

# **Synthesis and Photophysical and Photovoltaic Properties of a New Class of Two-dimensional Conjugated Polymers Containing Donor-Acceptor chromophore as pendant groups**

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## Supporting Information

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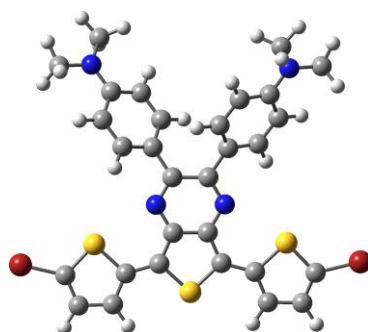
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## 1. Computational Details

Quantum-chemical calculations were performed with the Gaussian09 suite<sup>1</sup> employing the B3LYP density functional in combination with the 6-311G(d,p) basis set. Geometry optimizations were performed with solvation in toluene by applying the polarized continuum model (PCM) and with tight SCF and convergence criteria and an ultrafine integration grid by applying the GEDIIS optimization algorithm. The minimum nature of each stationary point was confirmed by a frequency analysis. Time-dependent density functional (TDDFT) calculations were performed including the keyword IOP(9/40=2) in order to output information on smaller contributions to each electronic transition. Electron density difference maps for electronic transitions were generated from TDDFT output by GaussSum 2.2 and visualized by GaussView 5.0. The electronic transitions can therefore be visualized through EDDMs. Red indicates a decrease in charge density, while green indicates an increase. Considering an insignificant effect on electronic properties, all the side-chain substituents were replaced with methyl groups for simplicity.

**Cartesian coordinates (Å) and energies (Hartree) of the Gaussian B3LYP/6-311G(d,p) optimized structures**

**DOATP**



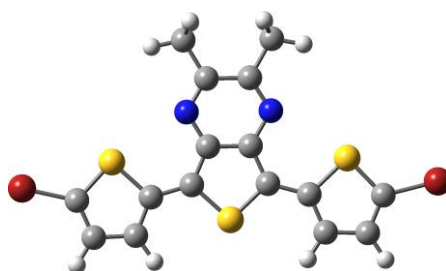
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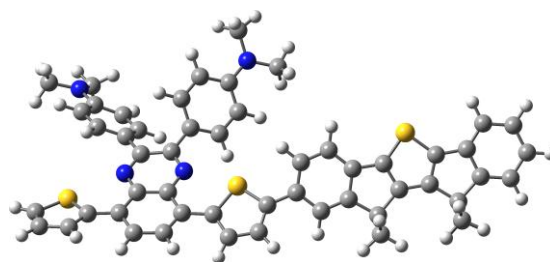


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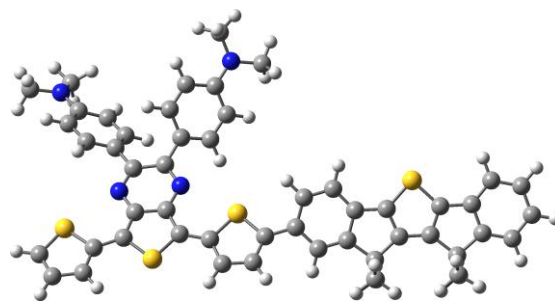
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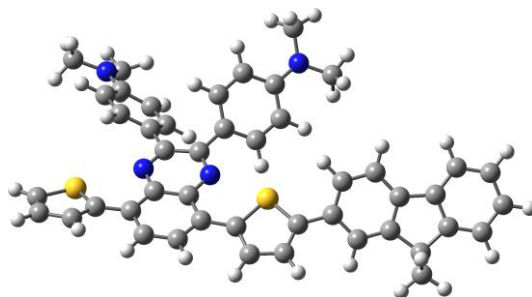
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| N | 9.884870657647  | 3.475018434706  | 1.140412670165  |
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| H | 11.904566597759 | 3.921411743359  | 0.903172764954  |
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| C | 0.797661124509  | 0.572071439277  | 0.080670845527  |
| N | 1.487277688415  | -0.553787823385 | 0.088991664767  |
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| H | 1.449028654033  | -5.087495471888 | 0.220499030201  |
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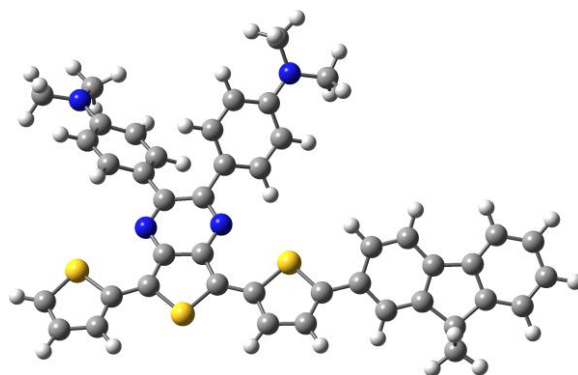
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| H | 5.318567740787  | 5.139988199251  | -0.928451205609 |
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| C | 7.126282118485  | -0.824387289384 | 1.067375232615  |
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| H | 11.069184741850 | 1.275969973367  | 1.779927863772  |
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| H | 11.949371926732 | -4.057386992613 | -0.982929504253 |
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| C | 10.499610996098 | -2.247959228471 | -2.508634843495 |
| H | 11.464245228969 | -2.490861688740 | -2.962719879547 |
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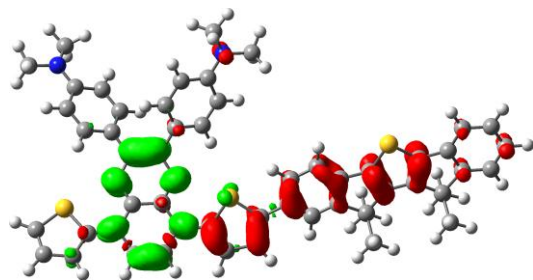
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| H | -0.200530977795 | 3.027940252101  | -1.644401025011 |
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| H | 3.204629139614  | 1.473593591019  | -1.042499422863 |
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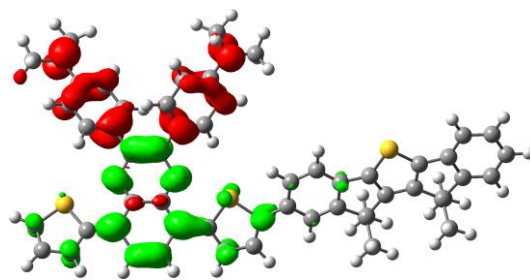
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| H | -5.375696202013 | 5.259509178091  | 0.746445345960  |
| C | -3.748190473565 | 6.303094019226  | -1.955414047628 |
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| H | -4.482927667433 | 7.106205246508  | -1.933026720470 |
| C | 5.318787114761  | 5.696844971386  | 0.070405488275  |
| H | 5.738601897427  | 6.689291287672  | 0.225635423678  |
| H | 5.989065073239  | 4.962438080642  | 0.537969585694  |
| H | 5.306956442899  | 5.507897354145  | -1.007001842761 |
| C | 3.594743900933  | 6.685674243141  | 1.584126215901  |
| H | 4.279362375639  | 7.527213581020  | 1.492223136663  |
| H | 2.585373707124  | 7.057230523765  | 1.384878805491  |
| H | 3.627455267291  | 6.327276899541  | 2.622426885870  |
| S | 0.248771442827  | -3.862905826444 | 0.239637864837  |
| C | 6.826982628914  | -2.623917301762 | 0.048898811609  |
| C | 7.783730671909  | -3.522472420485 | -0.468825473992 |
| C | 9.124509195313  | -3.181739578447 | -0.473406376850 |
| C | 9.549659544519  | -1.935204926299 | 0.023090628002  |
| C | 8.615533719035  | -1.032069690232 | 0.529903810952  |
| C | 7.270025411767  | -1.381370487834 | 0.543425838591  |
| H | 6.548852289056  | -0.689170673694 | 0.962538524947  |
| C | 11.005473786518 | -1.847149586245 | -0.116358980050 |

|   |                 |                 |                 |
|---|-----------------|-----------------|-----------------|
| C | 11.470236472008 | -3.040324106759 | -0.701034701106 |
| C | 12.825428879407 | -3.217775032652 | -0.945205704154 |
| H | 13.196064531717 | -4.132952216926 | -1.395221869655 |
| C | 13.719037822821 | -2.198202453518 | -0.603542531797 |
| H | 14.779330992765 | -2.327157338764 | -0.790079301467 |
| C | 13.257093491713 | -1.014438180684 | -0.023636404698 |
| C | 11.897619622737 | -0.829452067306 | 0.224359605320  |
| H | 11.545126987854 | 0.091904924588  | 0.675179709636  |
| H | 8.925433587144  | -0.069306063874 | 0.921301133231  |
| H | 7.455875193577  | -4.469970453562 | -0.881445457123 |
| H | 13.962643639012 | -0.233018500984 | 0.235882753421  |
| C | 10.312715729778 | -3.997469866767 | -0.983292902318 |
| H | -5.987986604573 | -3.092383606291 | 0.302015869087  |
| C | 10.468795407279 | -5.316151654727 | -0.194904118267 |
| H | 9.603882901865  | -5.965646111231 | -0.355728830427 |
| H | 11.361085073992 | -5.856628672568 | -0.522608429870 |
| H | 10.558694471754 | -5.124534448155 | 0.876599944423  |
| C | 10.185356621810 | -4.295748714051 | -2.493117435351 |
| H | 11.072921027060 | -4.820495538114 | -2.857322262306 |
| H | 9.315912516588  | -4.929311592960 | -2.688902955615 |
| H | 10.072944133400 | -3.373491351434 | -3.067308824168 |

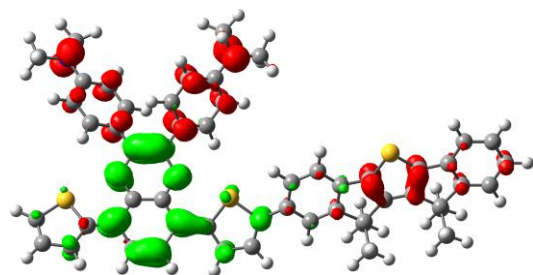
DIDTDOAQX



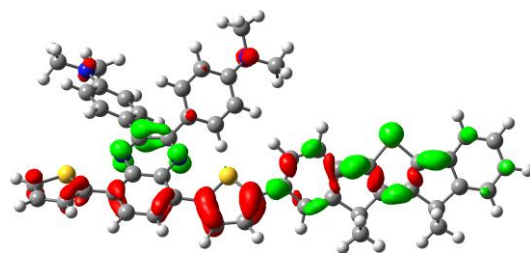
$\lambda_{\text{calc}} = 551 \text{ nm}$



$\lambda_{\text{calc}} = 514 \text{ nm}$

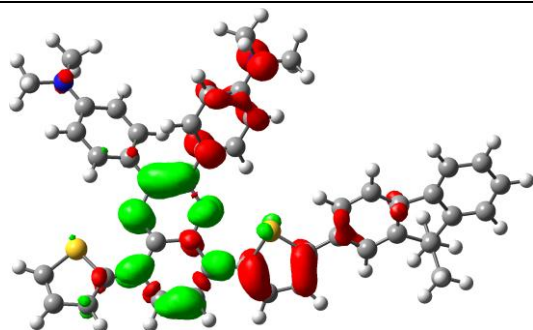


$\lambda_{\text{calc}} = 456 \text{ nm}$

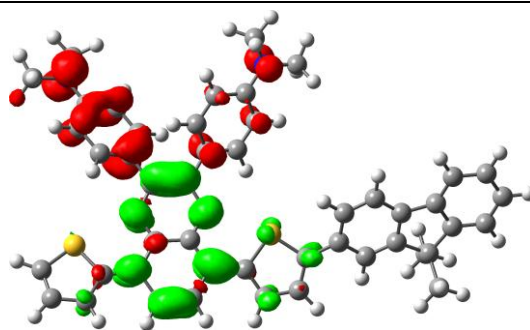


$\lambda_{\text{calc}} = 427 \text{ nm}$

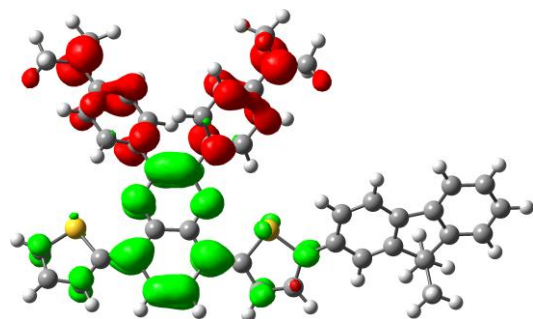
FDOAQX



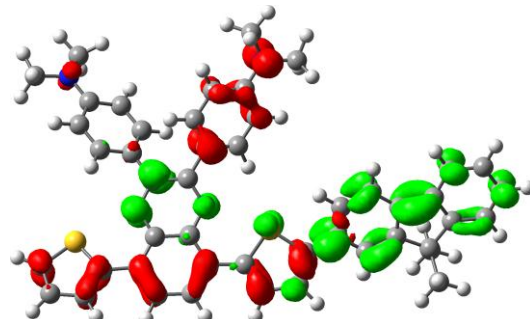
$\lambda_{\text{calc}} = 527 \text{ nm}$



$\lambda_{\text{calc}} = 508 \text{ nm}$

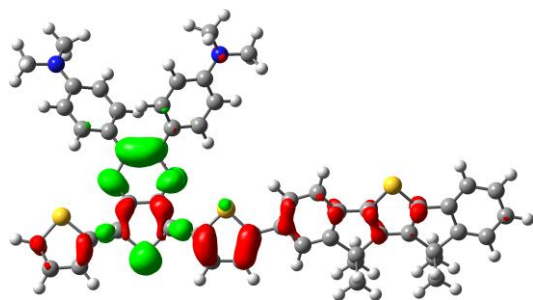


$\lambda_{\text{calc}} = 448 \text{ nm}$

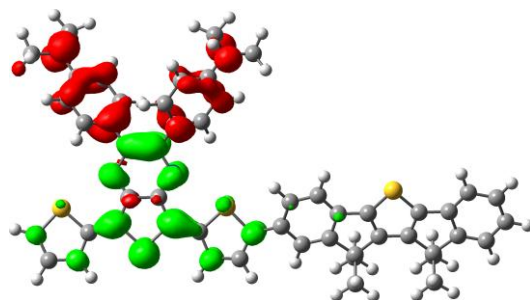


$\lambda_{\text{calc}} = 386 \text{ nm}$

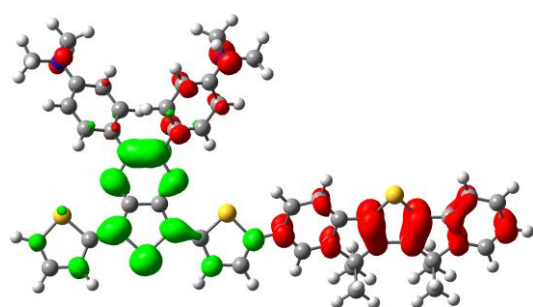
DIDTDOATP



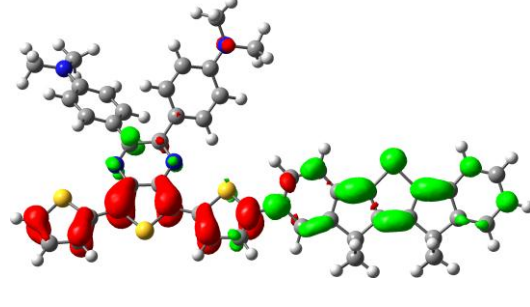
$\lambda_{\text{calc}} = 684 \text{ nm}$



$\lambda_{\text{calc}} = 570 \text{ nm}$

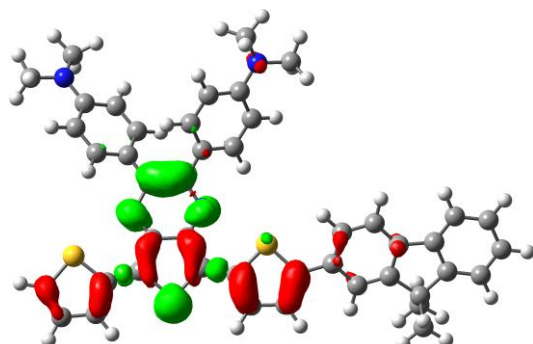


$\lambda_{\text{calc}} = 508 \text{ nm}$

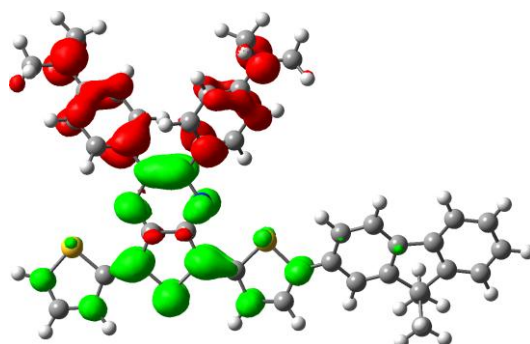


$\lambda_{\text{calc}} = 466 \text{ nm}$

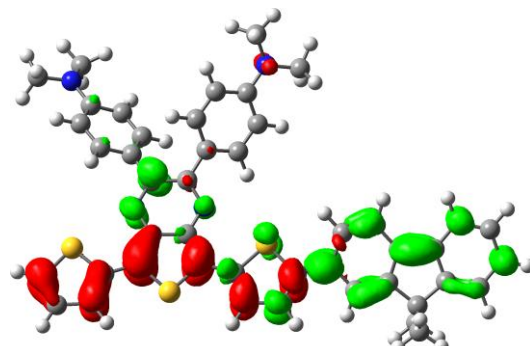
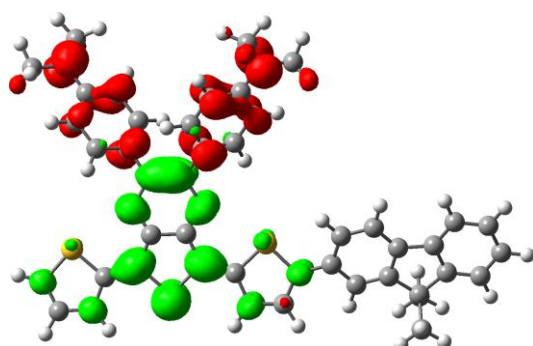
FDOATP



$\lambda_{\text{calc}} = 662 \text{ nm}$



$\lambda_{\text{calc}} = 569 \text{ nm}$



$$\lambda_{\text{calc}} = 493 \text{ nm}$$

$$\lambda_{\text{calc}} = 433 \text{ nm}$$

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Figure S1 Electron density difference maps (EDDMs) of selected singlet electronic transitions of **DIDTDOAQX** (at 551, 514, and 427 nm), **FDOAQX** (at 527, 508, 448, and 386 nm), **DIDTDOATP** (at 684, 570, 507, and 466 nm), and **FDOATP** (at 662, 569, 493, and 433 nm). Red indicates a decrease in charge density, while green indicates an increase. All EDMs are plotted with isovalue 0.0012 au.

## 2. NMR and Mass Spectra

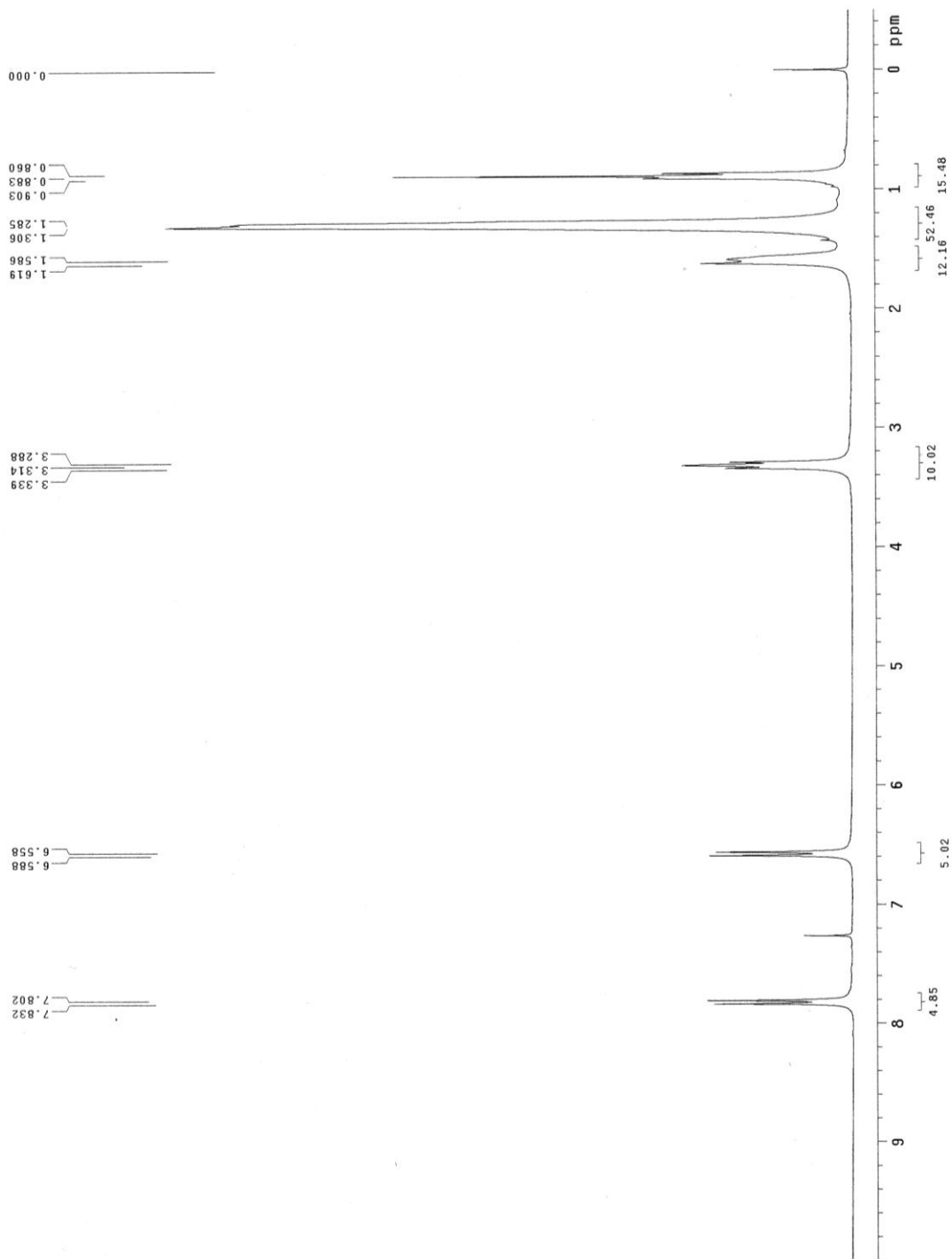


Figure S 2  $^1\text{H}$  NMR spectrum of 1,2-bis(4-dioctylaminophenyl)ethane-1,2-dione (4) in  $\text{CDCl}_3$



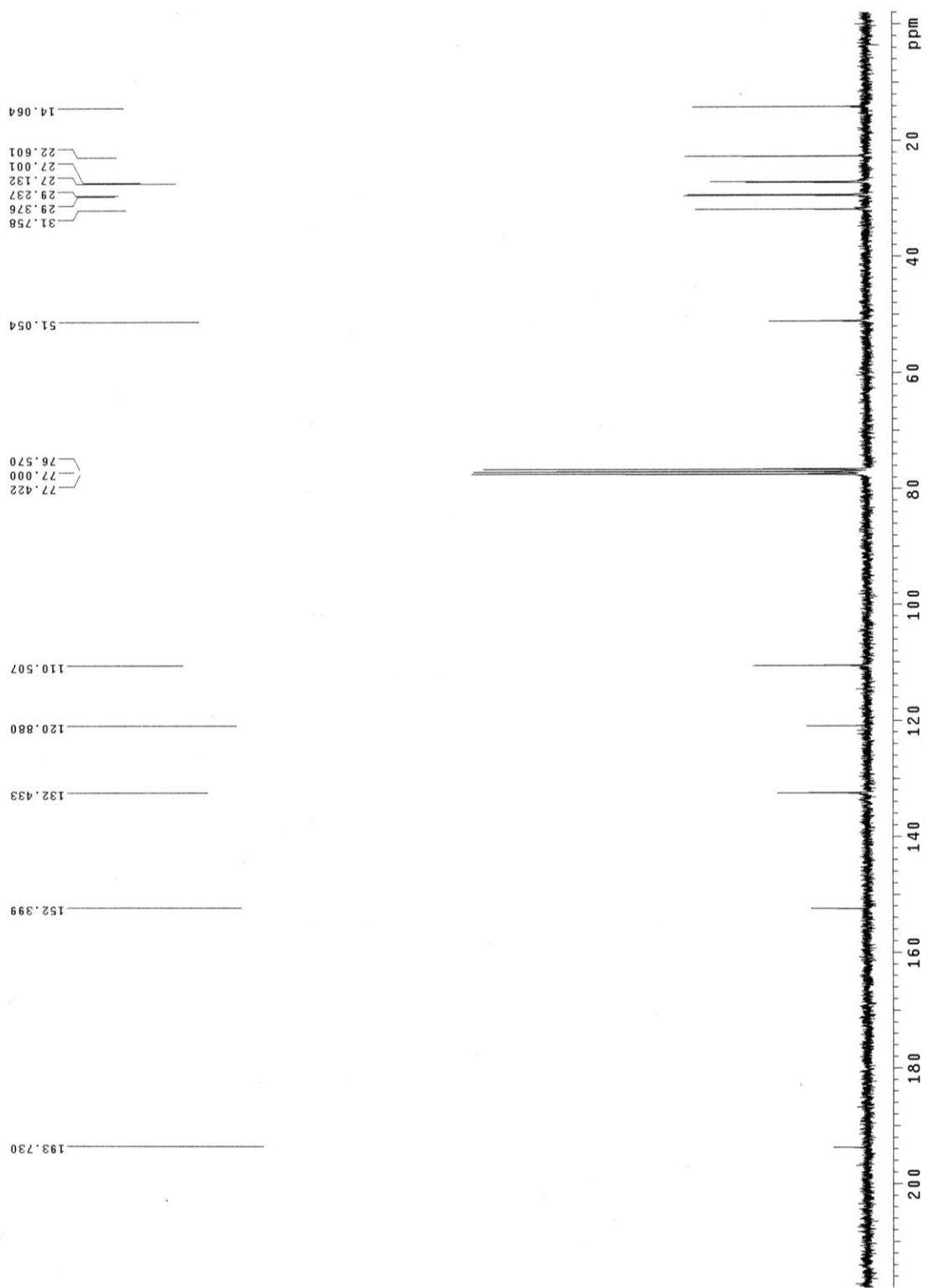


Figure S 3  $^{13}\text{C}$  NMR spectrum of 1,2-bis(4-dioctylaminophenyl)ethane-1,2-dione (4) in  $\text{CDCl}_3$

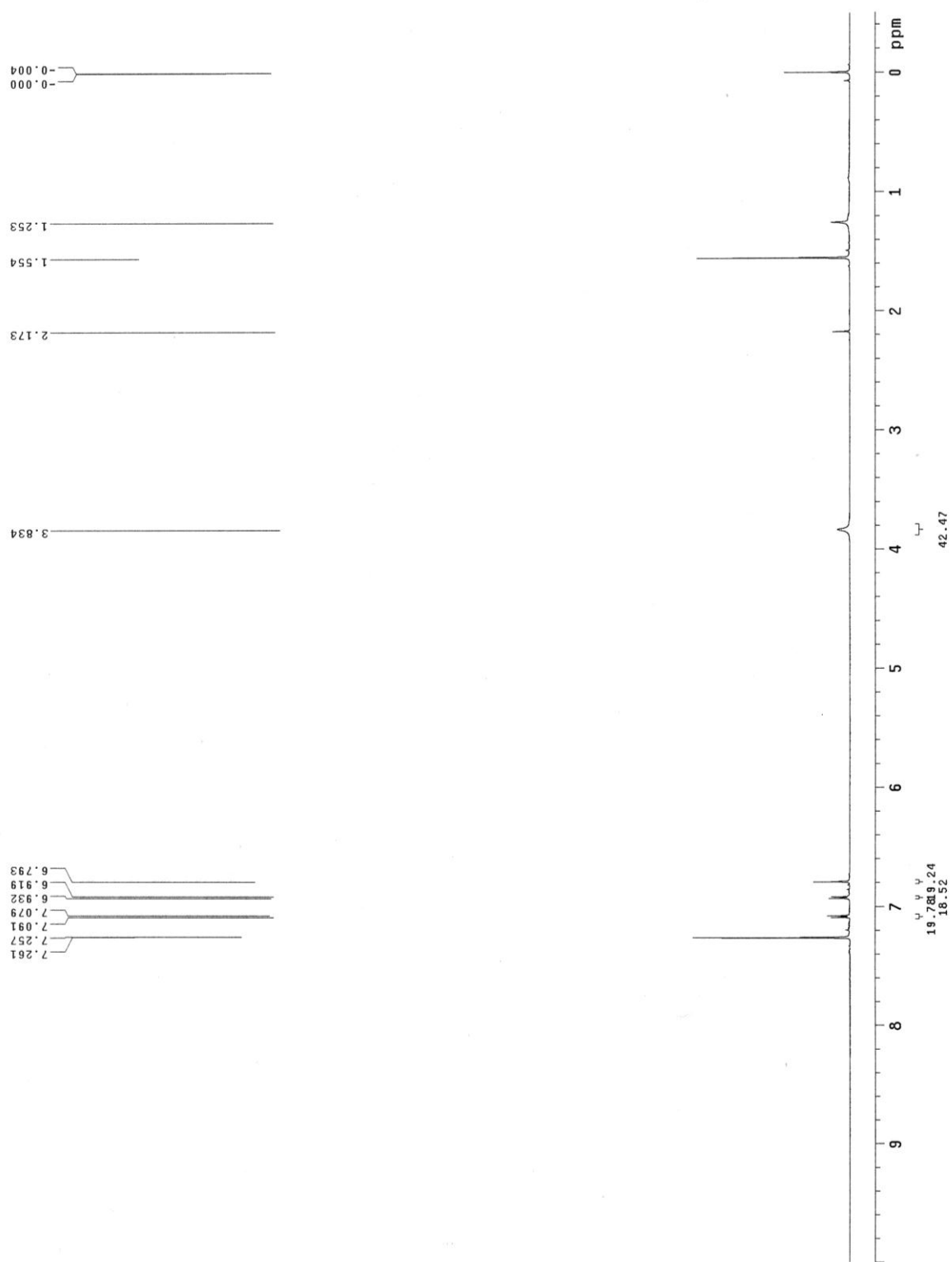


Figure S 4  $^1\text{H}$  NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)benzene-1,2-diamine (8) in  $\text{CDCl}_3$

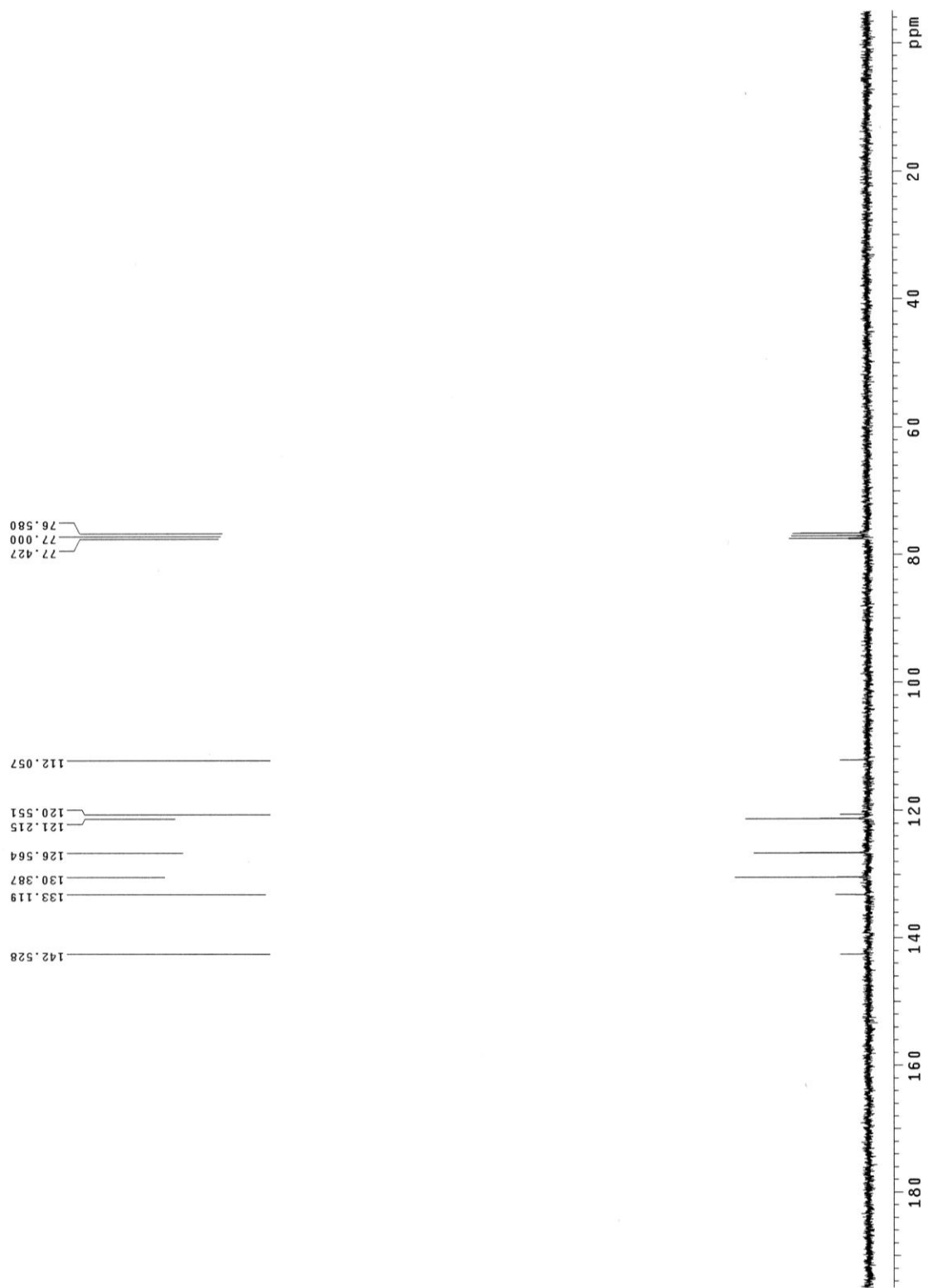


Figure S 5  $^{13}\text{C}$  NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)benzene-1,2-diamine (8) in  $\text{CDCl}_3$

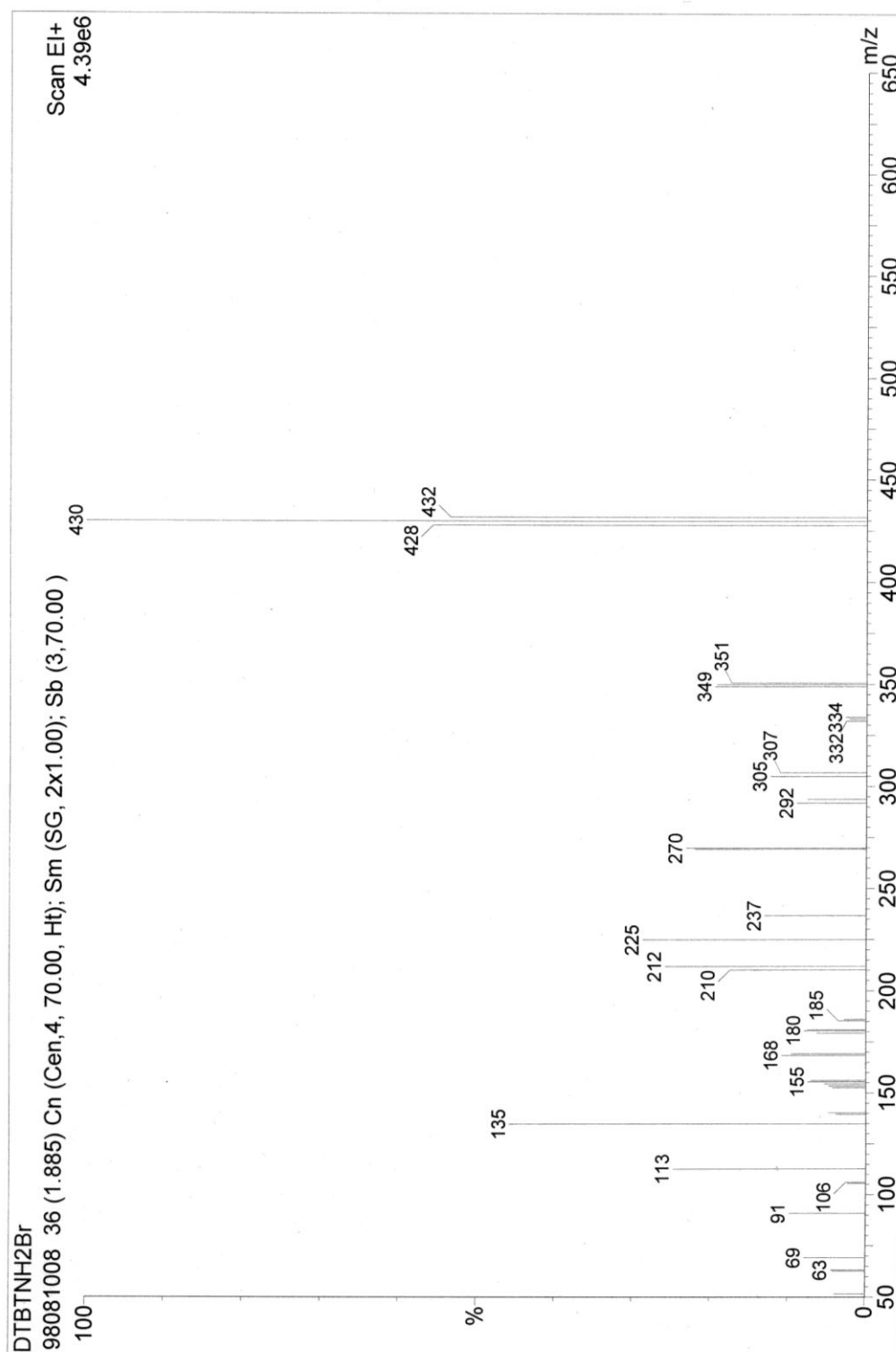


Figure S 6 EI spectrum of **3,6-bis(5-bromothiophen-2-yl)benzene-1,2-diamine (8)**

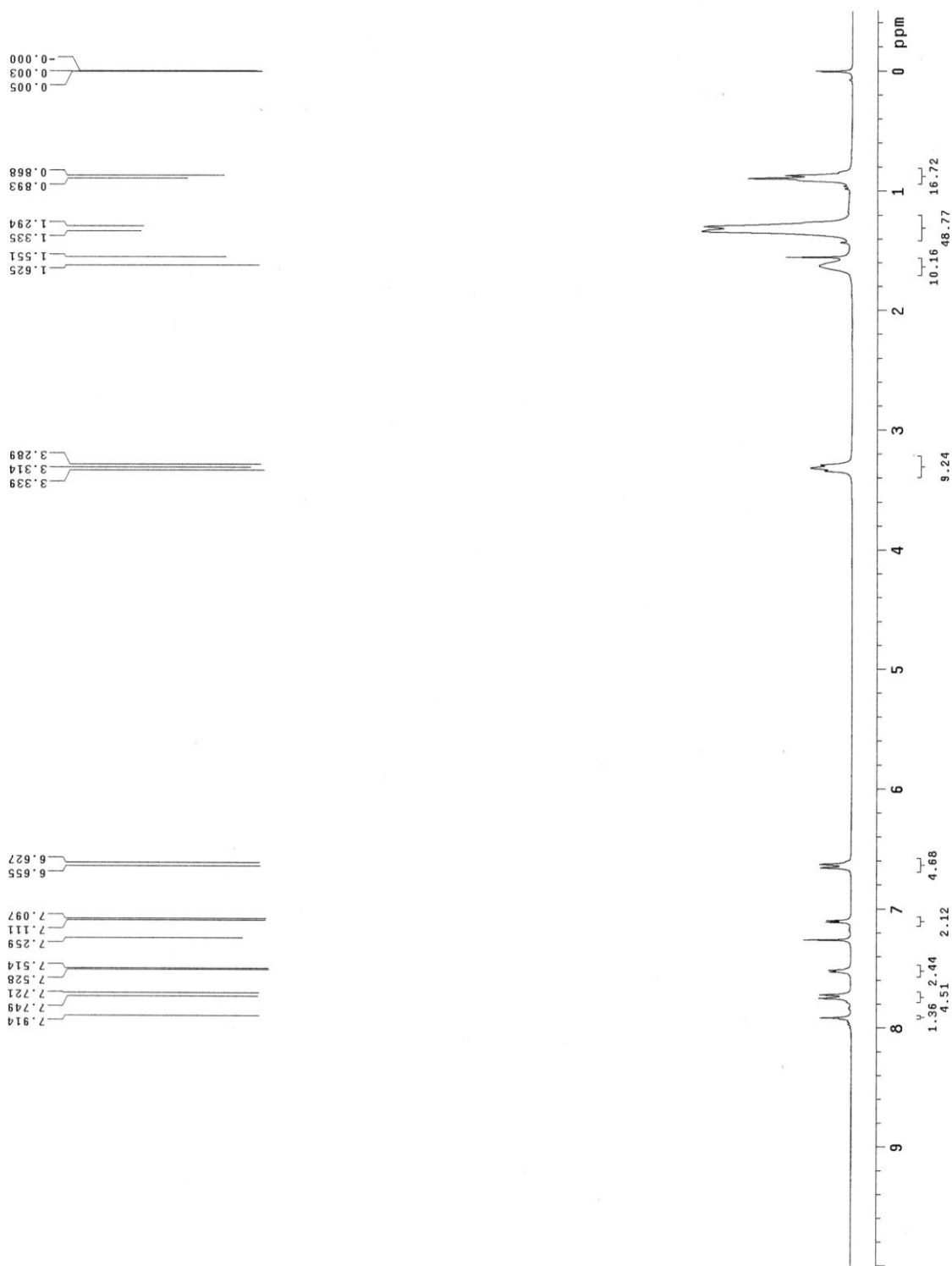


Figure S 7  $^1\text{H}$  NMR spectrum of

**2,3-bis(4-dioctylaminophenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (9)** in  $\text{CDCl}_3$

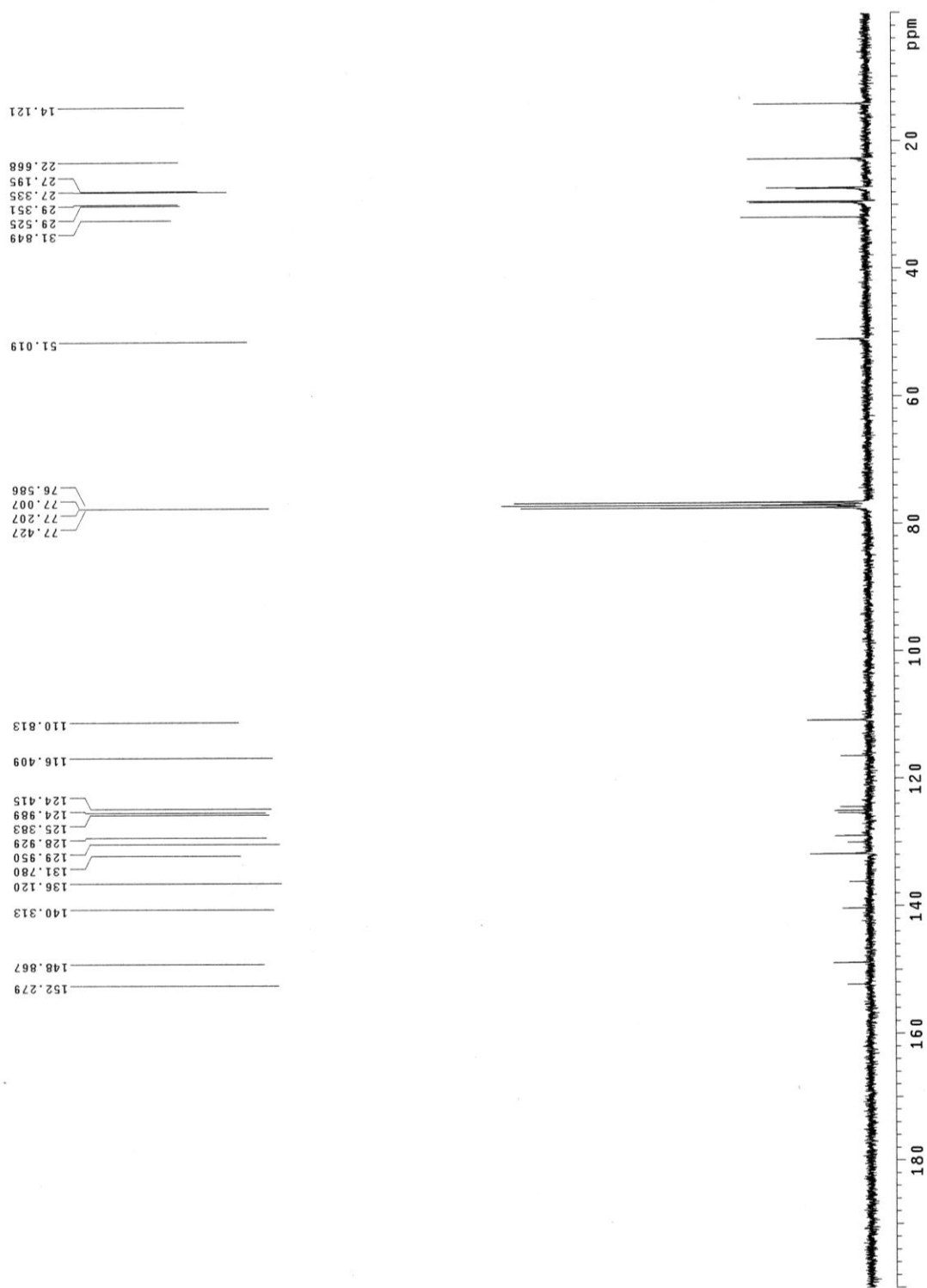


Figure S 8  $^{13}\text{C}$  NMR spectrum of

**2,3-bis(4-dioctylaminophenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (9)** in  $\text{CDCl}_3$

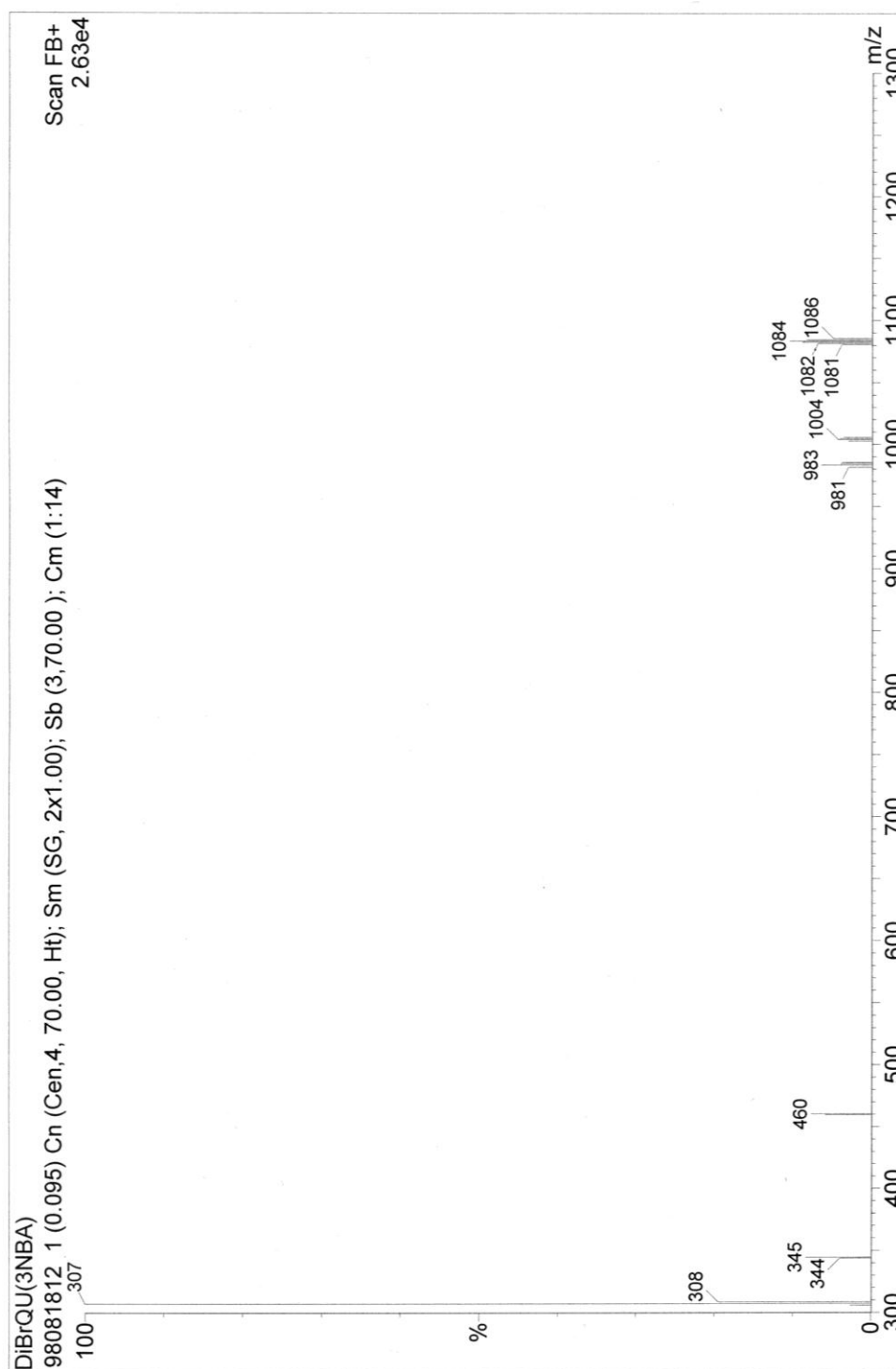


Figure S 9 FAB

spectrum

of

**2,3-bis(4-dioctylaminophenyl)-5,8-bis(5-bromothiophen-2-yl)quinoxaline (9)**

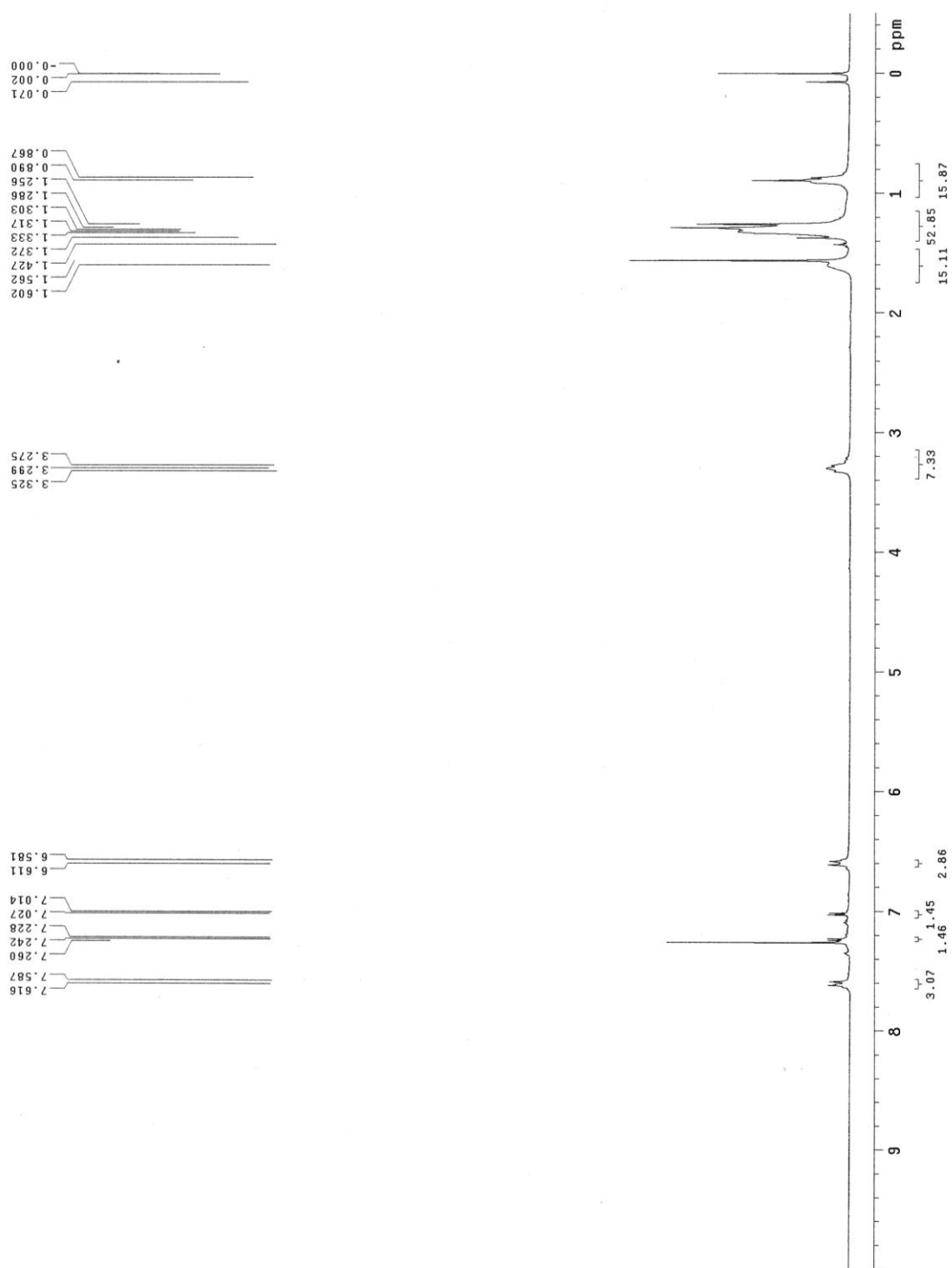


Figure S 10  $^1\text{H}$  NMR spectrum of

**2,3-bis(4-dioctylaminophenyl)-5,7-bis(5-bromothiophen-2-yl)thieno[3,4-*b*]pyrazine (14)** in  $\text{CDCl}_3$



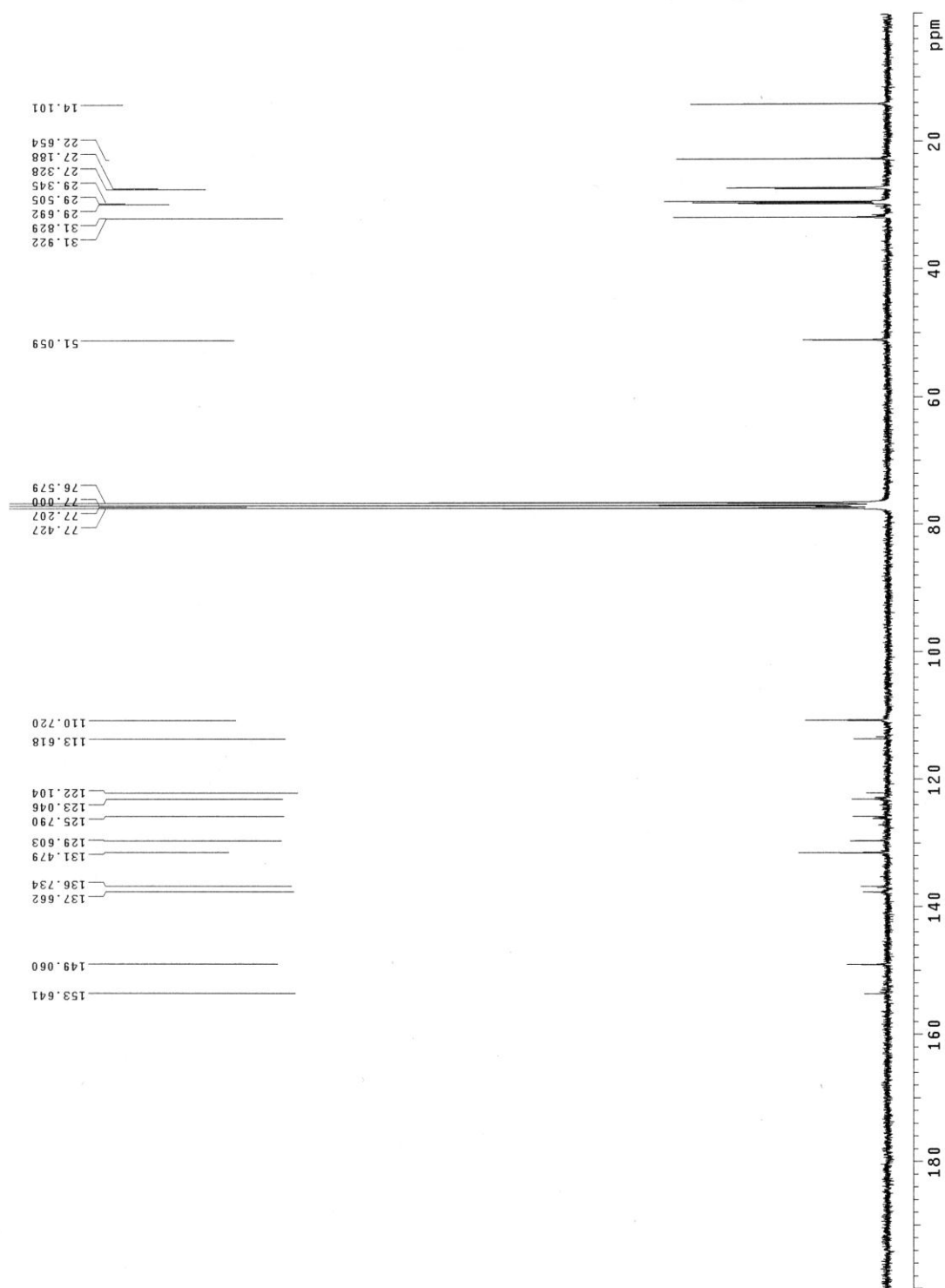


Figure S 11 <sup>13</sup>C NMR spectrum of

2,3-bis(4-dioctylaminophenyl)-5,7-bis(5-bromothiophen-2-yl)thieno[3,4-*b*]pyrazine (14) in CDCl<sub>3</sub>

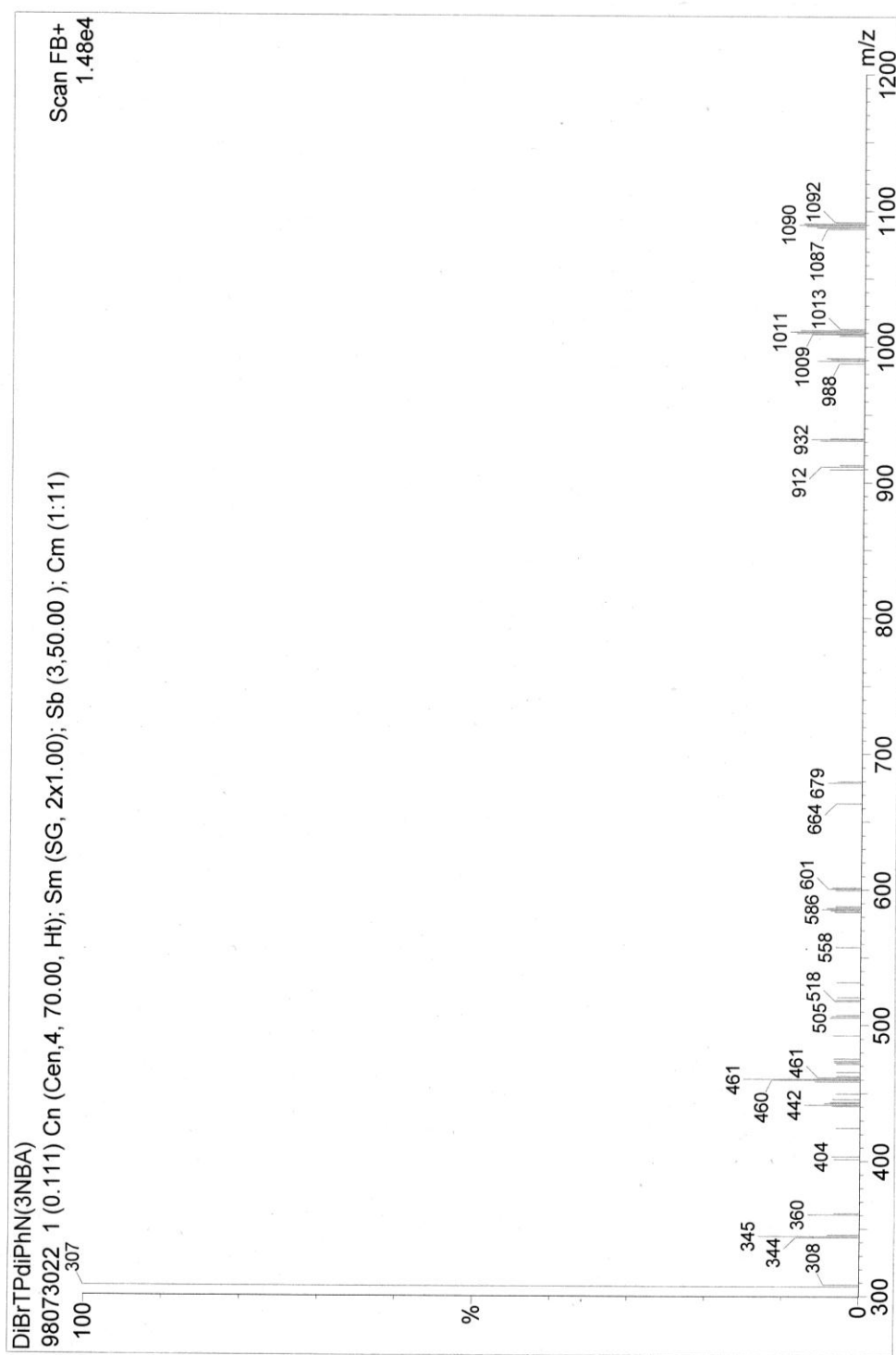


Figure S 12 FAB

spectrum

of

**2,3-bis(4-dioctylaminophenyl)-5,7-bis(5-bromothiophen-2-yl)thieno[3,4-*b*]pyrazine (14)**

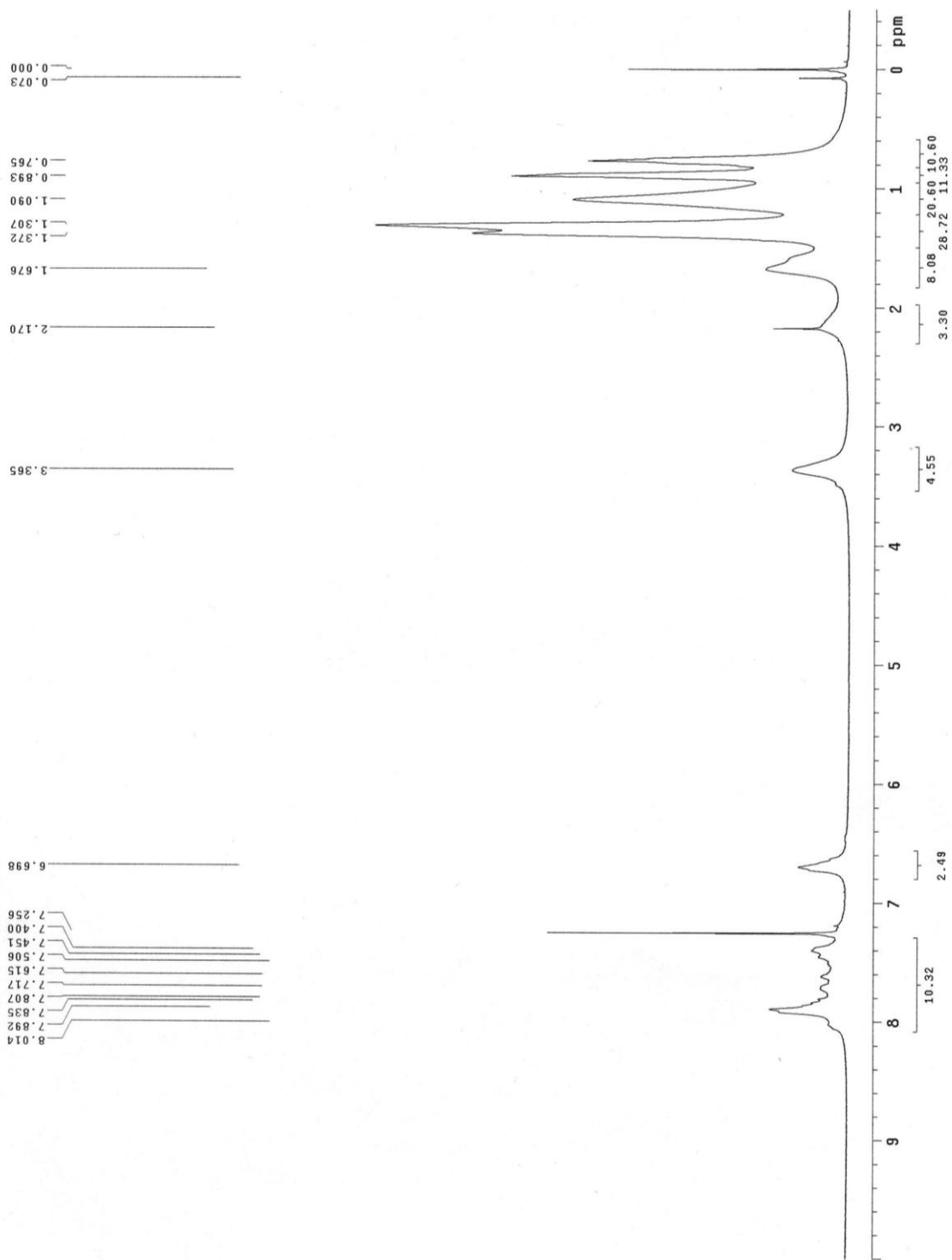


Figure S 13 <sup>1</sup>H NMR spectrum of PDIDTDOAQX in CDCl<sub>3</sub>

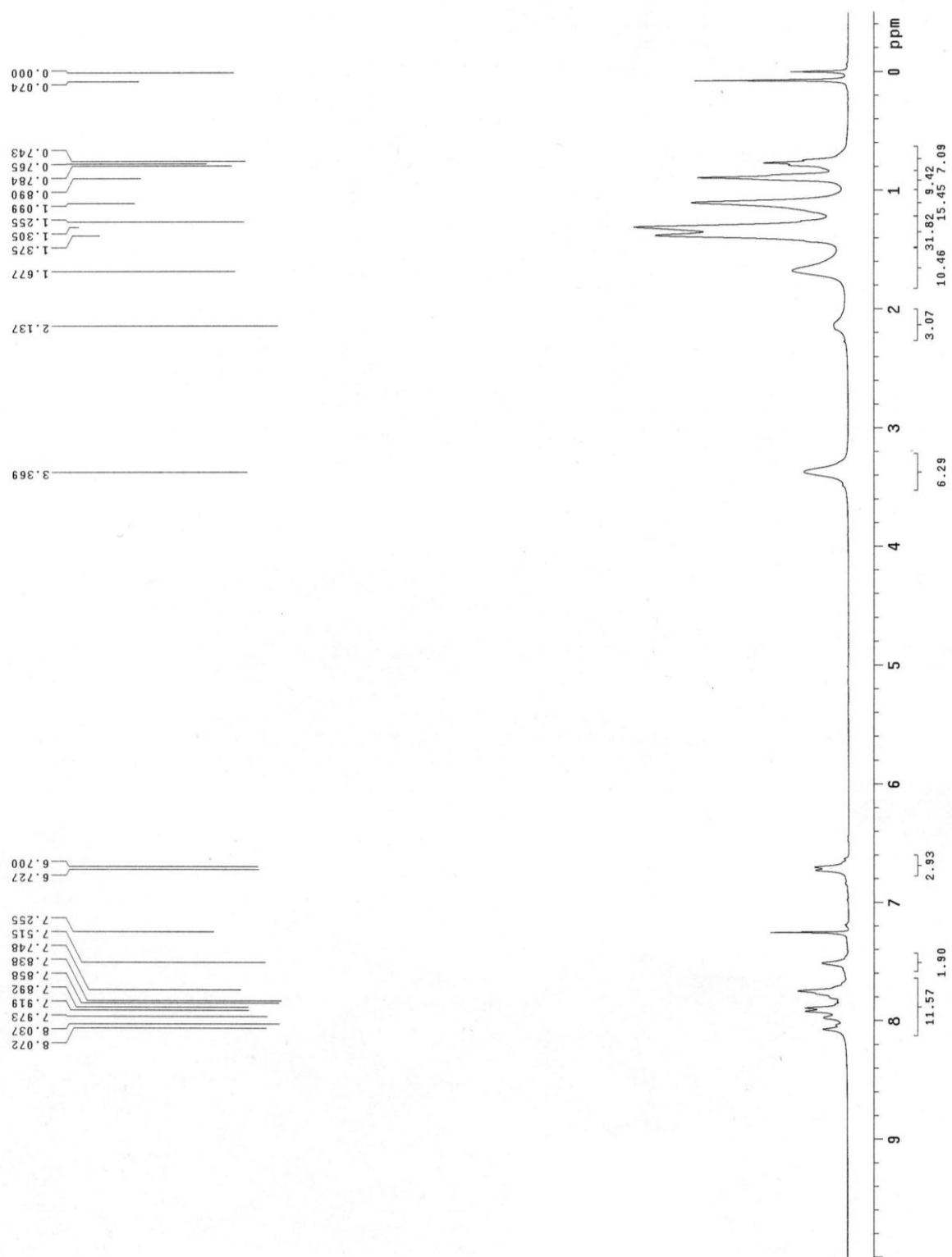


Figure S 14  $^1\text{H}$  NMR spectrum of **PFDOAQX** in  $\text{CDCl}_3$

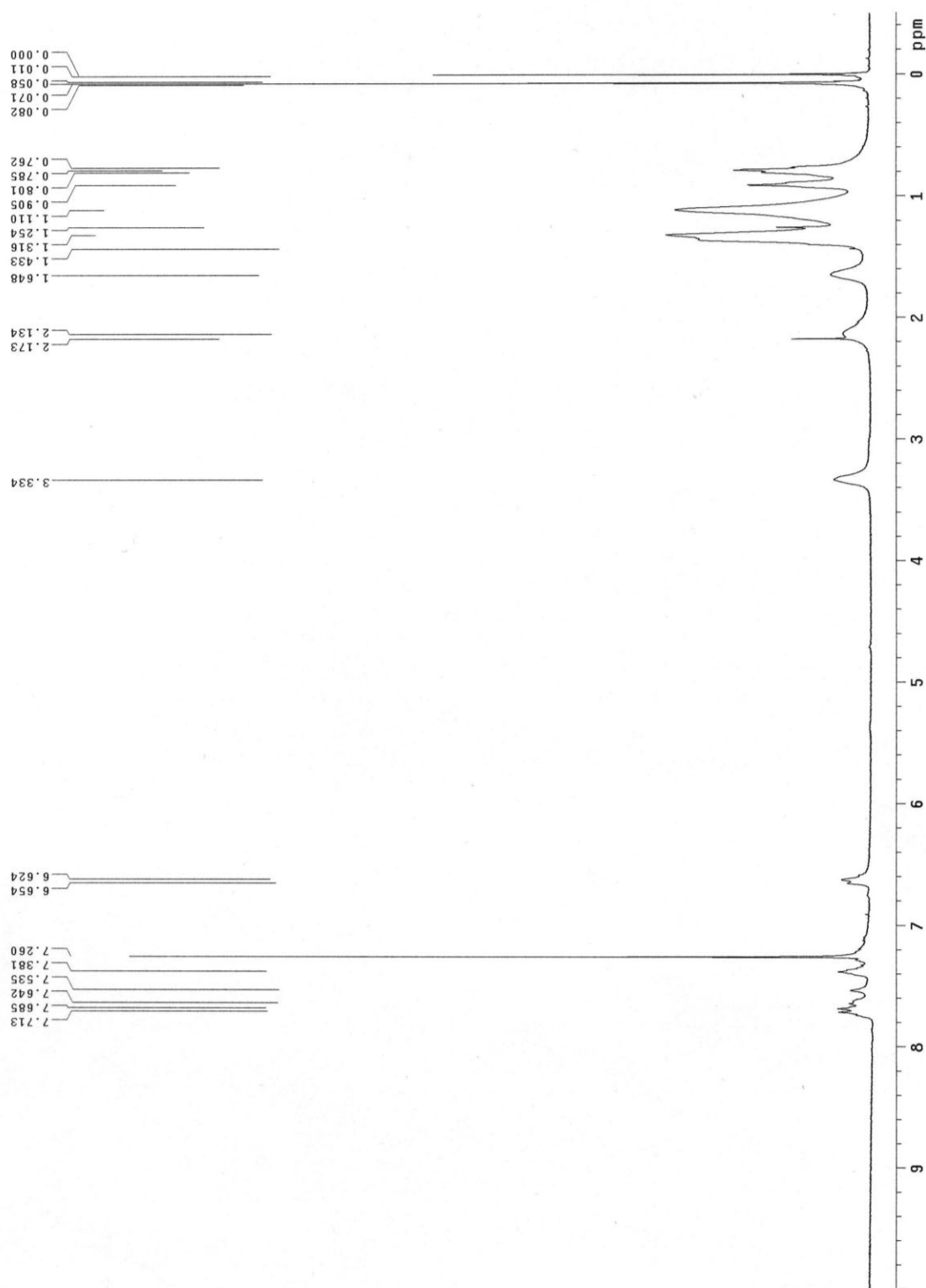


Figure S 15 <sup>1</sup>H NMR spectrum of PDIDTDOATP in CDCl<sub>3</sub>

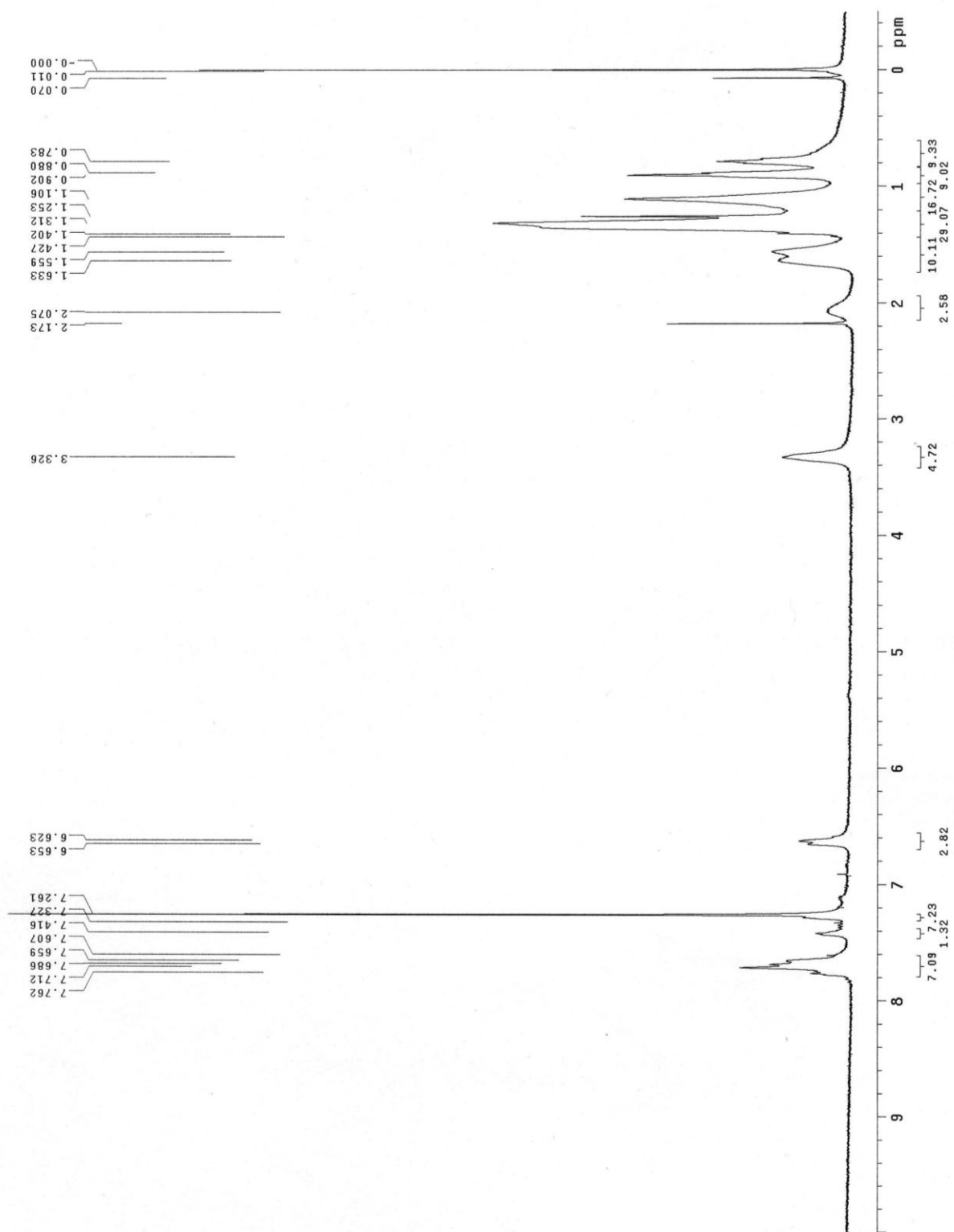


Figure S 16  $^1\text{H}$  NMR spectrum of PFDOATP in  $\text{CDCl}_3$

### 3. Reference

(1) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.