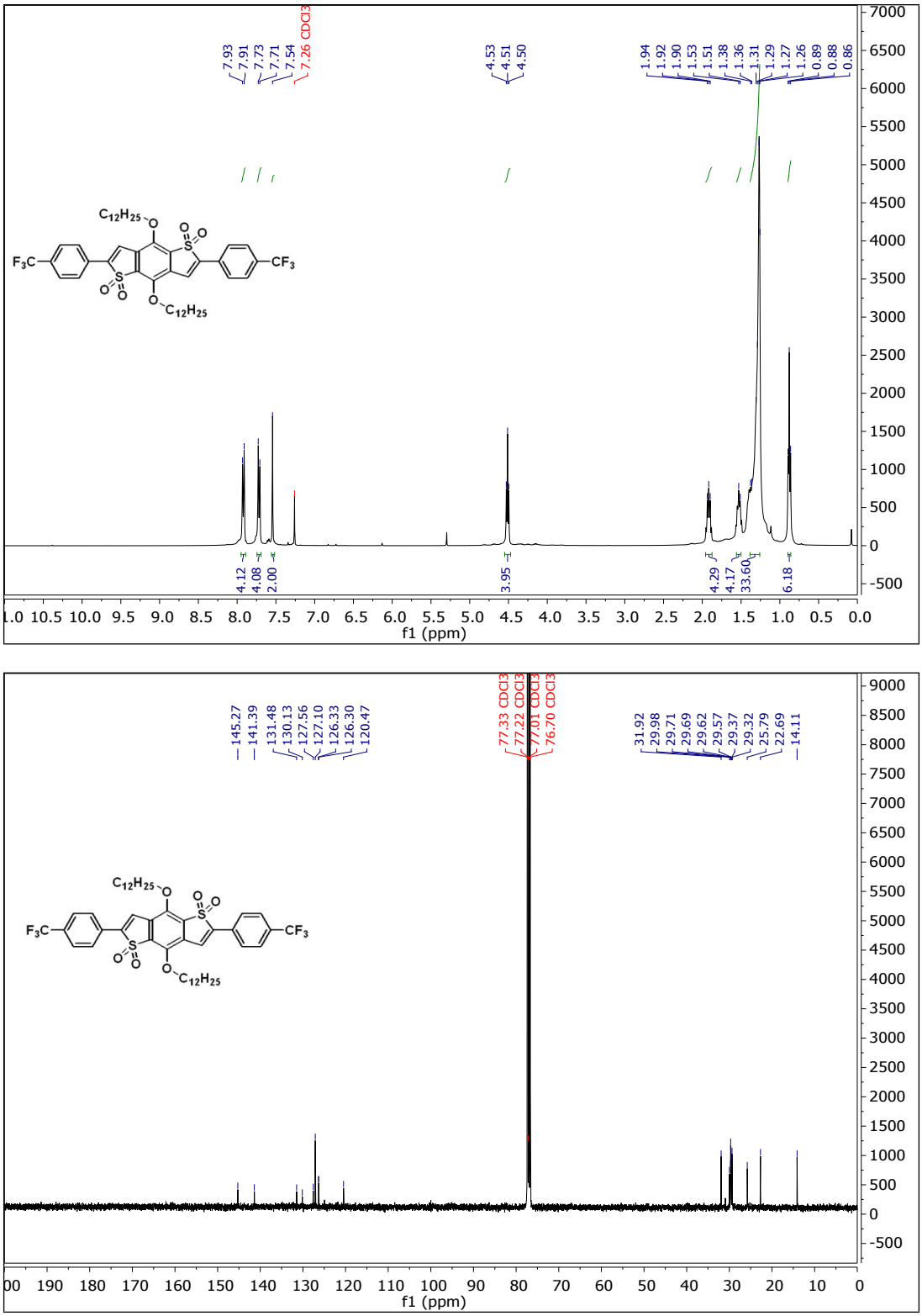
Compound (**5**): ^{1}H NMR (above) and ^{13}C NMR (below)



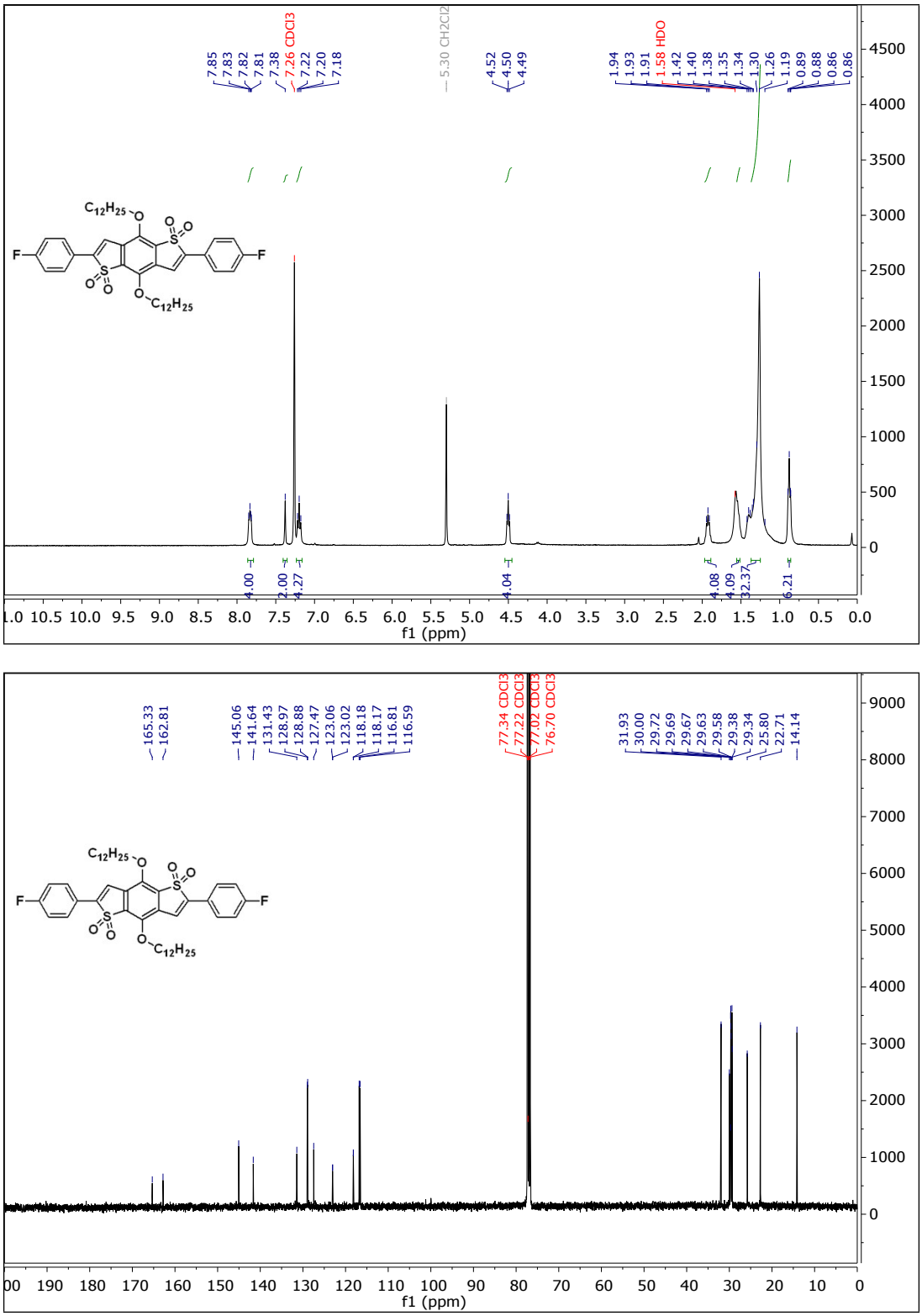
Compound (**6**): ^{1}H NMR (above) and ^{13}C NMR (below)



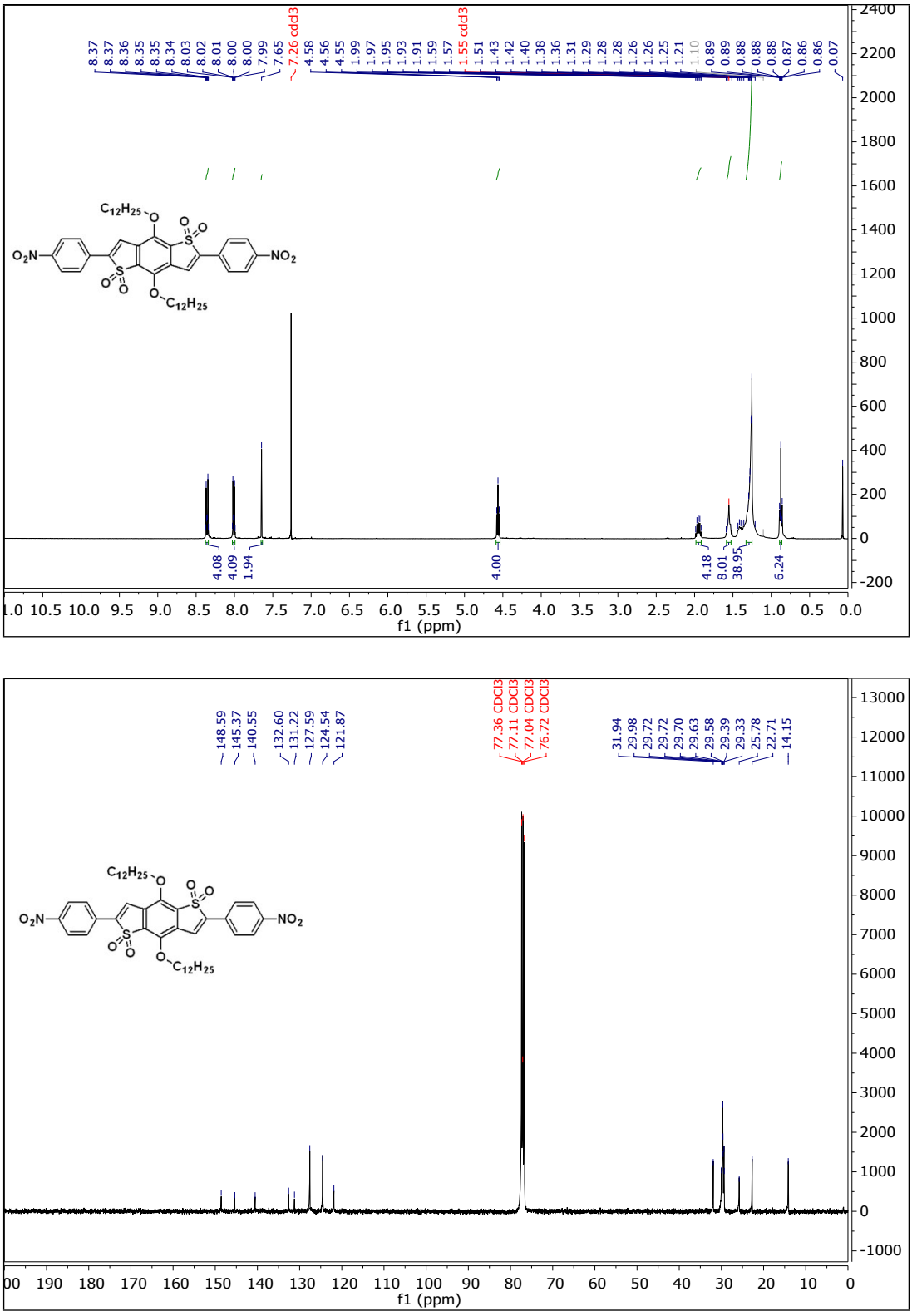
Compound (**7**): ^{1}H NMR (above) and ^{13}C NMR (below)



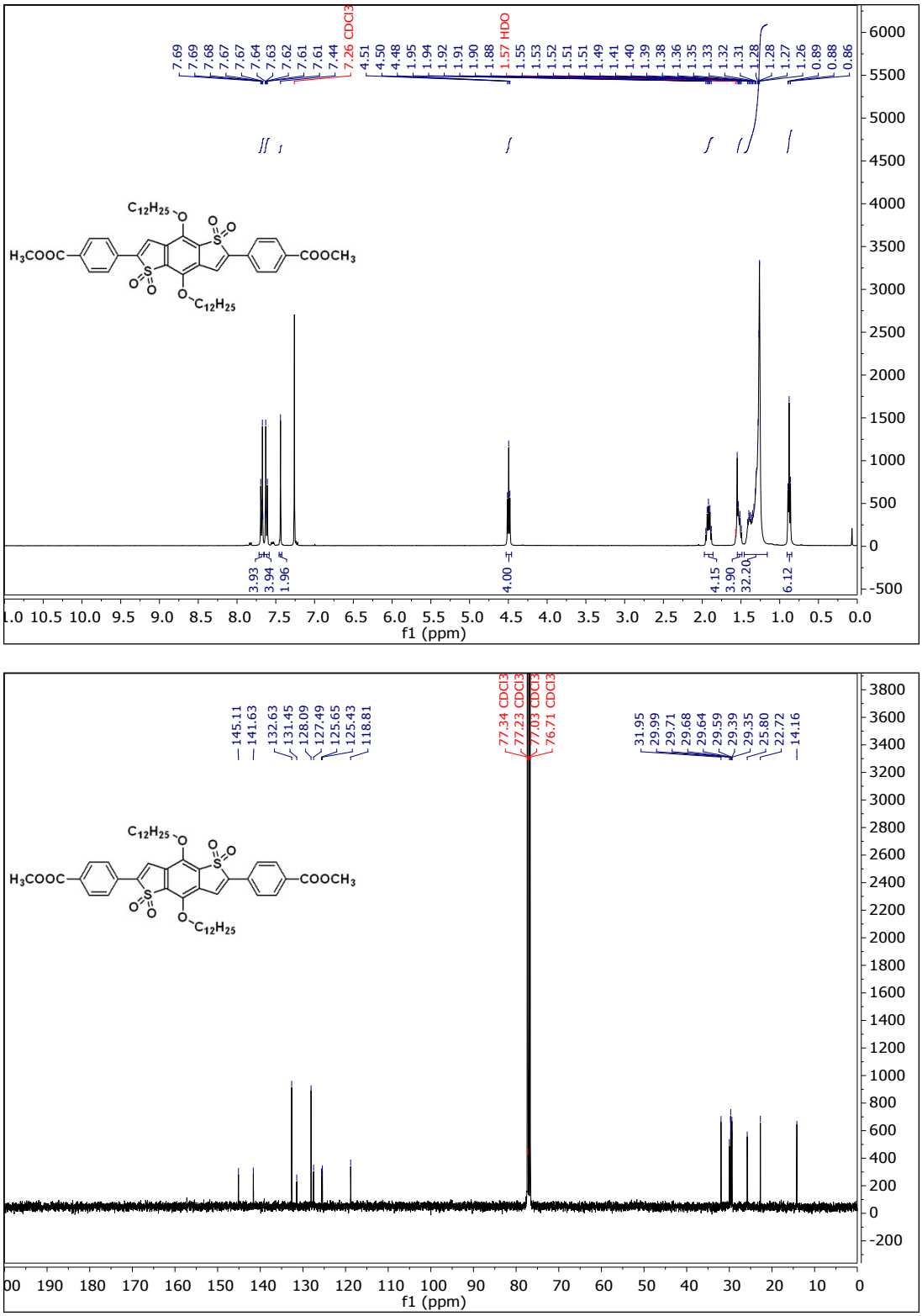
Compound (**8**): ^{1}H NMR (above) and ^{13}C NMR (below)



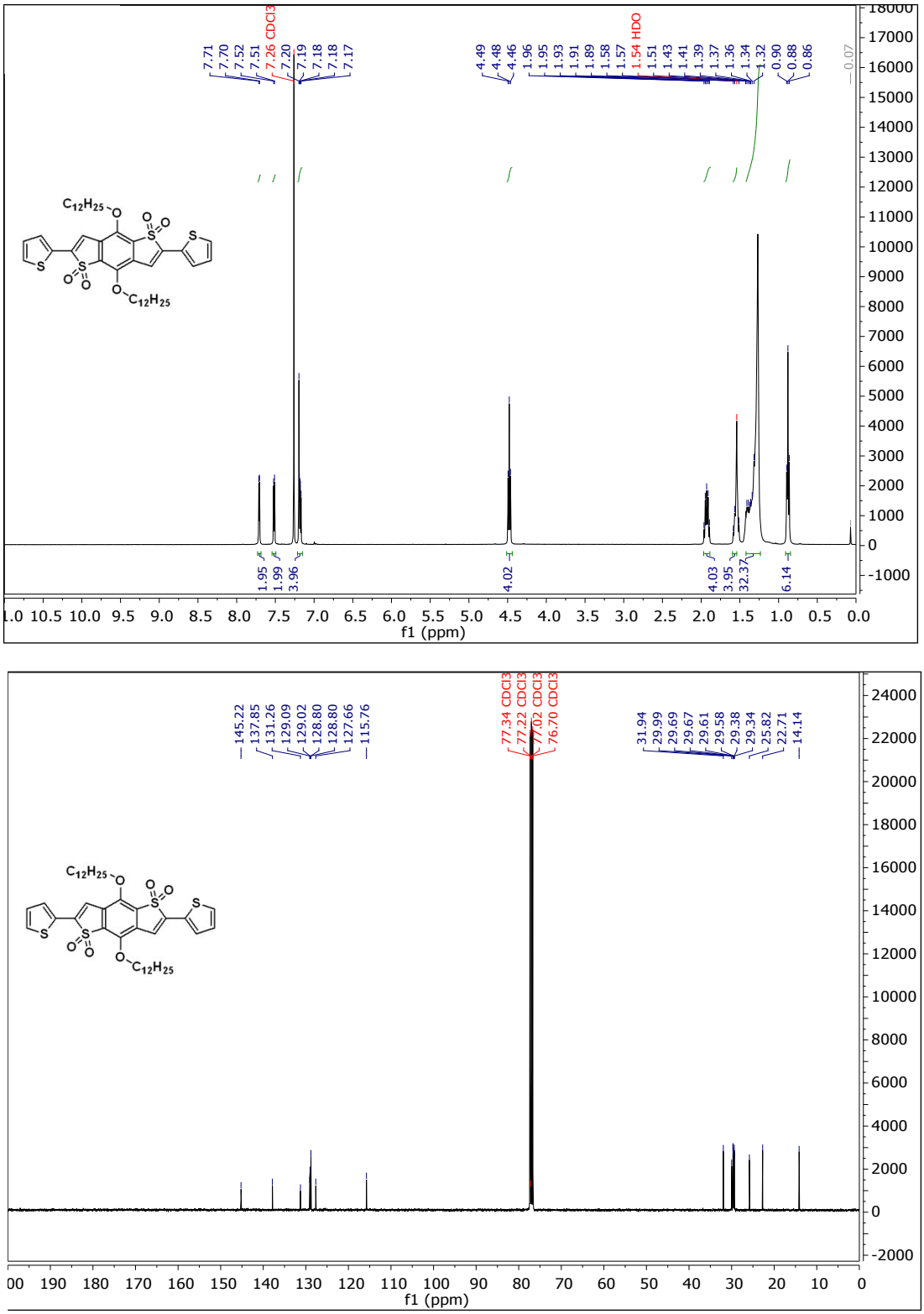
Compound (**9**): ^{1}H NMR (above) and ^{13}C NMR (below)



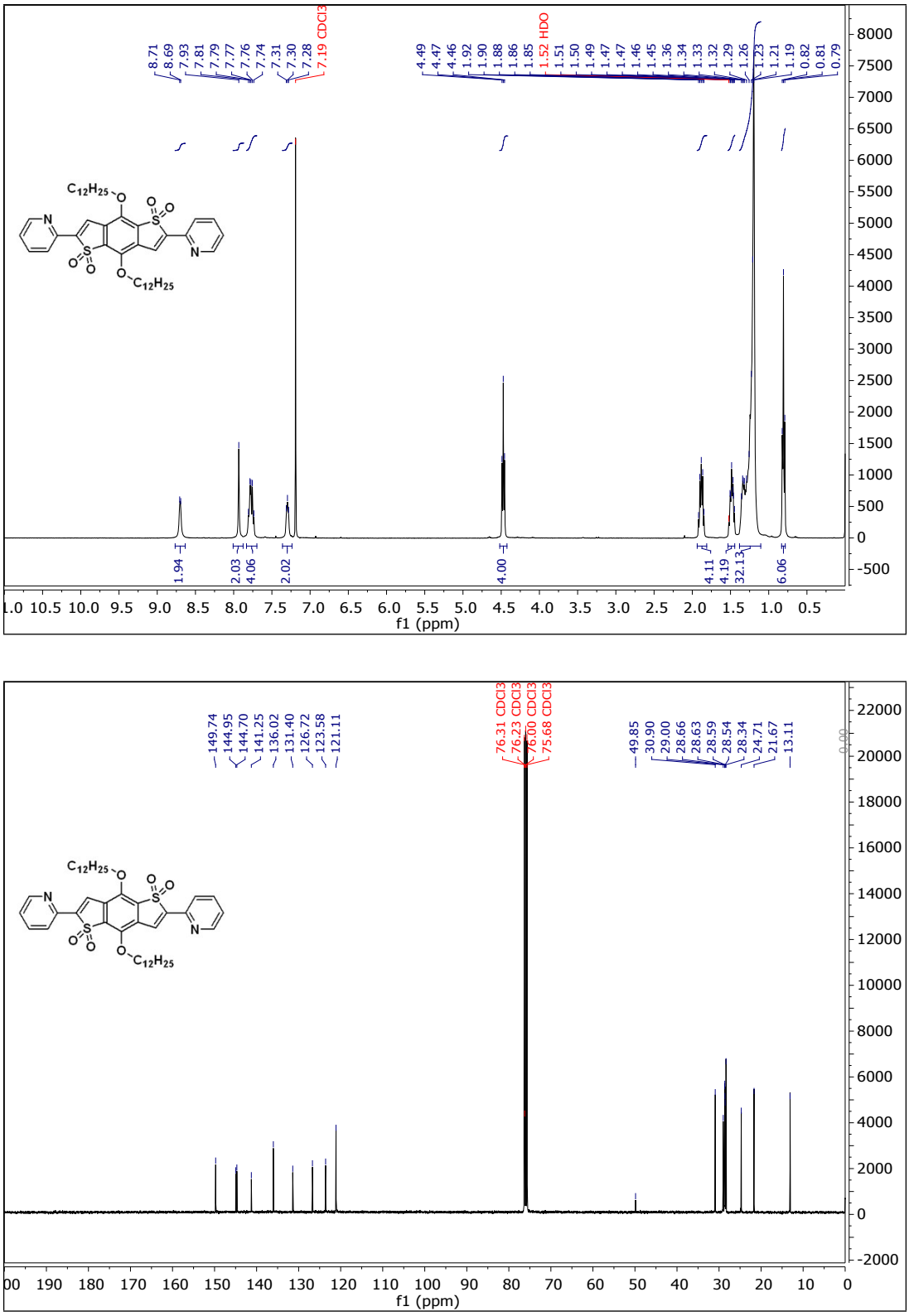
Compound (**10**): ^{1}H NMR (above) and ^{13}C NMR (below)



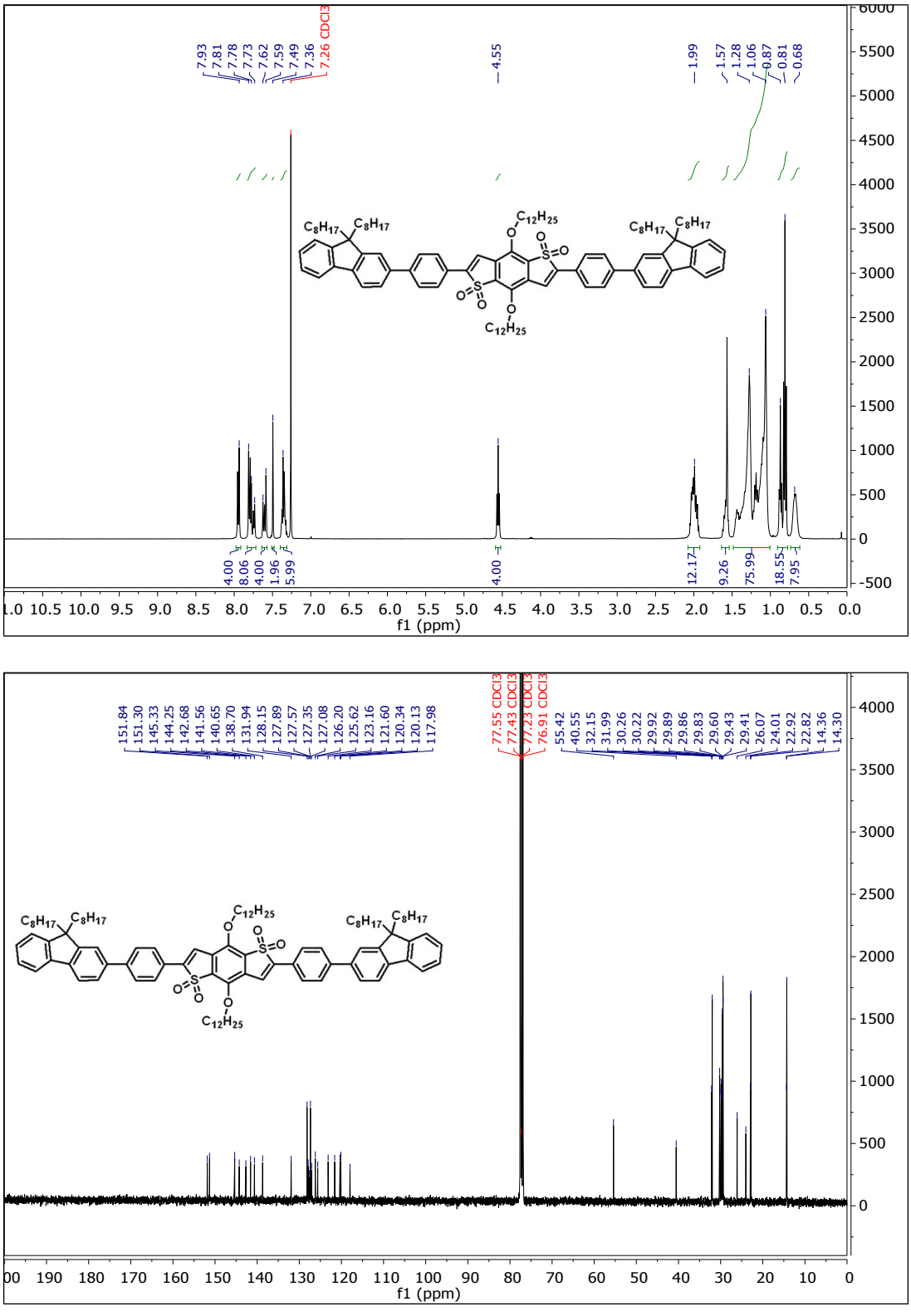
Compound (**11**): ^{1}H NMR (above) and ^{13}C NMR (below)



Compound (**12**): ^{1}H NMR (above) and ^{13}C NMR (below)



Compound (**13**): ^{1}H NMR (above) and ^{13}C NMR (below)



Compound (**14**): ^{1}H NMR (above) and ^{13}C NMR (below)

Compound (**3**): Crystal structure

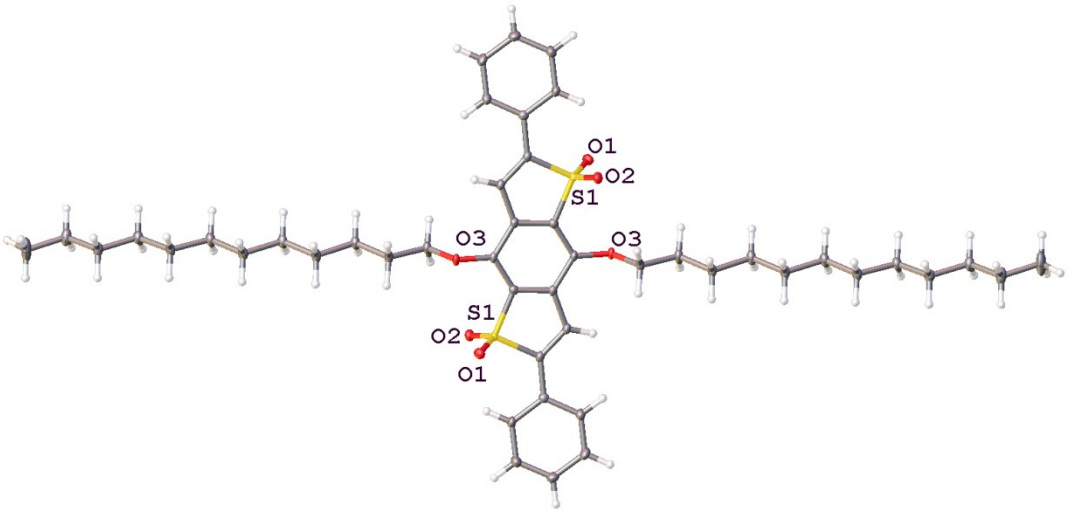


Table 1. Crystal data and structure refinement for compound (**3**)

Identification code	nelson12_0m_a	
Empirical formula	C46 H62 O6 S2	
Formula weight	775.07	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.9364(3) Å	α = 90°.
	b = 7.6637(2) Å	β = 97.5930(10)°.
	c = 18.4671(4) Å	γ = 90°.
Volume	2095.36(8) $Å^3$	
Z	2	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	1.521 mm^{-1}	
F(000)	836	
Crystal size	0.3 x 0.3 x 0.08 mm^3	
Theta range for data collection	2.985 to 68.609°.	
Index ranges	-15<=h<=18, -8<=k<=7, -22<=l<=19	
Reflections collected	17378	
Independent reflections	3784 [R(int) = 0.0545]	
Completeness to theta = 67.679°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6039	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3784 / 0 / 245	

Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0943
R indices (all data)	R1 = 0.0452, wR2 = 0.0975
Extinction coefficient	n/a
Largest diff. peak and hole	0.449 and -0.342 e.$Å^{-3}$

References:

1. J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012-6018.
2. M. Nandakumar, J. Karunakaran and A. K. Mohanakrishnan, *Organic Letters*, 2014, **16**, 3068-3071.