Electronic Supplementary Information

Enhanced open-circuit voltage in polymer solar cells by dithieno[3,2-*b*:2',3'-*d*]pyrrole N-acylation

Wouter Vanormelingen,[a,b] Jurgen Kesters,[a,b,c] Pieter Verstappen,[a,b] Jeroen Drijkoningen,[b,c] Julija Kudrjasova,[a,b] Simplice Koudjina,[d] Vincent Liégeois,[d] Benoît Champagne,[d] Jean Manca,[b,c] Laurence Lutsen,[b] Dirk Vanderzande[a,b] and Wouter Maes*[a,b]

[a] Design & Synthesis of Organic Semiconductors (DSOS), Institute for Materials Research (IMO-IMOMEC), Hasselt University, Agoralaan 1 - Building D, B-3590 Diepenbeek, Belgium.

[b] IMOMEC Assoc. Lab., IMEC, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium.

[c] Organic & Nanostructured Electronics and Energy (ONE^2), Institute for Materials Research (IMO-IMOMEC), Hasselt University, Universitaire Campus - Wetenschapspark 1, B-3590 Diepenbeek, Belgium.

[d] Laboratoire de Chimie Théorique, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium.

Corresponding author: Tel.: +32 11268312; Fax: +32 11268299; E-mail: wouter.maes@uhasselt.be

Table of contents

1. Analytical size exclusion chromatograms

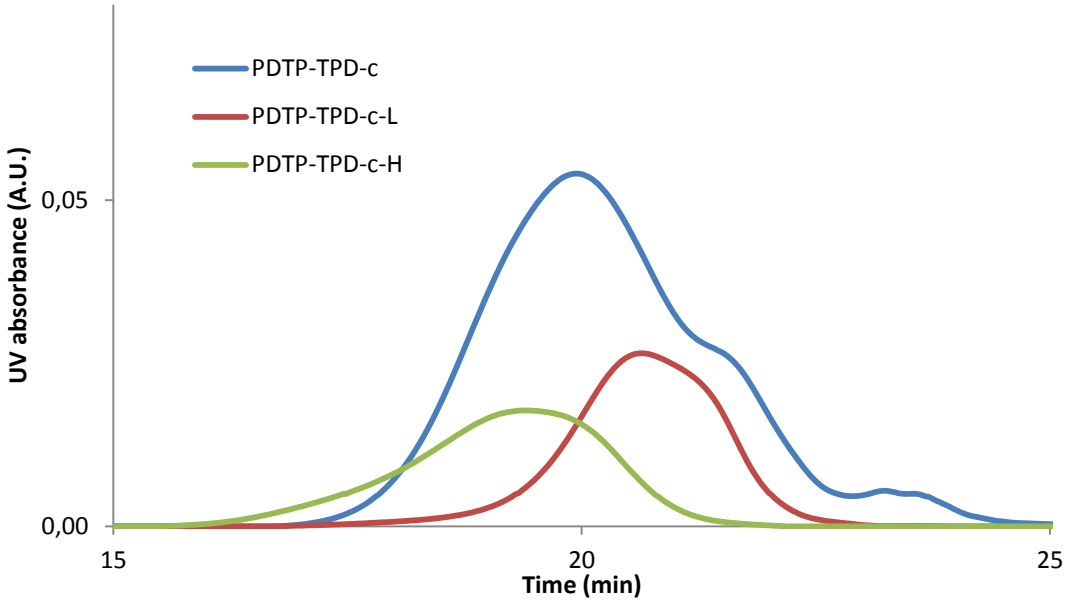


Fig. S1 Analytical size exclusion chromatograms (THF, 40 °C, UV detection at 254 nm) of the crude **PDTP-TPD-c** polymer (after Soxhlet extractions) and the low (**PDTP-TPD-c-L**) and high (**PDTP-TPD-c-H**) molar mass fractions obtained after fractionation by preparative SEC.

2. Visualization of the HOMO-LUMO energy levels for different DTP-based polymers

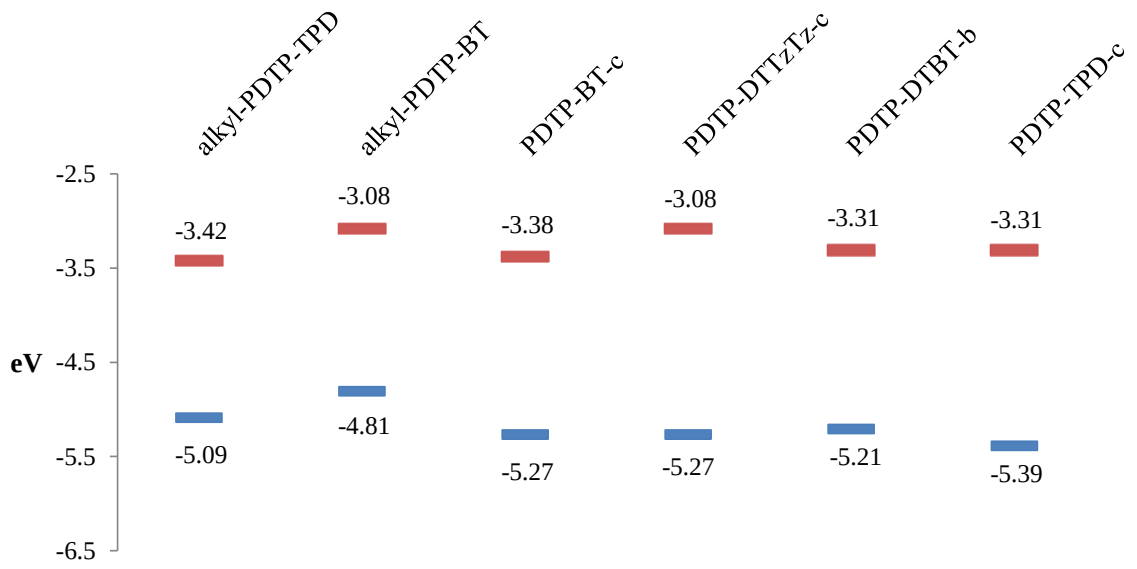


Fig. S2 Visualization of the HOMO (blue) and LUMO (red) energy levels for the N-acyl-DTP copolymers (as determined by CV) and previously reported N-alkyl-substituted PDTP-acceptor analogues.[1,2]

[1] **Alkyl-PDTP-BT**: W. Yue, Y. Zhao, S. Shao, H. Tian, Z. Xie, Y. Geng and F. Wang, *J. Mater. Chem.*, 2009, **19**, 2199.

[2] **Alkyl-PDTP-TPD**: a) M. Shi, L. Fu, X. Hu, L. Zuo, D. Deng, J. Chen and H. Chen, *Polym. Bull.*, 2011, **68**, 1867; (b) E. Zhou, J. Cong, L. Tajima, C. Yang and K. Hashimoto, *Macromol. Chem. Phys.*, 2011, **212**, 305; (c) X. Hu, M. Shi, L. Zuo, Y. Nan, Y. Liu, L. Fu and H. Chen, *Polymer*, 2011, **52**, 2559.

3. PeakForce AFM images

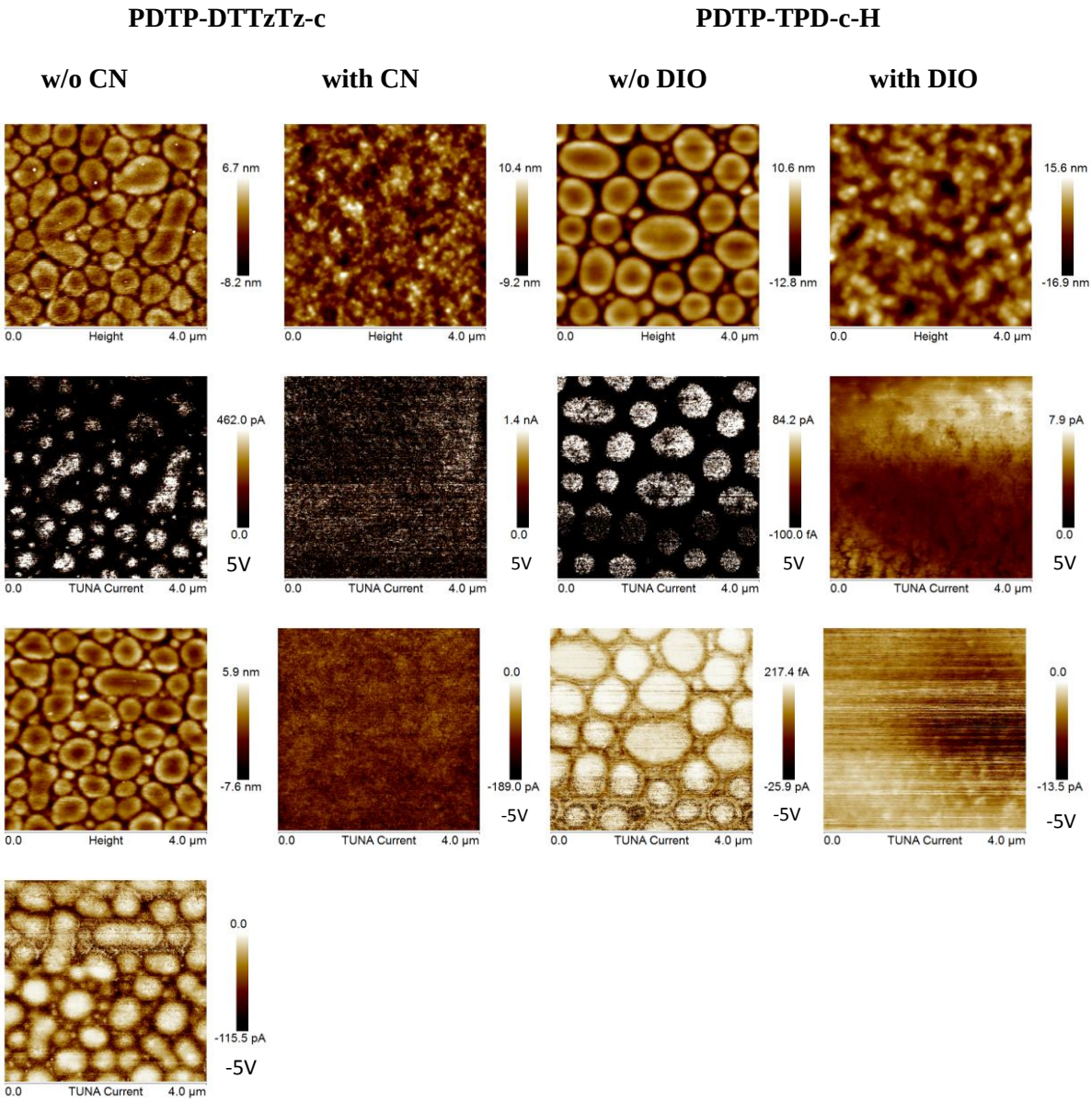


Fig. S3 Topographic and corresponding conductive AFM (under negative or positive sample bias of 5 V) images of spin-coated films of **PDTP-X** and $PC_{71}BM$ (measurements done on solar cell devices).

4. CPE interlayer materials

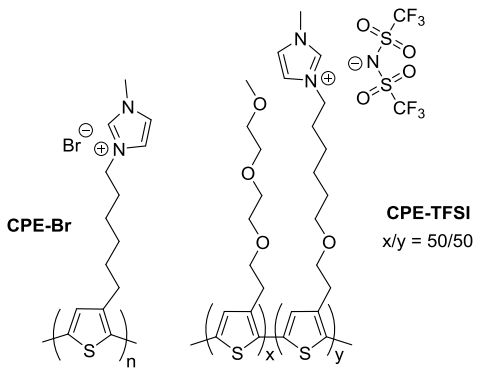


Fig. S4 Structures of the CPE's applied as interlayer materials: imidazolium-functionalized (co)polythiophenes with a bromine or bis(trifluoromethylsulfonyl)imide (TFSI) counter ion.[3]

5. EQE spectra for PDTP-TPD-c-H with and without cathode interlayers

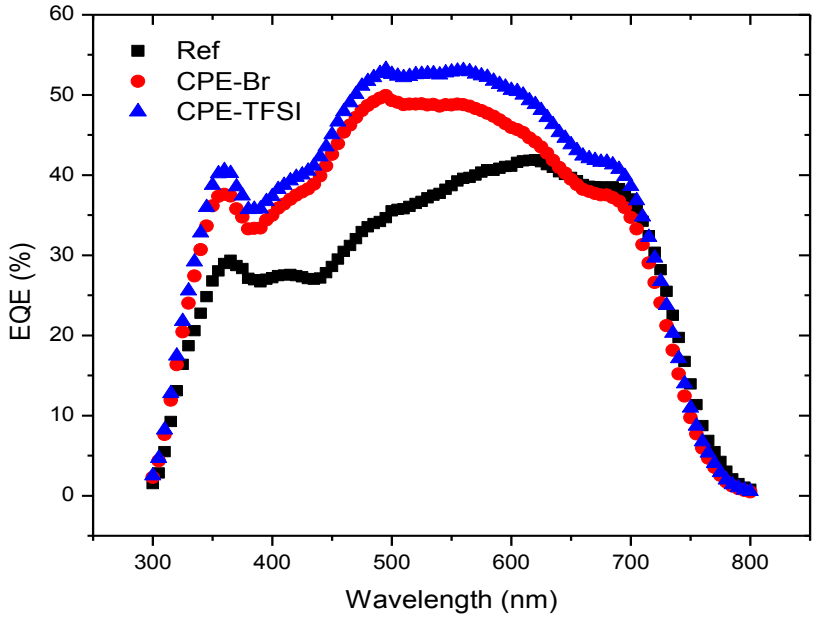
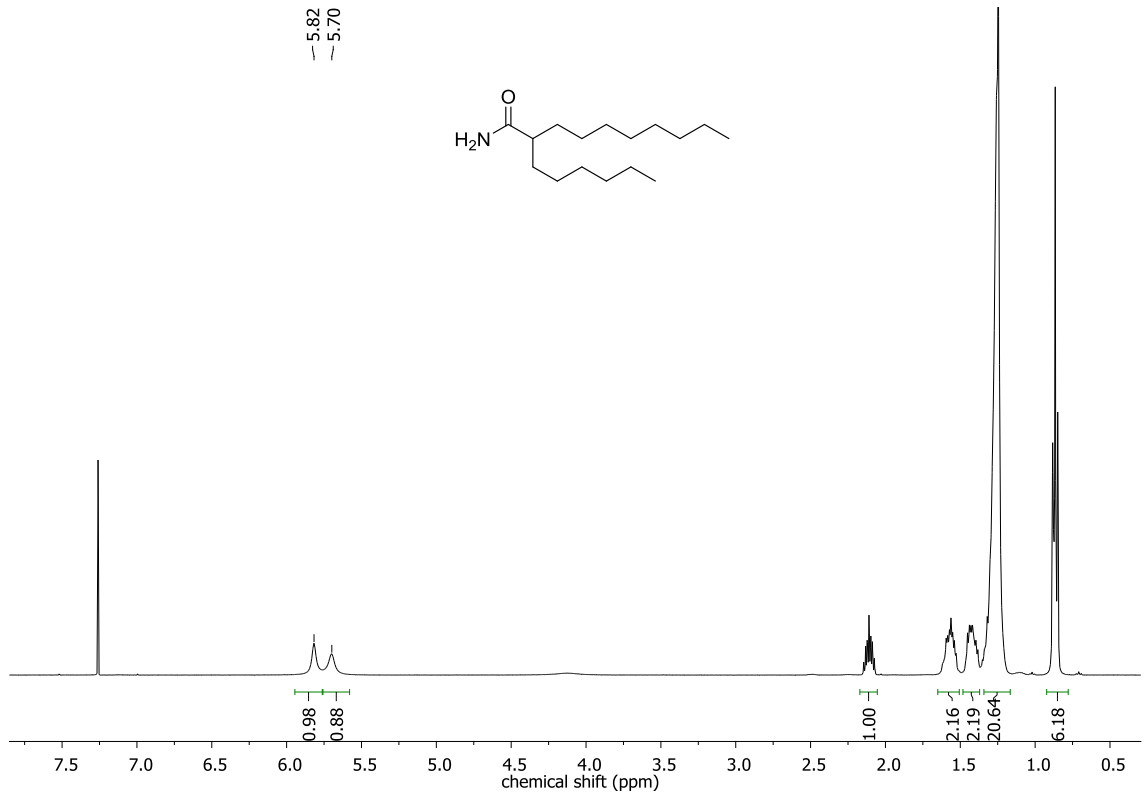


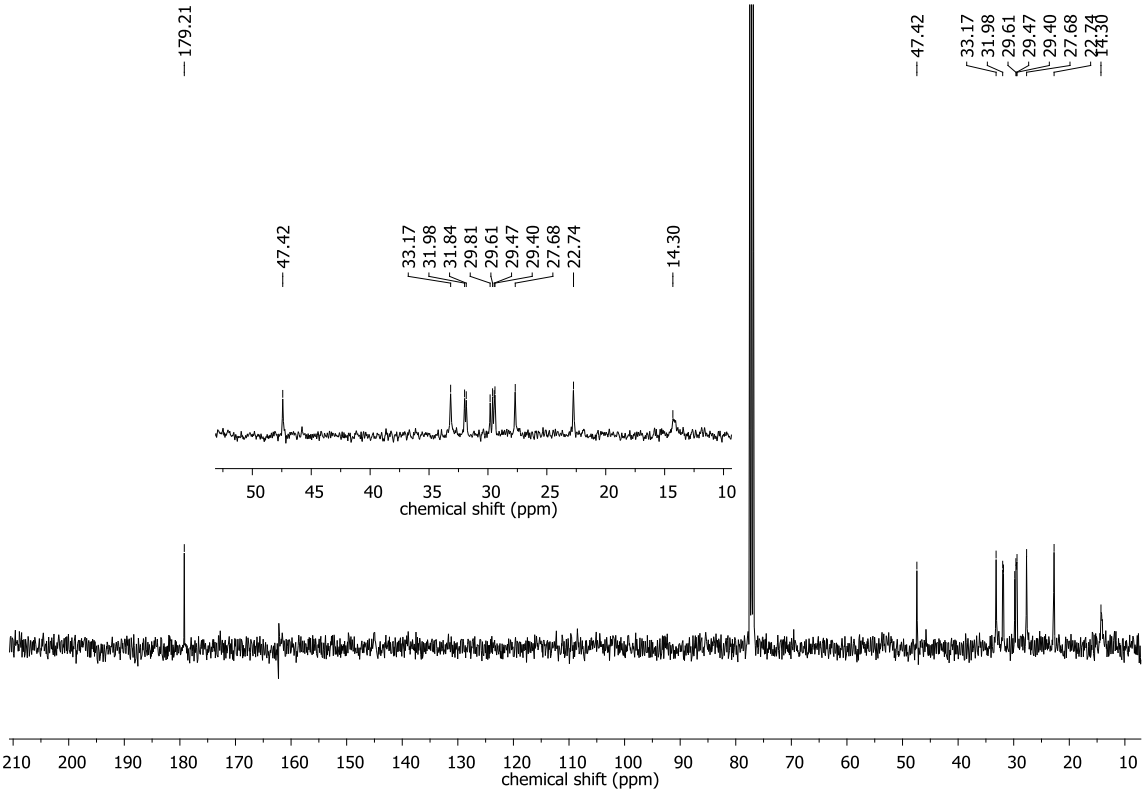
Fig. S5 EQE spectra for **PDTP-TPD-c-H** with and without CPE interlayers.

[3] (a) T. Ghoos, J. Brassinne, C.-A. Fustin, J.-F. Gohy, M. Defour, N. Van den Brande, B. Van Mele, L. Lutsen, D. J. Vanderzande and W. Maes, *Polymer*, 2013, **54**, 6293; (b) T. Ghoos, O. Malinkiewicz, B. Conings, J. Manca, L. Lutsen, D. Vanderzande, H. J. Bolink and W. Maes, *RSC Adv.*, 2013, **3**, 25197; (c) T. Ghoos, N. Van Den Brande, M. Defour, J. Brassinne, C.-A. Fustin, J.-F. Gohy, S. Hoeppener, U. S. Schubert, W. Vanormelingen, L. Lutsen, D. J. Vanderzande, B. Van Mele and W. Maes, *Eur. Polym. J.*, 2014, **53**, 206.

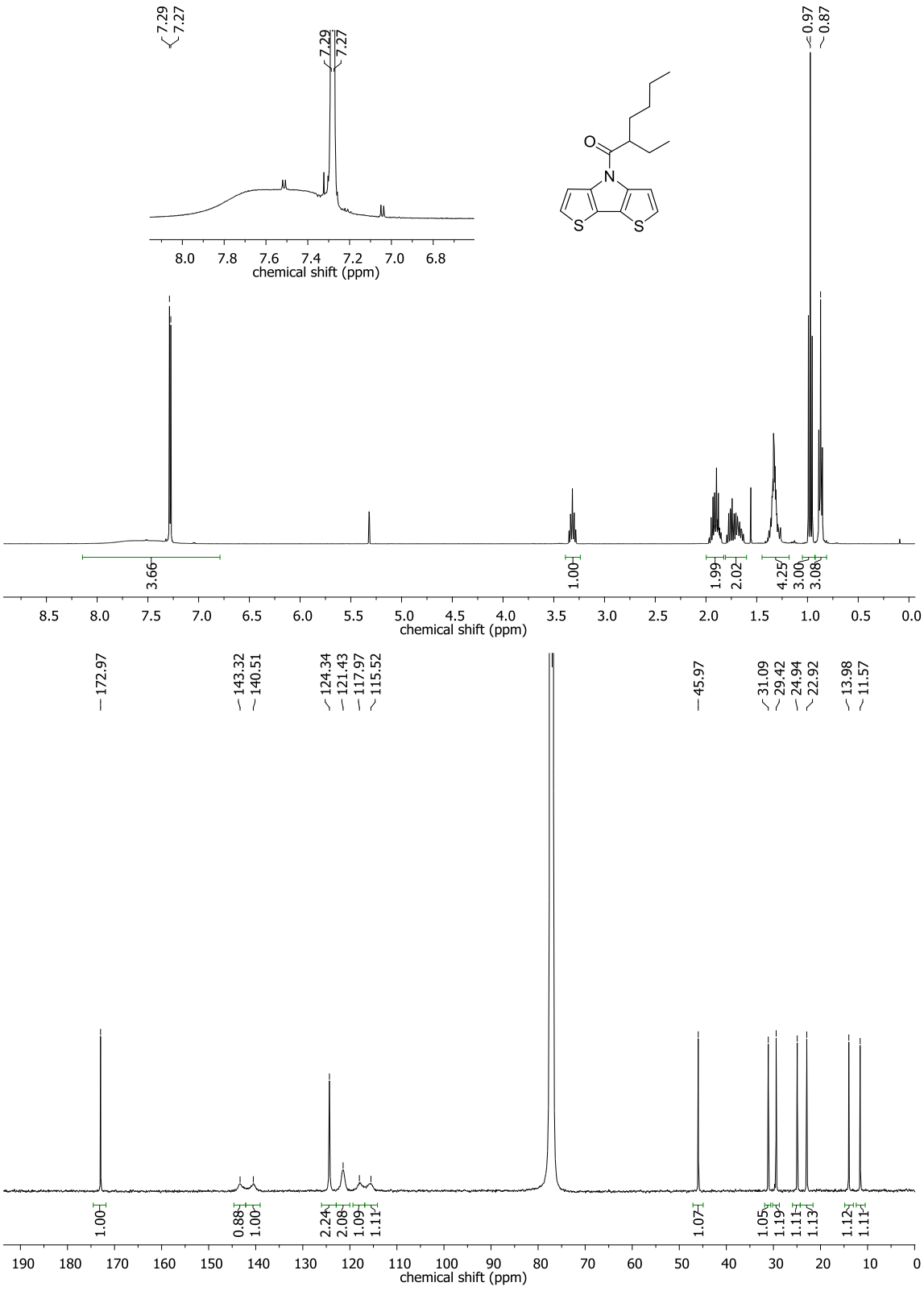
6. ^{1}H and ^{13}C NMR spectra

2-hexyldecanamide

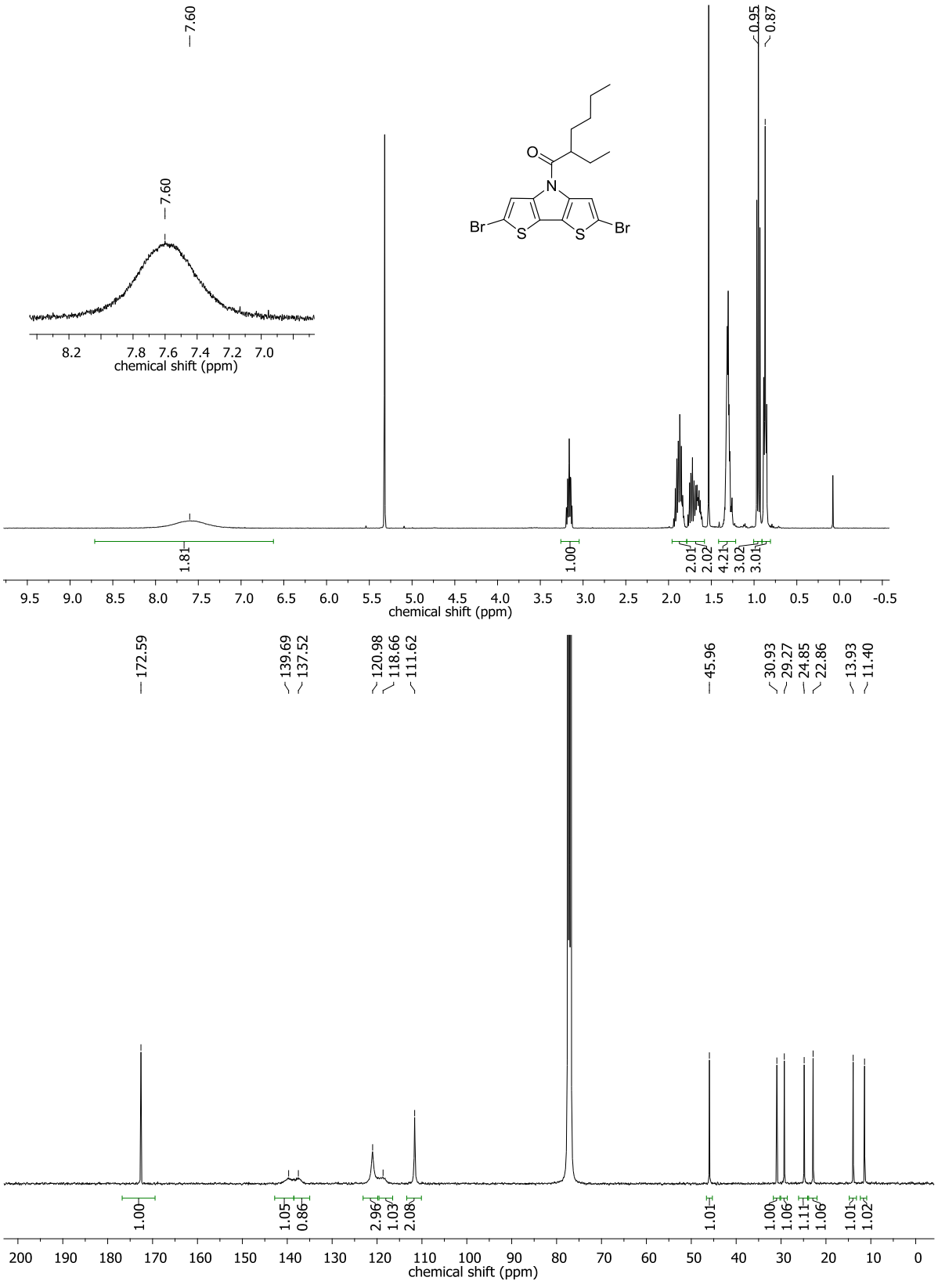




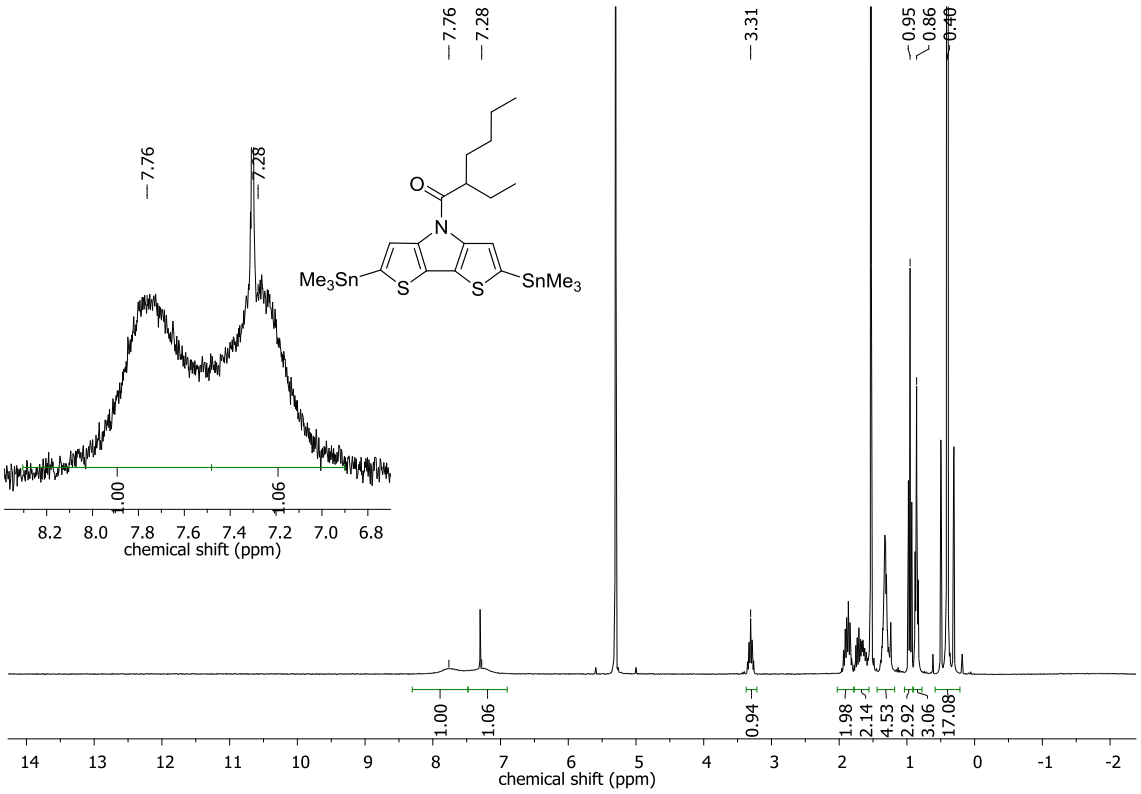
*N-(2-ethylhexanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**2a**)*



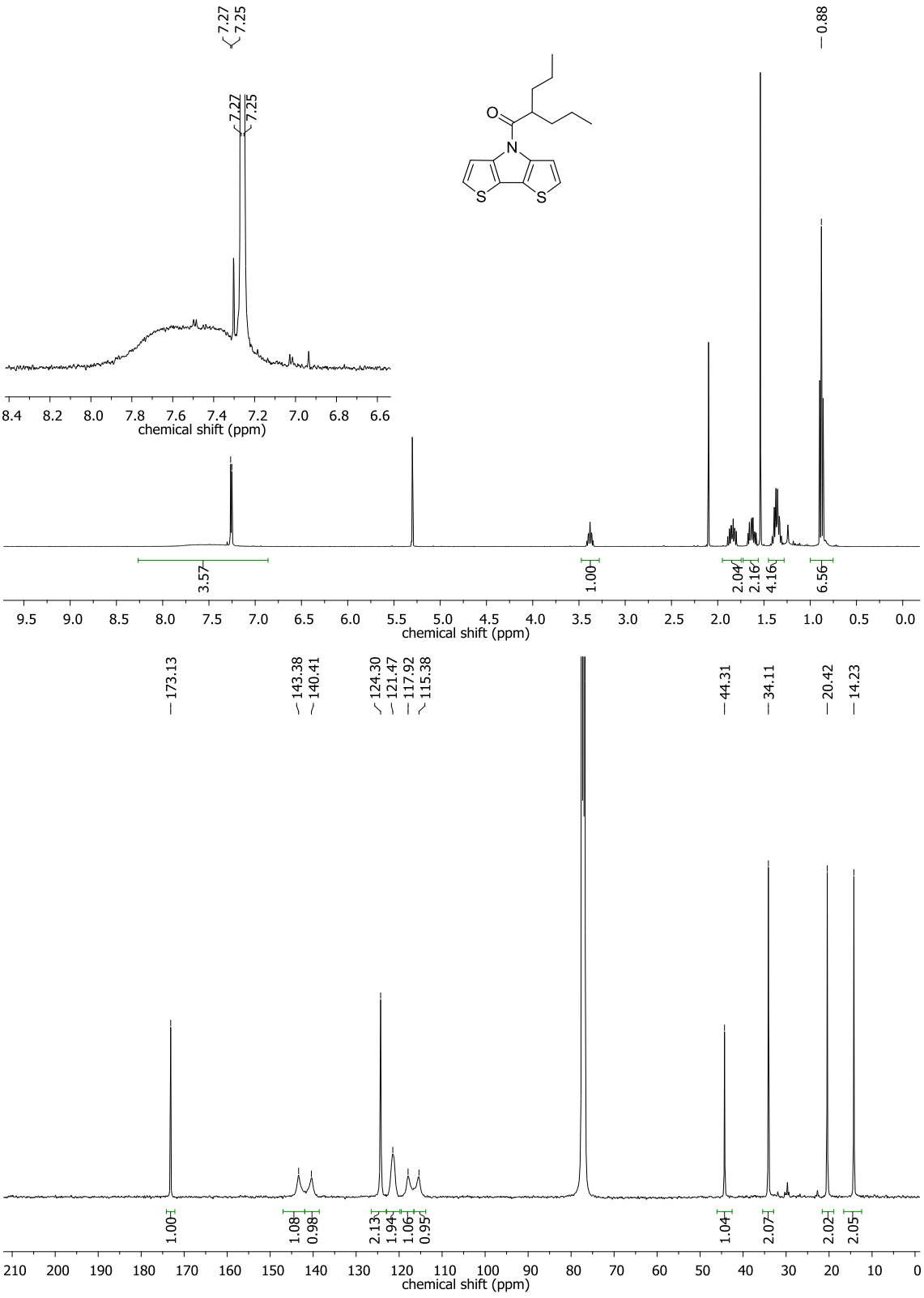
*2,6-dibromo-N-(2-ethylhexanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**3a**)*



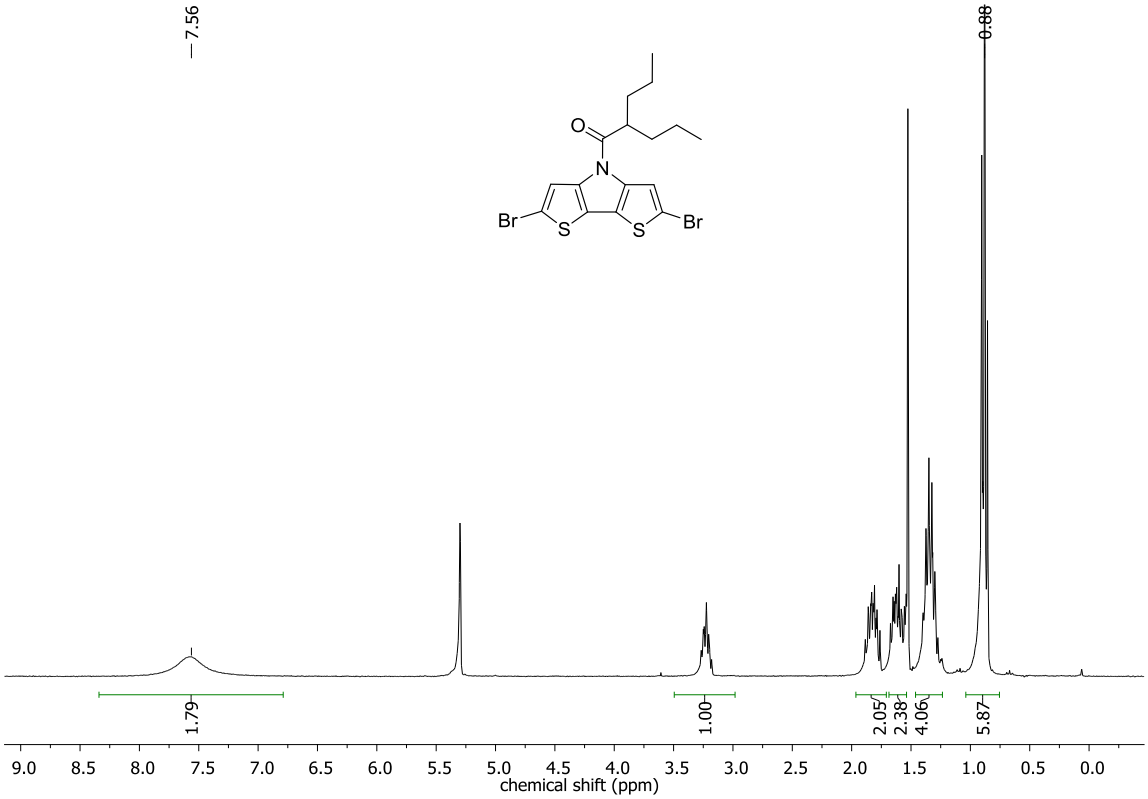
*2,6-bis(trimethylstannyl)-N-(2-ethylhexanoyl)-dithieno[3,2-b:2',3'-d]pyrrole (**4a**)*

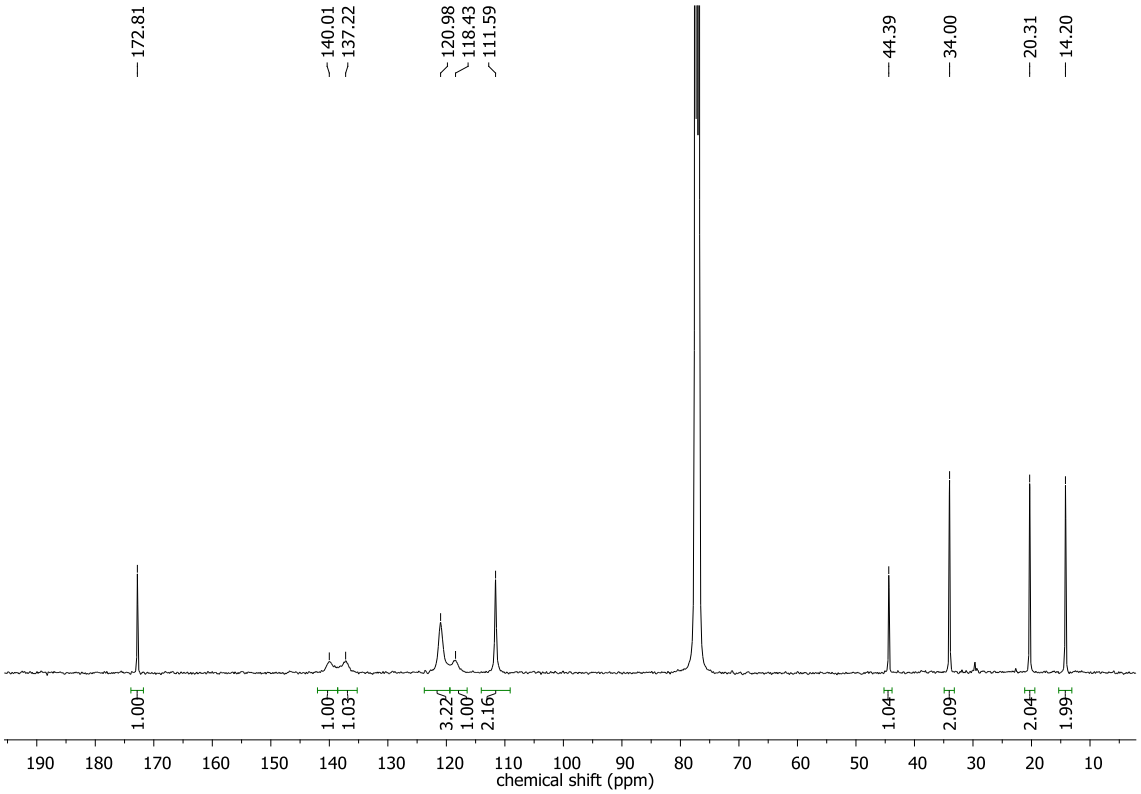


*N-(2-propylpentanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**2b**)*

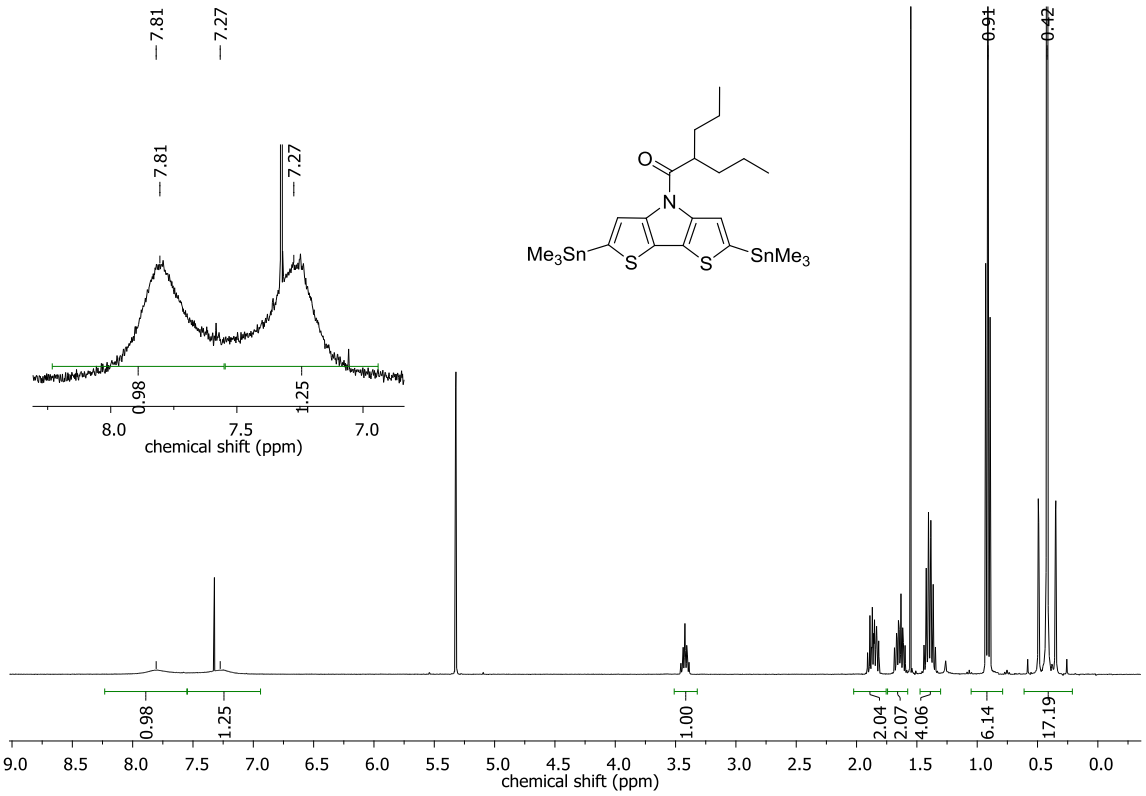


*2,6-dibromo-N-(2-propylpentanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**3b**)*

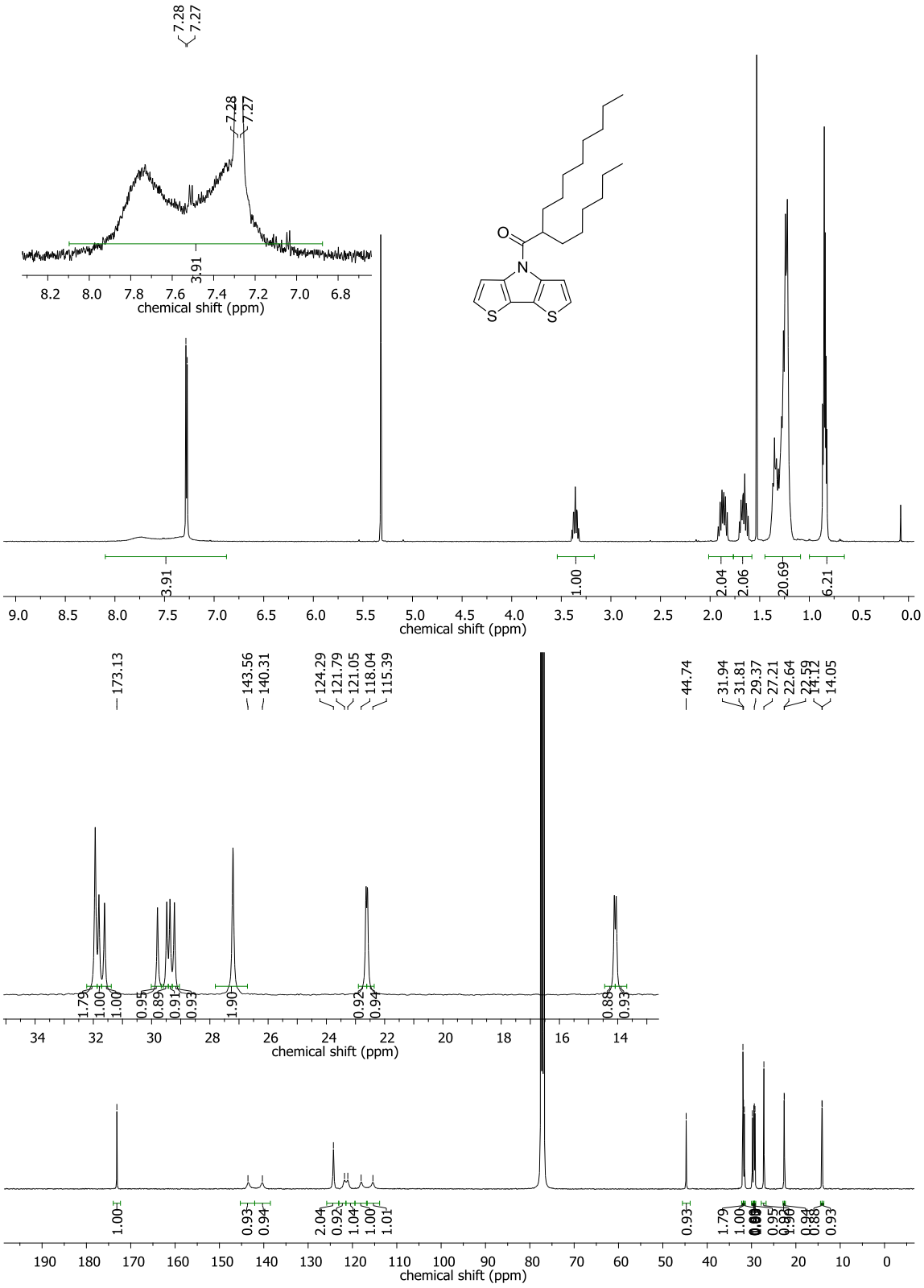




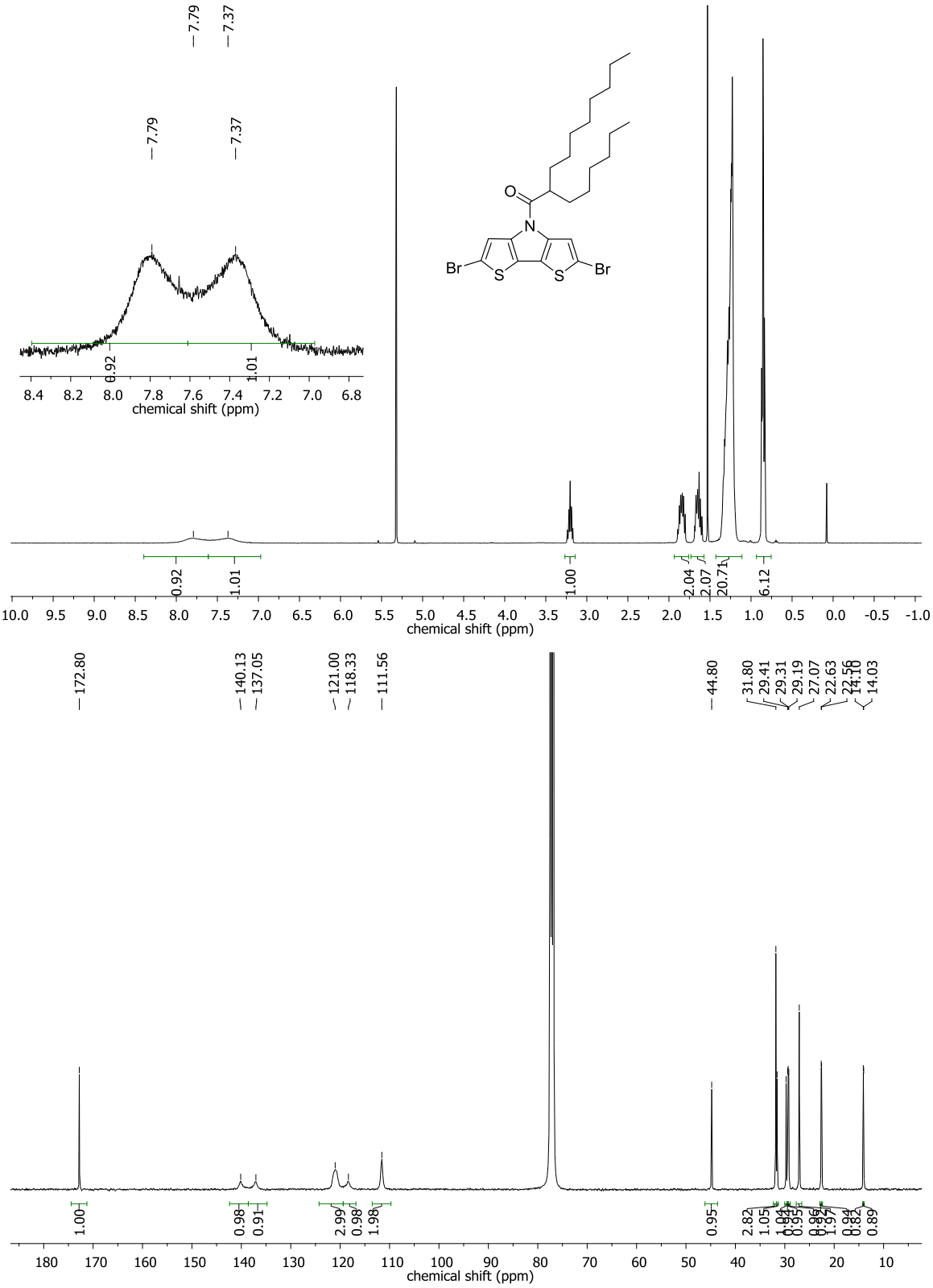
*2,6-bis(trimethylstannyl)-N-(2-propylpentanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**4b**)*



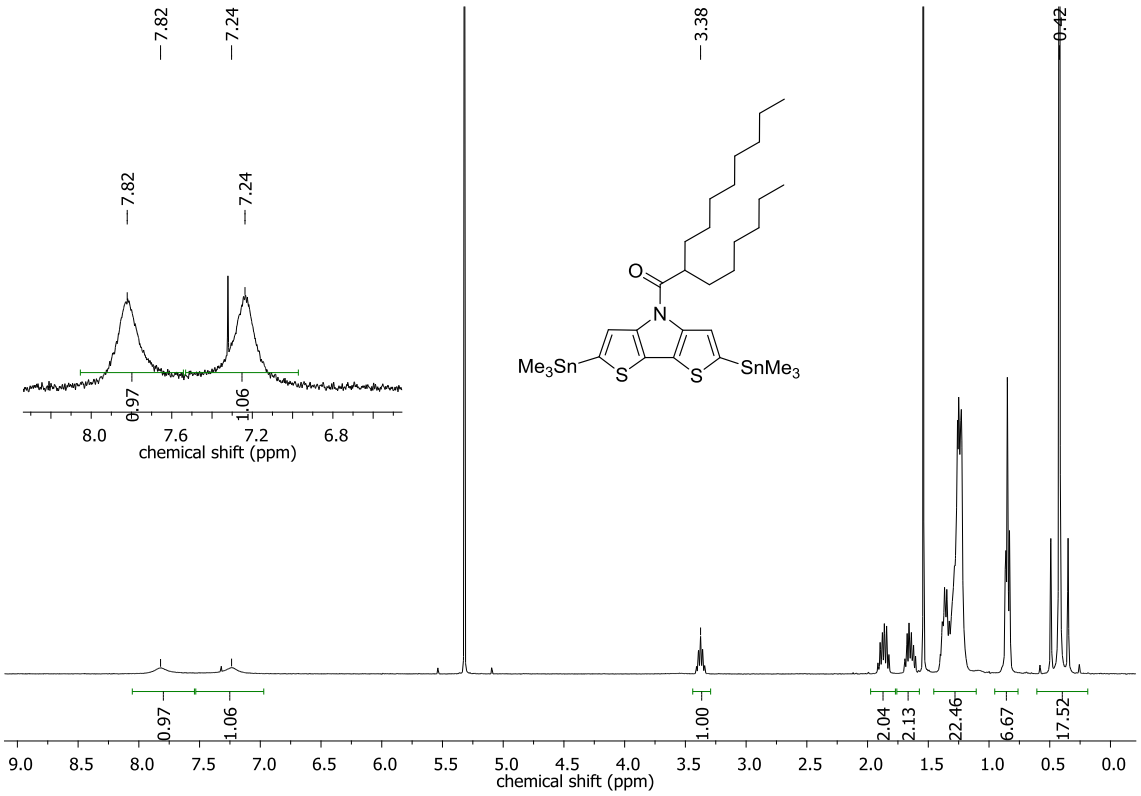
*N-(2-hexyldecanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**2c**)*



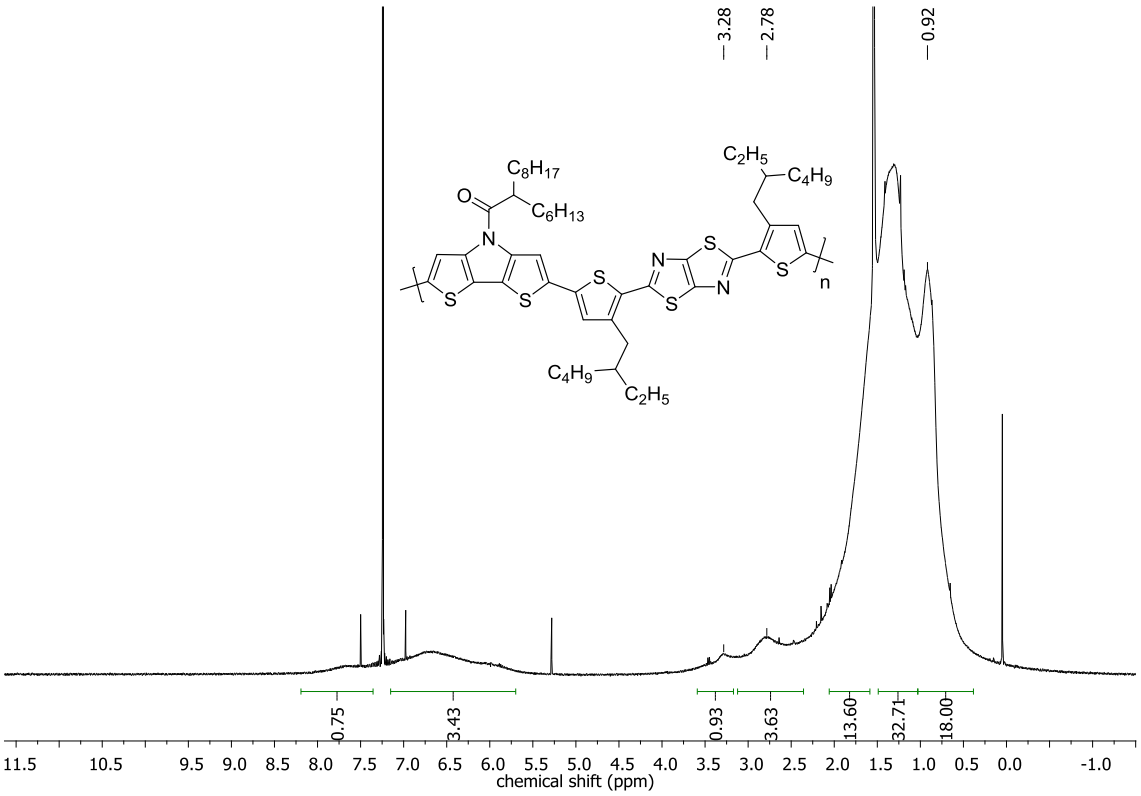
*2,6-dibromo-N-(2-hexyldecanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**3c**)*



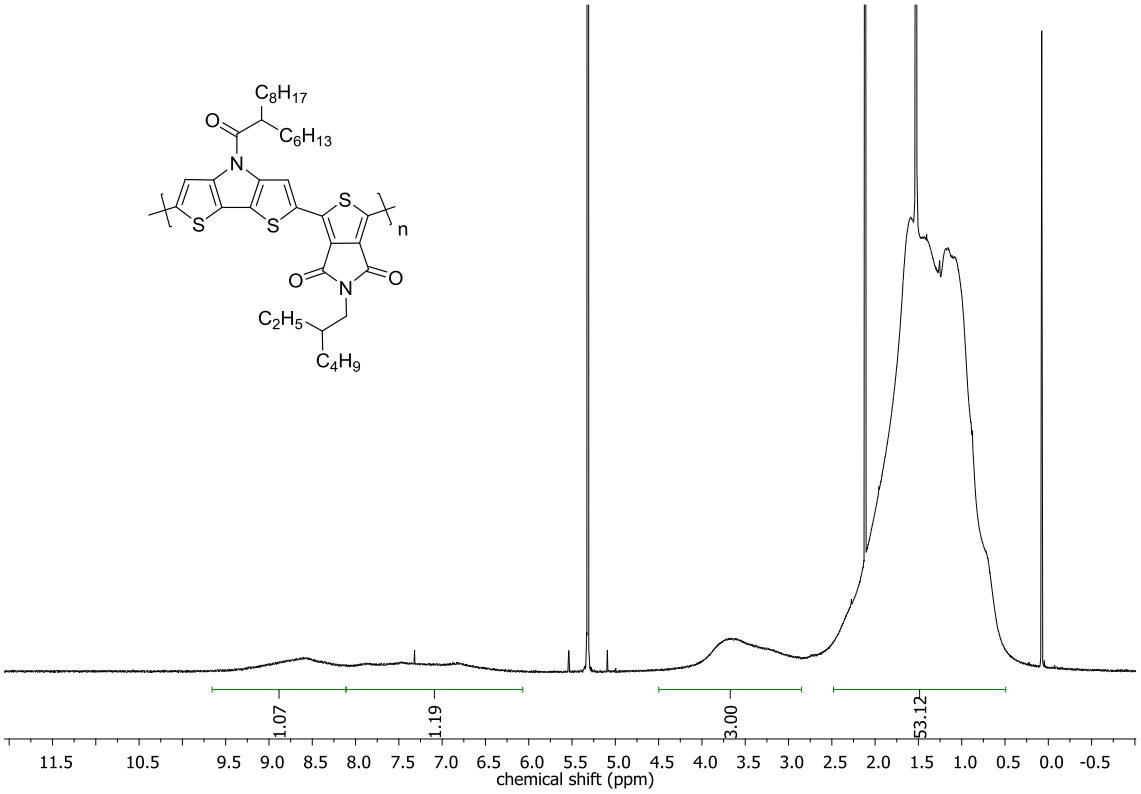
*2,6-bis(trimethylstannyl)-N-(2-hexyldecanoyl)dithieno[3,2-b:2',3'-d]pyrrole (**4c**)*



PDTP-DTTzTz-c



PDTP-TPD-c


C8H17
C6H13
O
N
S
S
S
n
O
N
O
C2H5
C4H9
1.07
1.19
3.00
53.12
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
chemical shift (ppm)