SUPPORTING INFORMATION

Highly Fluorescent Oligothiophenes Through the Incorporation of Central Dithieno[3,2-*b*:2',3'-*d*]pyrrole Units

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General. *N*-Octyldithieno[3,2-*b*:2',3'-*d*]pyrrole (**1**) was prepared as previously reported.[1] Unless noted, all materials were reagent grade and used without further purification. Chromatographic separations were performed using standard column methods with silica gel (230-400 mesh). Dry THF was obtained by treatment with sodium metal followed by distillation under nitrogen atmosphere. All glassware was oven-dried, assembled hot, and cooled under a dry nitrogen stream before use. Transfer of liquids was done by standard syringe techniques and all reactions were performed under a stream of dry nitrogen.

Unless otherwise noted, the ^{1}H NMR and ^{13}C NMR spectra were carried out on a 300 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet. High-resolution mass spectrometry was performed in house using a Bruker BioTOF III with an Agilent ES tuning mix as the reference.

General procedure for synthesis of DTP terthiophene analogues (2a-c): N-Octyl dithieno[3,2-*b*:2',3'-*d*]pyrrole (145.7 mg, 0.5 mmol) was dissolved in dry THF (80 mL) and cooled in an acetone/dry ice bath for 20 minutes. Tert-butyllithium (0.3 mL, 0.5 mmol) was then added dropwise and the mixture was allowed to stir 1 hour. At this point the mixture was removed from the ice bath, allowed to warm to room temperature, and then returned to the ice bath. Tributyltin chloride (0.15 mL, 0.5 mmol) was then added dropwise and the mixture was allowed to warm to room temperature and stir for 1 hour.

Meanwhile, in a separate flask, $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol) was dissolved in THF (20 mL) and the appropriate 2-bromoaryl (2-bromothiophene, 2-bromo-3-butylthiophene or 2-bromothiazole) (0.5 mmol) was added. The 2,6-bis(tributylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole solution was transferred into the catalyst/bromoaryl solution and refluxed for 20 hours. The solution was then allowed to cool, quenched with water, and extracted with diethyl ether. The combined ether washes were concentrated via rotary evaporation and the crude product was purified by column chromatography over silica gel.

***N*-Octyl-2-(2'-thienyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (2a).** 90-95% yield; ^{1}H NMR ($CDCl_3$) δ 7.200 (m, 2H), 7.142 (d, *J* = 5.4 Hz, 1H), 7.104 (s, 1H), 7.032 (m, 1H), 6.988 (d, *J* = 5.4 Hz, 1H), 4.174 (t, *J* = 7.2 Hz, 2H), 1.873 (m, 2H), 1.295 (m, 10H), 0.878 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 145.53, 145.32, 139.68, 135.18, 128.61, 124.53, 124.01, 123.66, 115.53, 114.48, 111.65, 108.38, 48.14, 32.56, 31.12, 29.97, 29.91, 27.75, 23.38, 14.86; IR (neat) 3104, 3079, 2926, 2853, 1524, 1464, 1428, 1408, 1376, 1214, 1093, 907, 823, 795, 705, 646 cm^{-1}; R_f 0.11 (Hexanes); HRMS calcd for $C_{20}H_{23}NS_3$ 373.0993, found 373.0993.

***N*-Octyl-2-(3'-butylthien-2'-yl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (2b).** 90-95% yield; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.181 (d, *J* = 5.6 Hz, 1H), 7.141 (d, *J* = 5.6 Hz, 1H), 7.027 (s, 1H), 7.001 (d, *J* = 5.6 Hz, 1H), 6.956 (d, *J* = 5.6 Hz, 1H), 4.195 (t, *J* = 7.2 Hz, 2H), 2.834 (t, *J* = 8.0 Hz, 2H), 1.886 (m, 2H), 1.665 (m, 2H), 1.428 (m, 2H), 1.288 (m, 10H), 0.947 (t, *J* = 7.6 Hz, 3H), 0.872 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 144.60, 144.44, 139.47, 133.29, 132.00, 130.10, 123.67, 123.17, 114.84, 114.76, 110.90, 109.97, 47.46, 33.08, 31.85, 30.42, 29.28, 29.21, 29.04, 27.08, 22.74, 22.68, 14.14, 14.05; IR (neat) 3102, 3080, 2926, 2855, 1525, 1464, 1428, 1406, 1376, 1215, 1095, 827, 795, 707, 646 cm^{-1}; R_f 0.15 (Hexanes); HRMS calcd for $C_{24}H_{31}NS_3$ 429.1619, found 429.1579.

***N*-Octyl-2-(2'-thiazolyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (2c).** 10-15% yield; mp 79.5-80.1 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.747 (d, *J* = 3.3 Hz, 1H), 7.468 (s, 1H), 7.209 (d, *J* = 5.4 Hz, 1H), 7.200 (d, *J* = 3.3 Hz, 1H), 6.982 (d, *J* = 5.4 Hz, 1H), 4.177 (t, *J* = 7.2 Hz, 2H), 1.869 (m, 2H), 1.262 (m, 10H), 0.859 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 163.28, 146.21, 144.36, 143.11, 133.66, 124.98, 117.23, 116.62, 114.82, 110.91, 110.35, 47.45, 31.80, 30.37, 29.23, 29.17, 27.01, 22.64, 14.12; IR (KBr) 3111, 3089, 3057, 2954, 2924, 2847, 1537, 1521, 1415, 1376, 1136, 709, 646 cm^{-1}; R_f 0.14 (5% EtOAc/Hexane); HRMS calcd for $C_{19}H_{22}N_2S_3$ 374.0945, found 374.0943.

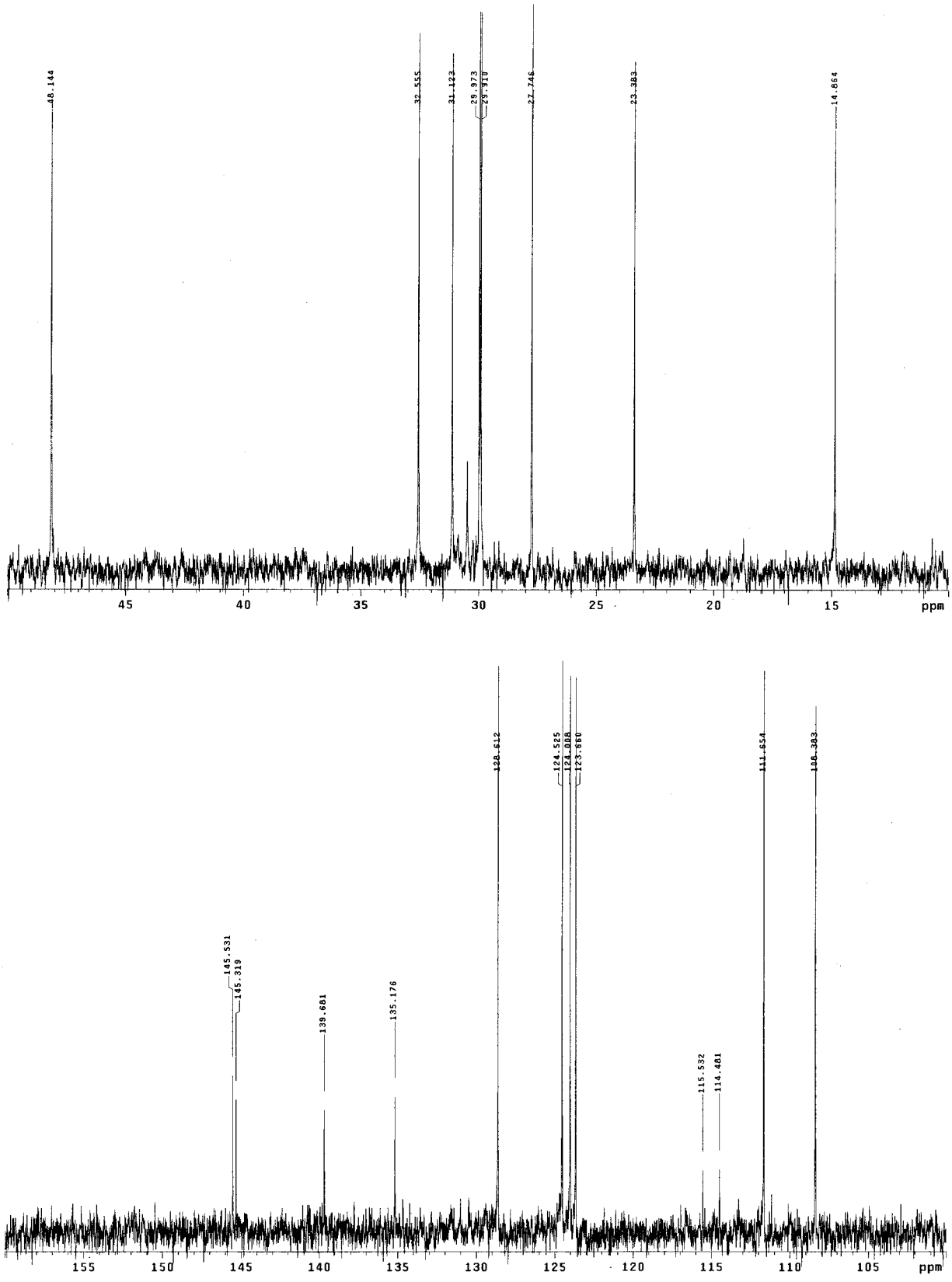

Figure S1. ^{13}C NMR of Compound **2a**

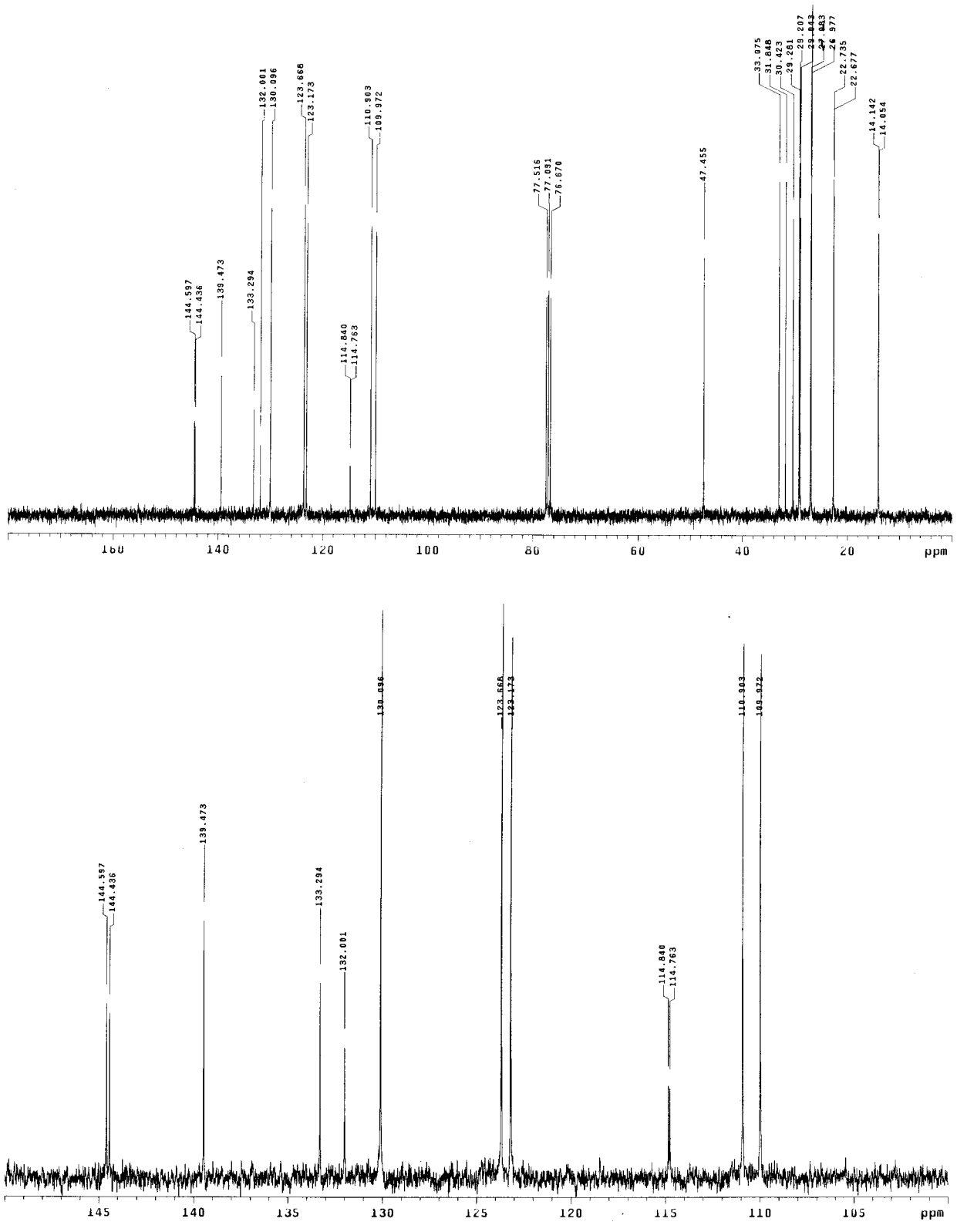

Figure S2. ^{13}C NMR of Compound **2b**

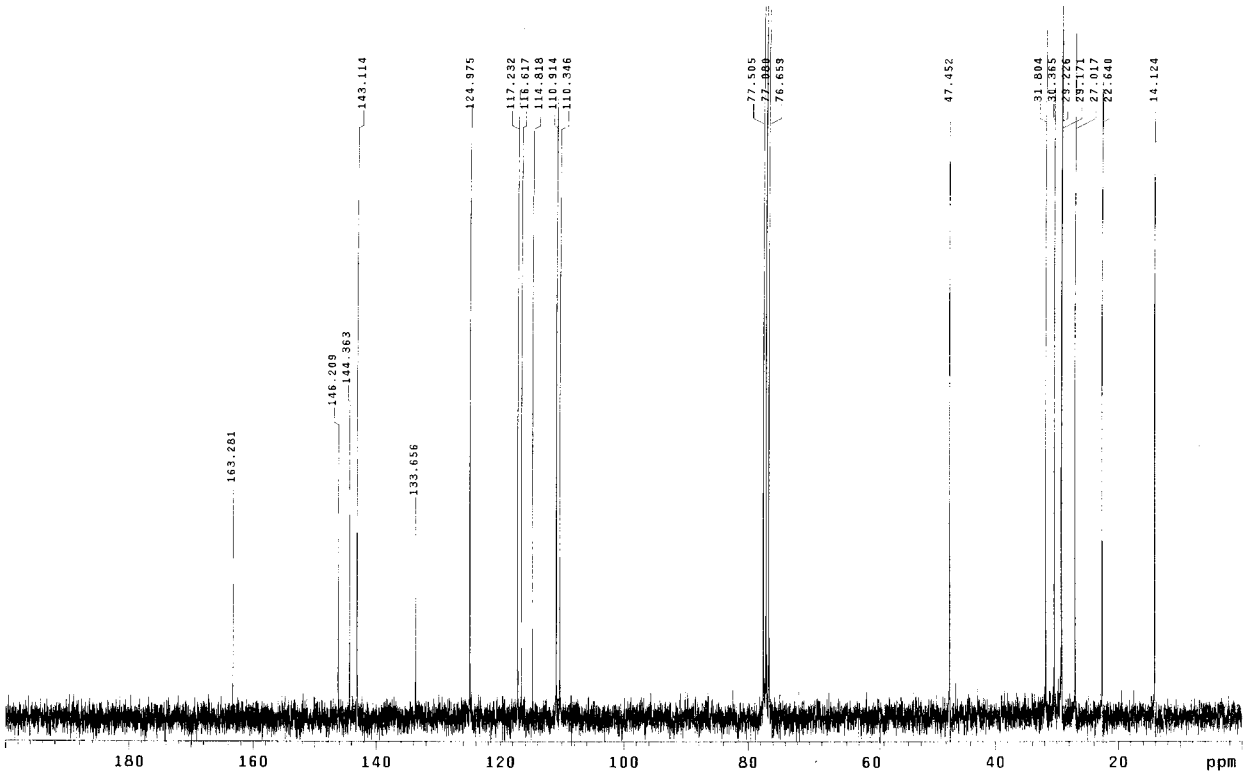

Figure S3. ^{13}C NMR of Compound **2c**

General procedure for synthesis of DTP quaterthiophene analogues (3a-c): N-Octyl dithieno[3,2-*b*:2',3'-*d*]pyrrole (2.0 mmol) was dissolved in dry THF (450 mL) and cooled in an acetone/dry ice bath for 20 minutes. Tert-butyllithium (2.4 mL, 4.0 mmol) was then added dropwise and the mixture was allowed to stir 1 hour. At this point the mixture was removed from the ice bath, allowed to warm to room temperature, and then returned to the ice bath. Tributyltin chloride (1.1 mL, 4.0 mmol) was then added dropwise and the mixture was allowed to warm to room temperature and stir for 1 hour.

Meanwhile, in a separate flask, $PdCl_2(PPh_3)_2$ (0.077 g, 0.11 mmol) was dissolved in THF (20 mL) and the appropriate 2-bromoaryl (2-bromothiophene, 2-bromo-3-butylthiophene or 2-bromothiazole) (4.0 mmol) was added. The 2,6-bis(tributylstannyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole solution was transferred into the catalyst/bromoaryl solution and refluxed for 20 hours. The solution was then allowed to cool, quenched with water, and extracted with diethyl ether. The combined ether washes were concentrated via rotary evaporation and the crude product was purified by column chromatography over silica gel (2% EtOAc/hexanes). Recrystallization was achieved using isopropyl alcohol.

***N*-Octyl-2,6-bis(2'-thienyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (3a).** 70-75% yield; mp 67.5-68.5 ^{o}C; ^{1}H NMR ($CDCl_3$): δ 7.200 (m, 4H), 7.069 (s, 2H), 7.029 (dd, *J* = 3.6, 5.1 Hz, 2H), 4.148 (t, *J* = 7.2 Hz, 2H), 1.873 (m, 2H), 1.266 (m, 12H), 0.873 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 144.70, 139.09,135.14, 128.14, 124.09, 123.20, 114.14, 107.69, 47.60, 32.06, 30.60, 29.47, 29.42, 27.22, 22.88, 14.36; IR (KBr) 3102, 3081, 2924, 2852, 1525, 1456, 1425, 1395, 1123, 1083, 1044, 847, 797, 688 cm^{-1}.); HRMS calcd for $C_{32}H_{41}NS_4$ 455.0869, found 455.0845

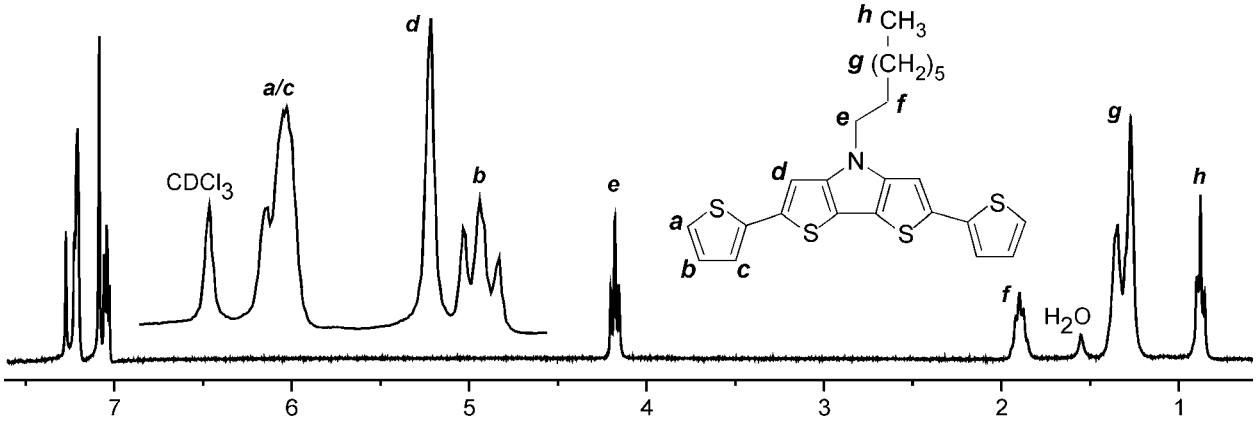

Figure S4. ^{1}H NMR Spectrum of Compound **3a**

***N*-Octyl-2,6-bis(3'-butylthien-2'-yl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (3b).** 40-45% yield; mp 28.5-30.0 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.183 (d, *J* = 5.1 Hz, 2H), 7.019 (s, 2H), 6.956 (d, *J* = 5.1 Hz, 2H), 4.195 (t, *J* = 7.2 Hz, 2H), 2.835 (t, *J* = 7.5 Hz, 4H), 1.892 (m, 2H), 1.662 (m, 4H), 1.419 (m, 4H), 1.265 (m, 12H), 0.947 (t, *J* = 7.2 Hz, 6H), 0.863 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 144.27, 139.71,133.86, 132.17, 130.35, 123.89, 115.09, 109.97, 47.66, 33.25, 32.04, 30.62, 29.47, 29.41, 29.26, 27.30, 22.93, 22.86, 14.33, 14.25; HRMS calcd for $C_{32}H_{41}NS_4$ 567.2123, found 567.2117

***N*-Octyl-2,6-bis(2'-thiazolyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (3c).** 15-20% yield (65-70% of **2c** isolated); mp 149.7-150.5 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.755 (d, *J* = 3.0 Hz, 2H), 7.389 (s, 2H), 7.217 (d, *J* = 3.0 Hz, 2H), 4.168 (t, *J* = 7.2 Hz, 2H), 1.870 (m, 2H), 1.279 (m, 10H), 0.848 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 162.86, 145.42, 143.31, 135.56, 117.69, 116.44, 109.948, 47.46, 31.79, 30.35, 29.22, 29.17, 27.01, 22.64, 14.12; IR (KBr) 3112, 3075, 3024, 2951, 2924, 2851, 1540, 1525, 1417, 1375, 1143, 705, 650 cm^{-1}; R_f 0.10 (10% EtOAc/Hexane); HRMS calcd for $C_{22}H_{23}N_3S_4$ 457.0775, found 457.0762

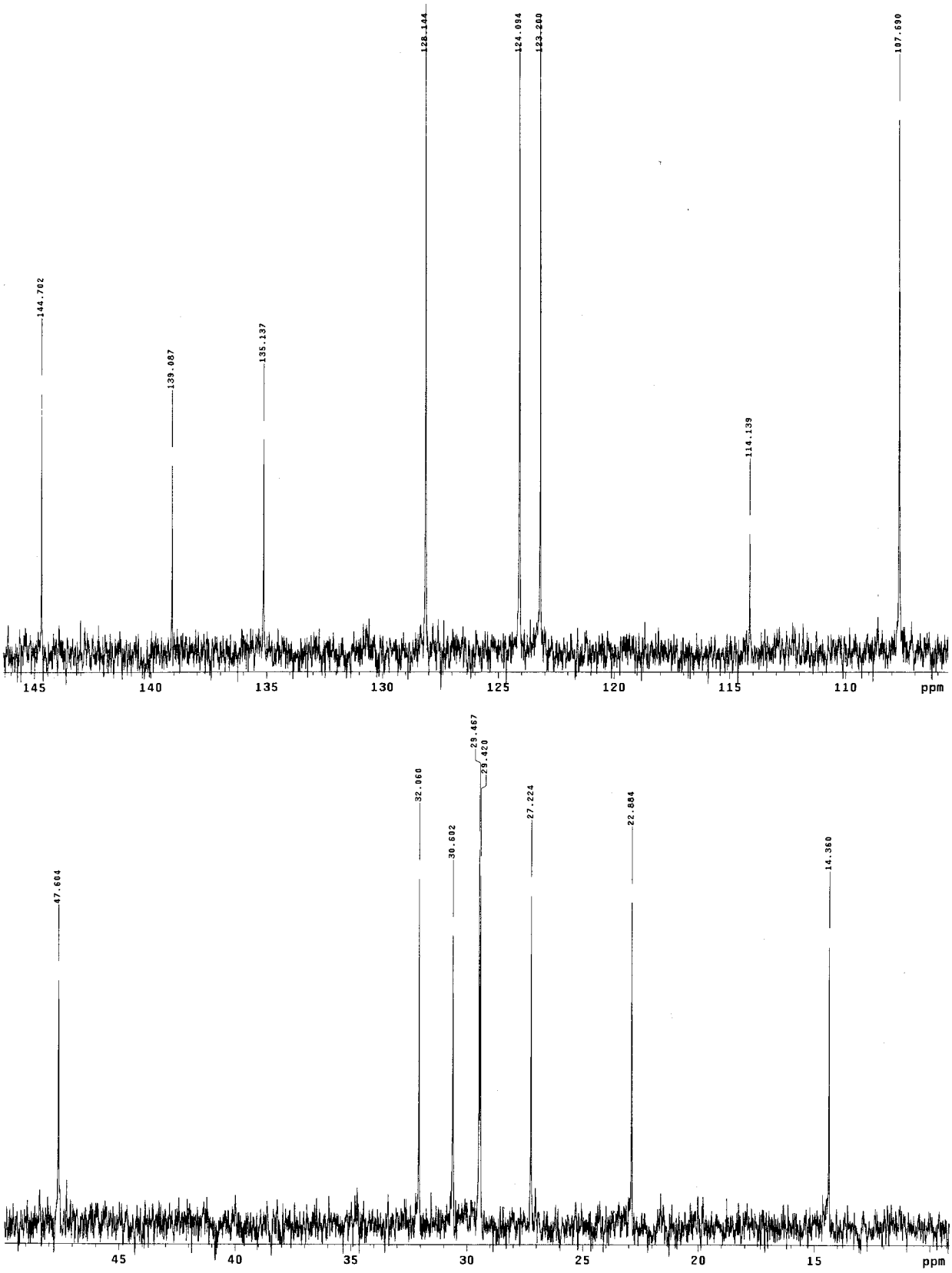

Figure S5. ^{13}C NMR Spectrum of Compound **3a**

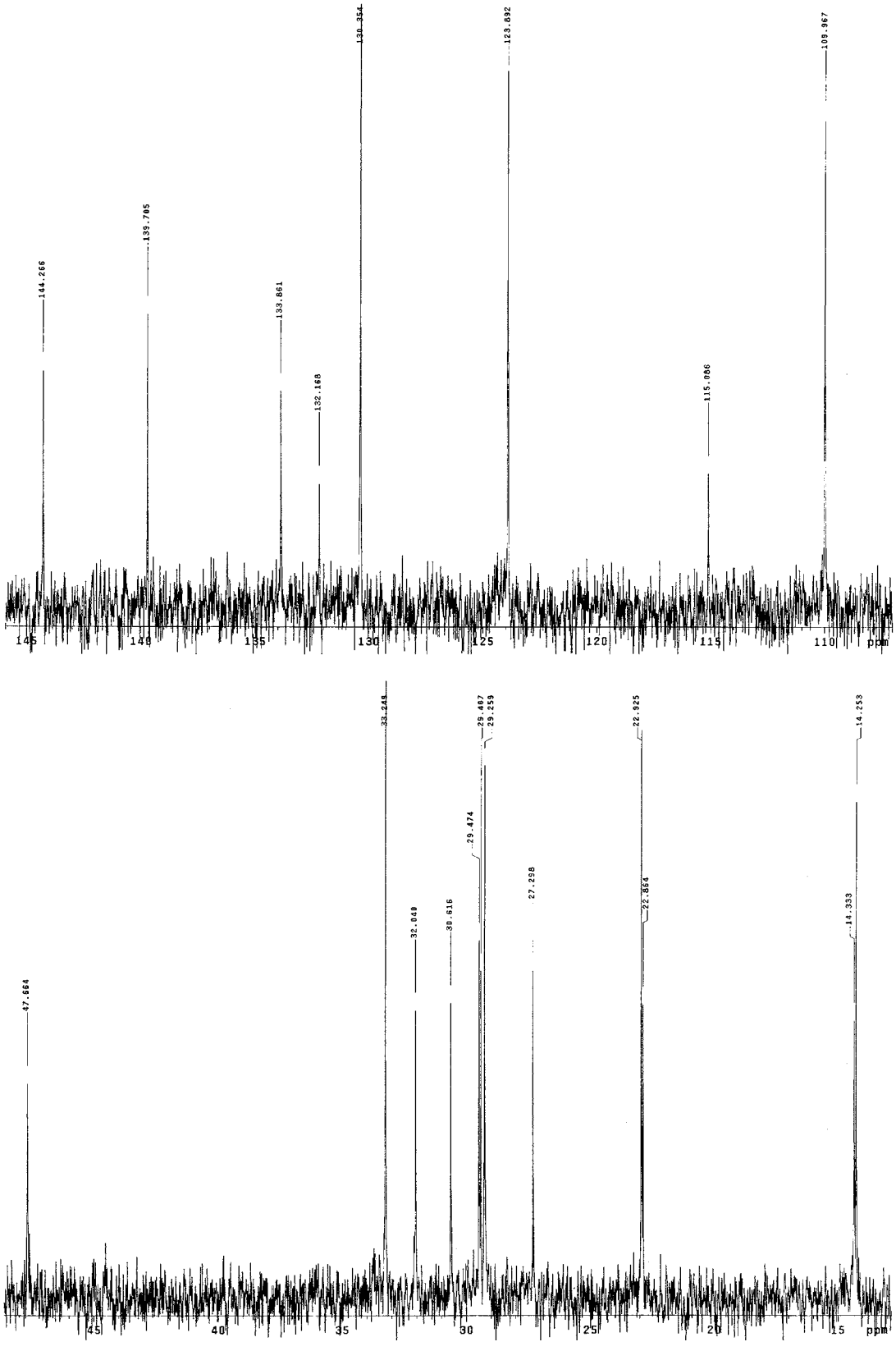

Figure S6. ^{13}C NMR Spectrum of Compound **3b**

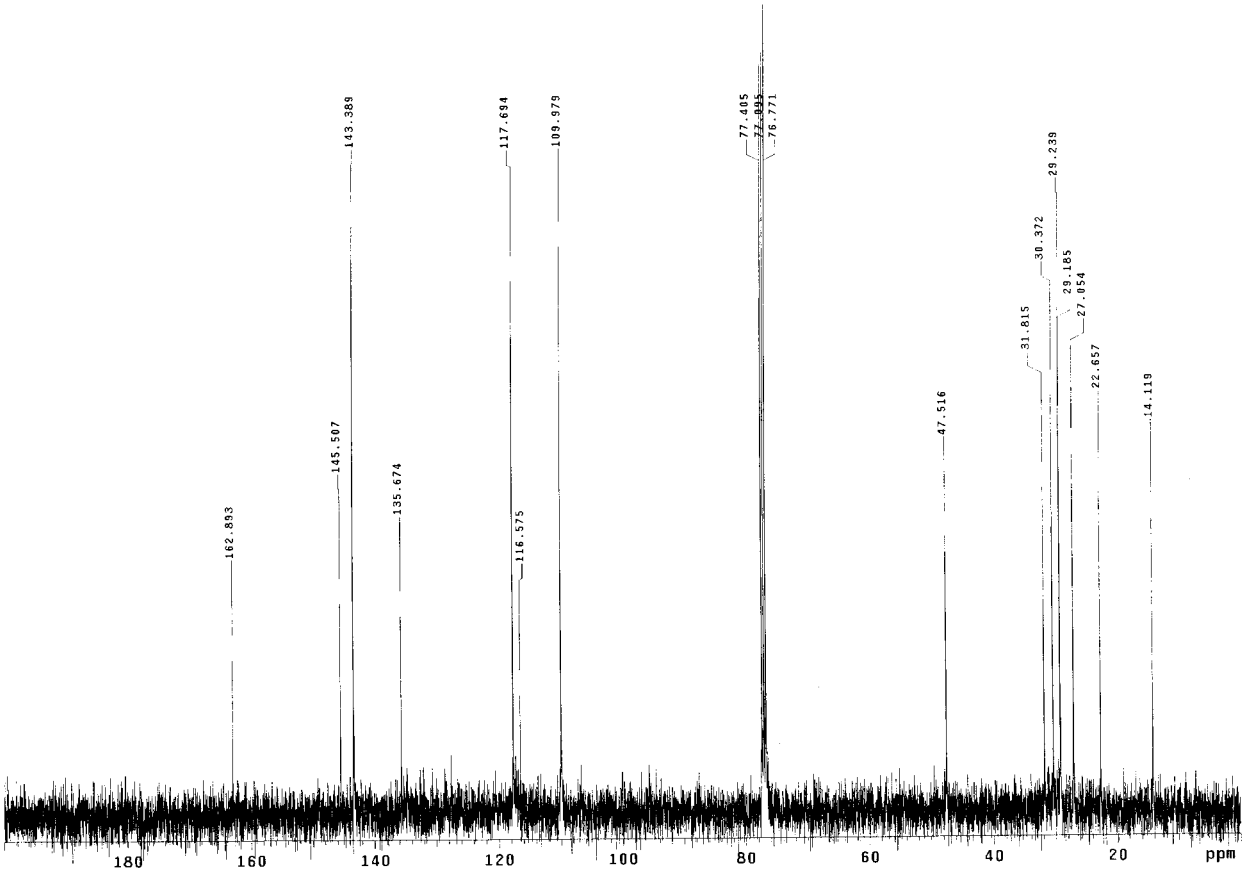

Figure S7. ^{13}C NMR Spectrum of Compound **3c**

Spectroscopy. UV-vis spectroscopy was performed on a dual beam scanning UV-vis-NIR spectrophotometer using samples prepared as dilute solutions in quartz cuvettes. Spectroscopy solvents were dried over molecular sieves prior to use. The solvent CH_2Cl_2 was chosen as the primary solvent for absorption characterization as it is one of the most commonly used solvents for oligothiophenes measurements in the literature and would thus allow the most convenient spectral comparisons. For the emission measurements, however, cyclohexane was chosen to reduce the error associated with the quantum efficiency measurements. When quantum yields are determined using secondary methods, it is best if both the unknown and reference sample are measured in the same solvent.[3] As the known quantum efficiency of the reference, 9,10-diphenylanthracene, is from its measurement in cyclohexane, cyclohexane is the most appropriate solvent to use for those measurements. Emission spectroscopy was performed using dilute solutions ($<10^{-5}$ M) at room temperature. Prior to each fluorescence measurement, the absorption spectrum was measured to ensure that the maximum absorption of the solution was

less than 0.1. Samples were excited at the corresponding absorption maxima and all spectra were obtained by averaging five scans.

REFERENCES

1. Ogawa, K.; Rasmussen, S. C., *J. Org. Chem.,* 2003, **68**, 2921.
2. *Standards in Fluorescence Spectrometry*, Miller, J. N., Ed., Chapman and Hall: New York, 1981, pp. 68-78; *Handbook of Organic Photochemistry*, Scaiano, J. C., Ed., CRC Press: Boca Raton, FL, pp. 233-236.